Formerly Utilized Sites
Remedial Action Program
(FUSRAP)

Maywood Chemical Company Superfund Site

ADMINISTRATIVE RECORD

Operable Unit 2 - Groundwater

Document Number

GW-015

US Army Corps
of Engineers®
New York District

FUSRAP
Maywood Superfund Site

Chemical Data Quality Management Plan

Formerly Utilized Sites Remedial Action Program
Maywood Superfund Site

Prepared by:

Shaw Environmental, Inc.
100 West Hunter Avenue
Maywood, New Jersey 07607

Prepared for:

US Army Corps of Engineers®

Contract No. DACW41-99-D-9001

June 2009, Revision 2

CHEMICAL DATA QUALITY MANAGEMENT PLAN

FUSRAP MAYWOOD SUPERFUND SITE
MAYWOOD, NEW JERSEY

SITE-SPECIFIC ENVIRONMENTAL RESTORATION
CONTRACT No. DACW41-99-D-9001
TASK ORDER No. 0003
WAD 01 WBS 01

Submitted to:

Department of the Army
U.S. Army Engineer District, New York
Corps of Engineers
FUSRAP Project Office
26 Federal Plaza
New York, New York 10278

Department of the Army
U.S. Army Engineer District, Kansas City
Corps of Engineers
700 Federal Building
Kansas City, Missouri 64106

Submitted by:

Shaw Environmental, Inc.
100 West Hunter Ave.
Maywood, NJ 07607

June 2009
Revision 2

Volumes 1 and 2

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Maywood Superfund Site

CDQMP Volume 1, Quality Assurance Project Plan

Formerly Utilized Sites Remedial Action Program
Maywood Superfund Site

Prepared by:

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100 West Hunter Avenue
Maywood, New Jersey 07607

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CHEMICAL DATA QUALITY MANAGEMENT PLAN
VOLUME 1 – QUALITY ASSURANCE PROJECT PLAN

FUSRAP MAYWOOD SUPERFUND SITE
MAYWOOD, NEW JERSEY

SITE-SPECIFIC ENVIRONMENTAL RESTORATION
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ABBREVIATIONS AND ACRONYMS

CAR	Corrective Action Report
CCQC	Contractor Chemical Quality Control
CCOR	Construction Close-Out Report
CDQMP	Chemical Data Quality Management Plan
CERCLA	Comprehensive Environmental Response, Compensation, and Liabilities Act of 1980
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CO	Contracting Officer
COC	contaminant of concern
cpm	counts per minute
CQCP	Contractor Quality Control Plan
CQCSM	Contractor Quality Control System Manager
%D	percent difference
DOD	Department of Defense
DOE	U. S. Department of Energy
DOJ	U. S. Department of Justice
dpm	disintegrations per minute
dps	disintegrations per second
DQCR	Daily Quality Control Report
DQO	Data Quality Objective
EDMS	Electronic Document Management System
EM	Engineering Manual
EPA	U.S. Environmental Protection Agency
FCO	Field Change Order
FCRF	Field Change Request Form
FFA	Federal Facilities Agreement
FMSS	FUSRAP Maywood Superfund Site
FSP	Field Sampling Plan
FSS	Final Status Survey
FUSRAP	Formerly Utilized Sites Remedial Action Program
g	gram
GC	Gas Chromatography
GEPP	General Environmental Protection Plan
GWQC	Groundwater Quality Criteria
ha	hectare
HPLC	High Performance Liquid Chromatography
HTRW	Hazardous, Toxic, and Radiological Waste
ICP	Inductively Coupled Plasma
km	kilometers
KPA	kinetic phosphorescence analysis
L_c	Critical Level
L_d	Detection Limit
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
MARSSIM	Multi-Agency Radiation Survey and Site Investigation Manual
MCL	Maximum Contaminant Level
MCW	Maywood Chemical Works

MD	matrix duplicate
MDA	Minimum Detectable Activity
MDL	Method Detection Limit
MEK	Methyl Ethyl Ketone
mi	mile
MISS	Maywood Interim Storage Site
MNA	Monitored Natural Attenuation
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NaI	Sodium Iodide
NCR	Nonconformance Report
NELAP	National Environmental Laboratory Accreditation Program
NESHAP	National Emission Standards for Hazardous Air Pollutants
NJAC	New Jersey Administrative Code
NJDEP	New Jersey Department of Environmental Protection
NOAA	National Oceanic and Atmospheric Administration
NRC	Nuclear Regulatory Commission
NUREG	US Nuclear Regulatory Commission Regulation
PARCCS	precision, accuracy, representativeness, comparability, completeness, and sensitivity
pCi	picocurie
pCi/g	picocuries per gram
pCi/L	picocuries per liter
PCB	Polychlorinated biphenyl
PCOC	Primary Contaminant of Concern
PE	Performance Evaluation
PID	Photoionization Detector
POTW	Publicly Owned Treatment Works
ppb	parts-per-billion
PPE	Personal Protective Equipment
ppm	parts-per-million
PQCM	Program Quality Control Manager
PQL	Practical Quantitation Limit
PRAR	Post-Remedial Action Report
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QCSR	Quality Control Summary Report
%R	percent Recovery
Ra	Radium
^{226}Ra	Radium-226
^{228}Ra	Radium-228
RF	Response Factor
RL	Reporting Limit
^{222}Rn	Radon-222
ROC	Radionuclides of Concern
ROD	Record of Decision
RPD	Relative Percent Difference
RPT	Radiation Protection Technician
%RSD	% Relative Standard Deviation
RSO	Radiation Safety Officer
S	Standard Deviation
SA	Spike activity added
S&W	Stone & Webster, Inc.

SAP	Sampling and Analysis Plan
SEC	Safety and Ecology Corporation
SOP	Standard Operating Procedure
SR	Sample result
SSHO	Site Safety and Health Officer
SSHP	Site Safety and Health Plan
SSR	Spiked sample result
SVOC	semi-volatile organic compound
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
Th	Thorium
^{232}Th	Thorium-232
TIC	Tentatively Identified Compound
TKN	Total Kjeldahl Nitrogen
TRPH	Total Recoverable Petroleum Hydrocarbons
U	Uranium
^{238}U	Uranium-238
UFML	USACE FUSRAP Maywood Laboratory
µg	microgram
$U_{(tot)}$	Total Uranium
uR/hr or µR/hr	micro-Roentgen per hour (either abbreviation is acceptable)
USACE	U.S. Army Corps of Engineers
USACE KCD	U.S. Army Corps of Engineers Kansas City district
VOC	Volatile Organic Compound

1.0 PROJECT MANAGEMENT

This Quality Assurance Project Plan (QAPP) describes the project organization established to ensure attainment of quality data; data quality objectives; the quality assurance and quality control methods employed for sample collection, handling, and testing; documentation requirements; assessment and oversight activities including audits and reports to management; and data validation. The QAPP is the project document that establishes the data quality required for attainment of project data quality objectives, which are in turn determined by site cleanup levels dictated by regulatory authorities. The official approved QAPP is kept in the Project File and is maintained by the Project Chemist, Brian Tucker.

1.1 PROJECT ORGANIZATION

This section of the Chemical Data Quality Management Plan (CDQMP) summarizes the project organization for the Formerly Utilized Sites Remedial Action Program (FUSRAP) Maywood Superfund Site (FMSS) project. It provides specific Shaw Environmental, Inc. (Shaw) and subcontractor personnel responsibilities and lines of authority and communication. Names of personnel fulfilling these responsibilities are also provided.

1.1.1 Quality Assurance / Quality Control Organization

Project Quality Assurance (QA) will be maintained under the direction of the Contract Quality Control System Manager (CQCSM) in accordance with the CDQMP and the Contractor Quality Control Plan (CQCP) (USACE 1999). In addition, the CQCSM will direct field audits. Quality Control (QC) for the following tasks will be the responsibility of the individuals and organizations listed in **Table 1-1**.

Table 1-1
QC Responsibilities

General Responsibility	General Tasks	Responsibility for Quality Control
Field Sampling	Environmental sampling of soil, water, and building materials	Shaw
Sample Management	Maintenance of correct custody and proper preservation of environmental samples	Shaw
Radiological Investigations	Radiological investigations	Shaw and Subcontractors
Laboratory Analyses	Radiological and chemical analysis of soil, water, air, and building materials	Analytical Laboratory(ies) and Shaw and Subcontractors
Data Validation	Validation of laboratory data using USACE guidelines	Data Validator and Shaw
Field Measurement Activities	Performance of QA measurements on Field Measurement units.	Shaw and Subcontractors
Laboratory Audits	Performance of systems and performance audits of laboratory(ies)	Shaw, USACE, NJDEP, and/or Subcontractor auditors
Field Audits	Performance of field quality control audits	Shaw and USACE Personnel

The USACE Contracting Officer and the Corporate Vice President for Quality will be notified prior to any deviation from the approved CDQMP.

1.1.2 Personnel, Responsibilities, and Qualifications

The organizational chart shown in **Figure 1-1** outlines the management structure that will be used to implement the project's sampling and analysis activities. Shaw is the designated USACE contractor responsible for conducting the remedial action at the FMSS. The functional responsibilities of key personnel are described in this section. These roles will be filled by a combination of Shaw staff and subcontractors. The assignment of personnel to each position will be based on a combination of:

1. Experience in the type of work to be performed.
2. Experience working with USACE personnel and procedures.
3. A demonstrated commitment to high-quality and timely job performance.
4. Staff availability.

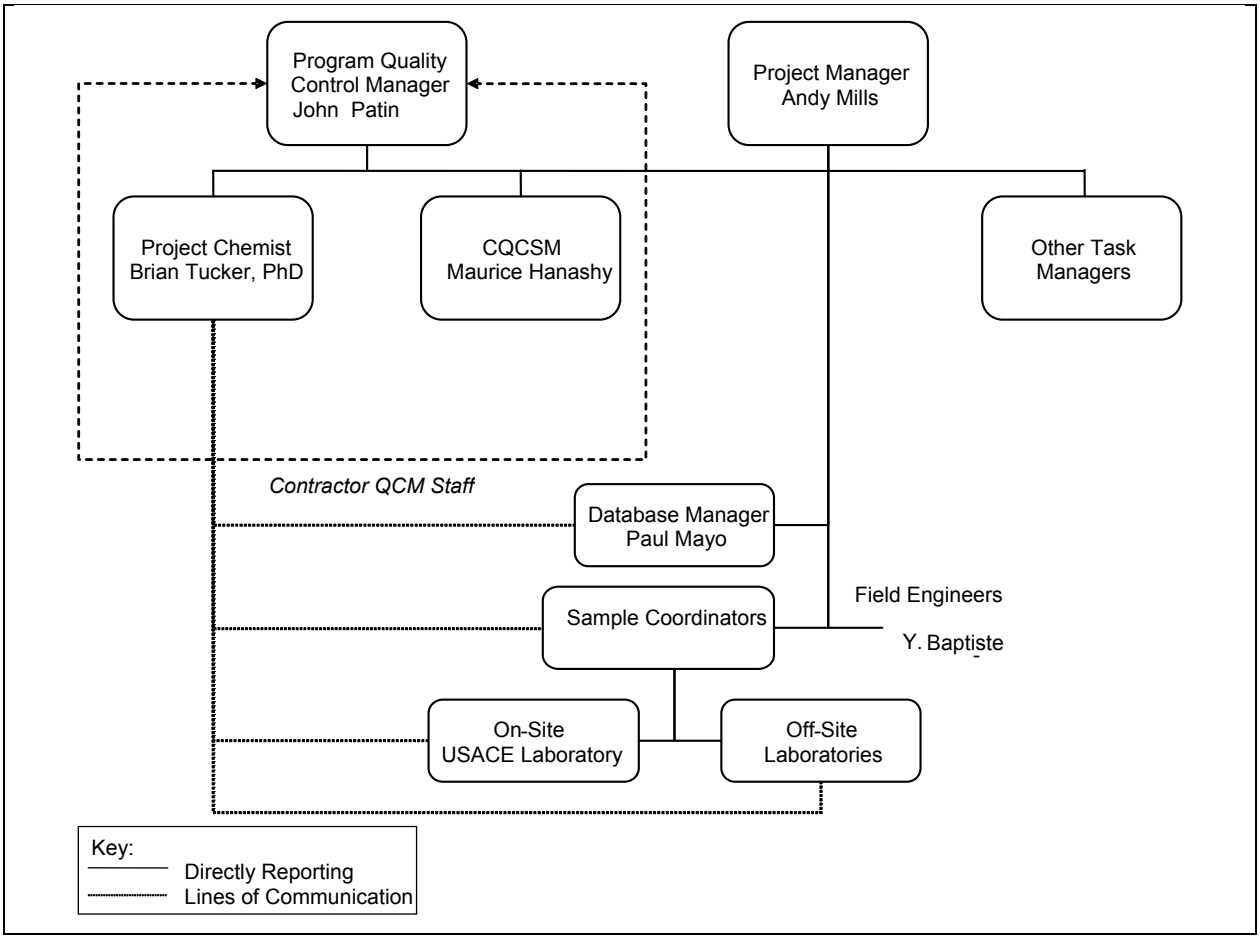

Figure 1-1
Chemical Data Quality Control Organization

1.1.2.1 Project Manager

The Project Manager ensures the overall management and quality of Shaw work on the FMSS project. This individual will ensure that all project goals and objectives are met in a high quality and timely manner. Project QA and nonconformance issues will be addressed by this individual for corrective action.

1.1.2.2 Project Environmental Engineer

The Project Environmental Engineer shall ensure that remediation goals, including required analytical data, are obtained consistent with applicable environmental laws and regulations. The Project Environmental Engineer reports directly to the Project Manager.

1.1.2.3 Task Managers

Task Managers will be assigned to the project to implement specific tasks. They will have direct responsibility for implementing the CDQMP, including all phases of work plan development, field activities, data management, and report preparation. These individuals will also provide the overall management of the tasks, and serve as the points of contact with the USACE. These activities will involve coordinating all personnel working on the assigned tasks, interfacing with USACE personnel, and tracking task budgets and schedules. Task Managers are responsible for ensuring proper technical performance of drilling operations and field sampling activities, adherence to required sample custody and other related QA/QC field procedures, coordination of field personnel activities, management of investigation-derived wastes, checks of all field documentation, and preparation of Field Change Orders (FCOs), if required. The Task Managers will also develop, monitor, and fill task staffing needs; delegate specific responsibilities to task team members; and coordinate with administrative staff to maintain a coordinated and timely flow of all project activities. The Task Managers report directly to the Project Manager, or designee.

1.1.2.4 Field Personnel

In addition to the Task Managers, other field personnel participating in the implementation of field activities are geologists, geotechnical engineers, environmental engineers, hydrogeologists, and sampling technicians. These individuals, in coordination with field subcontractor personnel, will be responsible for performance of drilling operations; collection of soil, groundwater, sediment, surface water, and air samples; radiation monitoring; and preparation of field logbooks and other required documentation. These individuals will be responsible for performing all field activities in accordance with the CDQMP, and will report directly to the Task Managers.

1.1.2.5 Contracted Field Support

Several team subcontractors provide support to the FMSS Project relating to the areas of data generation and quality. Many of the services are competitively bid on an annual basis so that the identified subcontractors may change over time. Within these areas, a few of the subcontractors currently supporting the project are listed is Table 1-2.

Table 1-2
Subcontractors Supporting the Project

Subcontractor	Support Service
Safety & Ecology Corporation 2800 Solway Road Knoxville, Tennessee 37931	Field Radiological Technicians, Laboratory Technicians, and Professional Support Services
Southern University CEES 315 Baranco Hall PO Box 9764 Baton Rouge, LA 70813	Offsite laboratory analysis of samples for chemical parameters
Kestrel Environmental Services 295 Lower Flying Point Road Freeport, ME 04032	Data Validation
Analytics 1380 Seaboard Industrial Blvd. Atlanta, GA 30318	Radiological Tracers and Standards
Ortec/Ametek 801 South Illinois Avenue Oak Ridge, TN 37830	Gamma spectrometer and alpha spectrometer systems
Protean Instrument Corporation 231 Sam Rayburn Parkway Lenoir City, TN 37771	Gas proportional detectors

Other subcontractors may also provide support on an as needed basis.

1.1.2.5.1 Subcontractor Field Personnel

Subcontractor field personnel, under the supervision of the Task Managers, will be responsible for performing their specific scopes of work that have been derived from the task-specific work plan. These individuals will be required to review the sampling sections of the work plan and the entire FMSS *Site Safety and Health Plan* (SSHP) (USACE 2006a) prior to field mobilization. All subcontractor field personnel report directly to the Task Managers who will be responsible for ensuring that all subcontractor activities comply with project requirements.

1.1.2.6 Subcontracted Laboratory Support

Analytical laboratory support specific to these investigations and remedial actions will be obtained from on-site testing and screening and one or more off-site laboratories.

On-site testing and screening for radiological parameters will be performed in the onsite laboratory (USACE FMSS Maywood Laboratory, or UFML) operated for USACE by Shaw and Safety and Ecology Corporation (SEC). UFML has the ability to dry and grind soil samples during the sample preparation phase. They can perform gamma spectrometry on these samples using one Canberra 30% germanium and two Canberra 40% Germanium one-hole detector systems. They can also take gamma counts on wet samples using a cross-correlation between dry equilibrated and wet unequilibrated samples. The on-site laboratory analyzes water samples for isotopic uranium (iso-uranium), isotopic thorium (iso-thorium), and radium-226 (Ra-226) using alpha spectrometry, and gross alpha, gross beta, and radium-228 (Ra-228) using a Protean Low-Background Gas Flow Proportional Counter. They can also analyze water samples using kinetic phosphorescence analysis (KPA). This laboratory also performs gross air sample and swipe counting using a combination of a gas proportional detector counting system and several Ludlum 2000/2929 alpha-beta scalers. The on-site laboratory is currently certified by the New Jersey Department

of Environmental Protection (NJDEP) to analyze soil samples by gamma spectrometry, and water samples by alpha spectrometry, gas proportional counting, and KPA. Sample testing by UFML reduces overall laboratory costs and improves turnaround time. This laboratory prepares and analyzes samples and generates data in accordance with the 600 series Standard Operating Procedures (SOPs) (located in the Electronic Document Management System (EDMS); see Section 4.7 of this QAPP) and uses the quality assurance principles described within their Quality Manual (USACE 2006b).

At this time, Test America Laboratories, Inc. of Earth City, Missouri (for QA split samples only) and ALS Laboratory Group (formerly Paragon) of Fort Collins, Colorado (subcontractor to Southern University for chemical testing) are the off-site contract laboratories for the FMSS tasks.

All current and future subcontract laboratories will be certified by the State of New Jersey to perform the pertinent tests. The subcontract labs are required to implement and maintain a QA/QC program in accordance with USACE and NJDEP guidelines. In addition, each subcontract laboratory must hold National Environmental Laboratory Accreditation Program (NELAP) accreditation. The Maywood onsite radiological laboratory must maintain State of New Jersey certification in their Environmental Laboratory Certification Program.

A relevant QA Manual, laboratory qualification statements, certifications, and license documentation will be made available upon request. Geotechnical laboratory support will be designated to a separate subcontractor certified by the State of New Jersey.

Organization charts outlining the key laboratory personnel and organization will be identified in their QA Plans. The responsibilities of key personnel are described in the following paragraphs. The assignment of personnel to each position will be based on a combination of

1. Experience in the type of work being performed.
2. Experience working with USACE personnel and procedures.
3. A demonstrated commitment to high quality and timely job performance.

Prior to commencement of project field activities for the project, Shaw will send a complete copy of the CDQMP to all subcontracted laboratories.

1.1.2.6.1 Laboratory Quality Assurance / Quality Control Manager

The subcontractor laboratory QA/QC Manager is responsible for the laboratory QA/QC in accordance with the requirements of this QAPP in conjunction with the established laboratory QA Program. In coordination with the Shaw CQCSM and Project Chemist, the laboratory QA/QC Manager will be responsible for documenting sample analysis in accordance with required methodologies. In addition, the laboratory QA/QC Manager will be responsible for documenting instrument calibration; field and internal laboratory QC sample analysis; and that analytical results for both field and QC samples are reported to the USACE and Shaw in the format required in the laboratory scope of work, this QAPP, and the task-specific Work Plans. Further, the laboratory QA/QC Manager is responsible for processing laboratory Nonconformance Reports (NCRs) in a timely manner and for implementing Corrective Action Report recommendations and requirements. The Subcontractor Laboratory Project Manager reports directly to the Shaw CQCSM and Project Chemist for issues related to this project.

1.1.2.6.2 Laboratory Project Manager

The responsibilities of each laboratory Project Manager include the following: initiation and maintenance of contact with Shaw on individual job tasks; preparation of laboratory-associated work plans, schedules,

and resource allocations; initiation of laboratory-associated procurement for the project; provision of day-to-day direction of the laboratory project team including analytical department managers, supervisors, QA personnel, and data management personnel; coordination of laboratory related financial and contractual aspects of the project; provision of formatting and technical review for laboratory reports; provision of day-to-day communication with Shaw; provision of final review and approval on all laboratory analytical reports to Shaw; and response to all post project inquiries.

1.1.2.6.3 Laboratory Manager

The responsibilities of the Laboratory Manager include the following: coordination of all analytical production activities conducted within the analytical departments; working with the Laboratory Project Manager to ensure all project objectives are met; provision of guidance to analytical department managers; and facilitation of transfer of data produced by the analytical departments to the report preparation and review staff for final delivery to the client.

1.1.2.6.4 Laboratory Section Heads, Department Managers, and Technical Leads

The responsibilities of each laboratory section or department include the following: coordination of all analytical functions related to specific analytical areas; provision of technical information to and oversight of all analyses being performed; review and approval of all analytical results produced by their specific analytical area of expertise; and maintenance of all analytical records and information pertaining to the analysis being performed.

1.1.2.7 Program Quality Control Manager

The Program Quality Control Manager (PQCM), John Patin, consults with the Shaw Director of Quality Assurance, Bryan Koehler, as required for direction on all quality matters. The PQCM is responsible for the planning, development, implementation, and effectiveness of the project-specific QC program included in the CQCP (USACE 2005). The effectiveness of the program is measured through the use of audits, surveillances, document reviews, and other QA monitoring activities defined throughout this document.

The PQCM's duties include, but are not limited to, reviewing and approving the project-specific CQCP (USACE 2005) and all revisions thereto, reviewing and approving supporting QC procedures, evaluating the effectiveness of the quality program, assigning qualified QC personnel to projects, directing and supporting project QC management staff, training and qualifications oversight, and ensuring the necessary QC resources are provided consistent with project needs.

1.1.2.8 Contractor Quality Control System Manager

The CQCSM, Maurice Hanashy, is responsible for implementation and documentation of all project QA/QC protocols during field activities. In this capacity the CQCSM will direct and implement the various components of the Contractor Chemical Quality Control (CCQC) program as identified in USACE Engineering Manual (EM) 200-1-3. This will include but not be limited to: documentation of QAPP instructions to field personnel; oversight of field sampling and analytical activities; documentation of field QC activities; and completion of Daily Quality Control Reports (DQCRs). The CQCSM reports directly to the Project Manager and consults with the PQCM and other project personnel as required to keep them informed and support their activities. The QC organization is also discussed in the CQCP (USACE 2005).

1.1.2.9 Site Safety and Health Officer and Radiation Safety Officer

The Site Safety and Health Officer (SSHO), Chad Miller, and Radiation Safety Officer (RSO), Mike Winters, are responsible for ensuring that health and safety procedures designed to protect personnel are maintained throughout the field activities. This will be accomplished by strict adherence to the project SSHP (USACE 2006a), which has been prepared as a separate document for this project. These individuals will have the authority to halt fieldwork if health or safety issues arise that are not immediately resolvable in accordance with the project SSHP (USACE 2006a). The SSHO and RSO report directly to the Project Manager.

1.1.2.10 Project Chemist

The Project Chemist, Brian Tucker, together with the CQCSM, will oversee the field sampling and sample handling activities, as well as laboratory quality control, to ensure that the requirements of the CDQMP are met. In particular, the Project Chemist is responsible for oversight of chemical and radiochemical analysis and reporting performed by the subcontract laboratory(ies), in accordance with the requirements defined in the CDQMP. The Project Chemist will also resolve questions the laboratory may have regarding QAPP requirements and deliverables, and will coordinate data reduction, validation, and documentation activities related to sample data package deliverables received from the laboratories. The Project Chemist is responsible for writing or overseeing the writing of the Quality Control Summary Reports (QCSRs) for each task, and for periodically revising the CDQMP. The Project Chemist reports directly to the Project Manager.

The Project Chemist is also currently identified as the QA Officer of UFML, as required under the certification designation of the NJDEP. The responsibilities of the QA Officer are defined under NJAC 7:18 of the NJDEP Office of Quality Assurance.

1.1.2.11 Sample Coordinator

The Sample Coordinators are responsible for coordination of sample shipment to the analytical laboratory(ies), and verification of the accuracy of chain-of-custodies. The Sample Coordinators will also coordinate the shipment of samples to the USACE QA Laboratory(ies), which will be designated by the USACE for the project. A Sample Coordinator is assigned to each task. These individuals are responsible for obtaining required sample containers from the laboratory(ies) for use during field sample collection. Along with the Project Chemist, the Sample Coordinators ensure that off-site laboratories understand the FMSS project QC requirements, and that quality concerns and problems are resolved in a timely manner. The Sample Coordinators also track the samples of a given task from shipment to the laboratory through delivery of results and transmittal to a data validation subcontractor, if required.

1.1.2.12 Project Environmental Sampler

The Project Environmental Sampler must be familiar with all of the SOPs pertaining to sampling in this CDQMP. Specifically, the sampler must be familiar with methods of collecting various matrices; the types of containers and preservatives required; how and how often to collect field sample quality control samples; safety guidelines described in the FMSS Site Safety and Health Plan; documentation including how to fill out a Field Notebook and Chain-of-Custody; and labeling, packaging, and shipping requirements as per project guidelines. The Project Environmental Sampler interacts with the Sampling Coordinator on a regular basis.

1.1.2.13 USACE QA Laboratory

The USACE QA Laboratory for this project will be assigned by the USACE Kansas City District (KCD) Project Chemist in Kansas City, MO. This laboratory is responsible for analyzing designated project QA samples. The QA laboratory designated by the KCD for testing of QA split samples is Test America Laboratories, Inc., at 13715 Rider Trail North, Earth City, Missouri 63415 (referred to as Test America-St. Louis), for both chemical and radiological parameters. The point of contact at the Test America-St. Louis facility is Terry Romanko (314-298-8566).

1.2 PROBLEM DEFINITION / BACKGROUND

1.2.1 Problem Definition

Shaw will perform remedial actions at the FMSS, a FUSRAP site under the jurisdiction of the USACE Kansas City and New York Districts. Task-specific Work Plans will contain a problem definition section that describes the problem to be solved and project goals. Site-specific maps, diagrams, existing data, and possible regulatory requirements shall be discussed.

Soils located on the FMSS contain thorium and radium, and to a lesser degree uranium, above the site-specific cleanup levels established for the FMSS. Deposition of radionuclides was either by soil and sediment transport along the former Lodi Brook and Westerly Brook channels, by emplacement of fill containing radionuclides, or by past waste disposal practices. Properties with FUSRAP waste include 88 designated commercial, government, and residential tracts. Sixty-four (64) of these properties have previously been remediated by removal actions as authorized under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The Maywood Feasibility Study addresses soil and building contamination meeting the definition of FUSRAP waste at the remaining 24 properties (including the MISS and the Stepan Company) within the FMSS. Maximum concentrations of these radionuclides of approximately 37500 picoCuries per gram (pCi/g) ^{232}Th, 609 pCi/g ^{226}Ra, and 7600 pCi/g ^{238}U have been detected in buried residues or soils.

Chemicals are also known to be present on some of these properties. In particular, the soils have exhibited elevated concentrations of volatile organics (methylene chloride, acetone, methyl ethyl ketone [MEK], benzene, toluene, and ethylbenzene in the parts per million [ppm] range); acid extractables; and metals (aluminum, arsenic, barium, cadmium, chromium, copper, cobalt, lead, manganese, mercury, beryllium, silver, thallium, zinc, and nickel varying in concentrations from 1 ppm to several hundred ppm). In addition, all of the target compound list (TCL) pesticides have been detected infrequently in the low part-per-billion (ppb) range. Some soil borings also exhibited the presence of gasoline and fuel oil components, various methylated benzenes, caffeine, and the essential oils alpha-pinene and d-limonene.

Groundwater analyses have detected volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), including but not limited to benzenes, toluene, xylenes, 1,2-dichloroethene, and phenol; the pesticide gamma-BHC at a maximum concentration of 0.03 ppb; and metal contaminants including aluminum, arsenic, lead, chromium, copper, cobalt, nickel, vanadium, and barium.

The USACE is responsible for FUSRAP waste as defined in the Federal Facilities Agreement that states:

- All radioactive and chemical contamination, whether commingled or not, occurring on the MISS.
- All radioactive contamination exceeding the action levels agreed to in the Record of Decision and related to thorium processing at the Maywood Chemical Works (MCW), occurring on a vicinity property.

- Non-radioactive chemical contamination that occurs on vicinity properties if the contamination is mixed or commingled with radioactive contamination that exceeds cleanup criteria.
- Non-radioactive contamination that originated at the MISS or is associated with specific thorium manufacturing or processing activities at (MCW) that resulted in the radioactive contamination.

Detection of these chemicals in various matrices has been accomplished as part of several tasks. Much of this effort was focused on characterization of soils and groundwater, as well as evaluation of a soil sorting and rinsing operation as a mechanism for reducing the volume of soil to be shipped and thus reducing cost.

The tasks completed to date on this project include:

- Pre-design investigations to delineate soil excavation limits at all commercial / government vicinity properties.
- On-site field demonstrations of gravel separation and rinsing and radiological sorting of soil technologies.
- Development and implementation of a work plan for the FMSS groundwater remedial investigation.
- Time critical removal action of contaminated sediments in the West Howcroft Road drainage swale, following heavy rains deposited by Hurricane Floyd on September 16-17, 1999.
- Characterization of radiological contamination in Stepan buildings.
- Remediation of the 72 Sidney Street, 170 Gregg Street, 150/160/174 Essex Street, 80 Hancock, 100 Hancock Street, former I-80 Right-of-Way, 167 NJ Route 17N, 8 Mill Street, 239 NJ Route 17N, 23 West Howcroft Road, 85-103 NJ Route 17N, 200 NJ Route 17N, 137 NJ Route 17N, and Ballod properties including shipment and off-site disposal of the contaminated soils.
- Construction of an on-site radiological laboratory.
- Ongoing water treatment of groundwater encountered during excavation and storm water runoff.
- On going work plan and report preparation associated with PRAR/CCOR, Master Construction Work Plan, Site Safety & Health Plan, Quality Control Plan, etc.

The tasks currently in progress are:

- Remediation at the 149-151 Maywood Avenue and 100 West Hunter Avenue properties and final restoration of 99 Essex Street and 113 Essex Street properties
- Associated soil load-out evolutions and wastewater processing

The scope of future work currently planned for this project includes the follow:

- General
  - Design, remediation, and restoration of MISS, Stepan, and remaining commercial / government vicinity properties.
  - Excavation, handling, sampling, analysis, and disposal of buried drums and contents currently located on the 149-151 property.
  - Excavation, handling, transportation, and off-site disposal of the remaining accessible radiological contaminated soils exceeding cleanup standards; and backfill and restoration at the commercial / government vicinity properties and MISS and Stepan properties.

  - Verification sampling of remaining excavations during final status surveys (FSS) using Environmental Protection Agency (EPA) document 402-R-97-016, *Multi-Agency Radiation Survey and Site Investigation Manual* (*MARSSIM*) (EPA 2000b).

- Structures
  - Further characterization of radiological contamination in buildings.
  - Demolition of Building 76, the pumphouse, and the reservoir on the MISS to allow access to contaminated soils.
  - Potential demolition of Buildings 11, 13, 15, 20, 67, and 78 on the Stepan property to allow access to contaminated soils.
  - Demolition and/or decontamination of Buildings 4, 10, 13, 15, 20, 67, and 78 to remediate contamination in buildings.

For each delivery order involving sampling and analysis of environmental media, the corresponding task-specific Work Plans will contain sampling and analysis sections. They will address the site- and task-specific issues that are not discussed in this CDQMP. A narrative describing the task will be included that will state the specific problem to be solved or the decision to be made. The goal of the investigation will be clearly stated. A description of the work site, including an area map, location map, site map, site history as it relates to the current work, and any unusual conditions will be included. The text will include diagrams detailing areas to be sampled as relevant to the definition of the investigation goals. These sections will also contain a summary of site geology / hydrogeology as known, prepared to a level of detail such as to provide a comprehensive description of the site. The discussion will include enough information about the problem, the past history, any previous work or data, the regulatory or legal context, and any relevant regulatory requirements to present a clear description of the project objectives. It also should specify rationale for selection of sampling locations and test methods and frequencies.

1.2.2 Goals of the Investigation and Remediation

Remedial action has been and will continue to be conducted at the FMSS to ensure that risks to human health or the environment from potential exposure to impacted materials are either eliminated or reduced to prescribed safe levels. Media of concern will be remediated to these levels.

To meet the overall project objective, procedures for sampling, chain-of-custody, laboratory instrument calibration, laboratory analysis, reporting of data, internal QC, audits, preventive maintenance of field equipment, and corrective action have been developed and implemented and are described in other sections of this CDQMP. They will provide information for site evaluation and assessment leading to remediation. The procedures will ensure technically sound and legally defensible data. Each task-specific Work Plan will be used to identify specific task objectives as they relate to site action levels and remediation. The task-specific Work Plan for each FMSS task or activity will also provide the details, in tabular form, of the analytical parameters, methods, and quantitation levels.

General objectives of this CDQMP are as follows:

- To provide data of sufficient quality and quantity to support ongoing remedial efforts and further define the project contaminants of concern, if possible.
- To provide data of sufficient quality to meet applicable State of New Jersey and federal concerns (e.g., reporting requirements) as identified in the FMSS *General Environmental Protection Plan* (GEPP) (USACE 1999).
- To ensure samples are collected using approved techniques and are representative of existing site conditions.

- To specify QA/QC procedures for both field and laboratory methodology to meet the USACE and other applicable guidance document requirements such as:
  - EPA SW-846, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, Version 2 (EPA 1997).
  - EPA, QA/R-5, *Requirements for Quality Assurance Project Plans for Environmental Data Operations*, March 2001 (EPA 2001).
  - USACE, EM 200-1-6, *Chemical Quality Assurance for HTRW Projects*, October 1997 (USACE 1997).
  - DoD Quality Systems Manual for Environmental Laboratories, Version 1, October 2000
  - USACE, *Radionuclide Data Quality Evaluation Guidance*. May 2009 (USACE 2009).

1.2.3 Work Sites Description

The FMSS is located in Bergen County, New Jersey, approximately 20 kilometers (km) (12 miles [mi]) north-northwest of New York City and 21 km (13 mi) northeast of Newark, New Jersey. It is described in detail in the GEPP (USACE 1999). The reader is directed there.

1.2.4 Site History

The MCW was constructed in 1895. In 1916, the plant began extracting thorium and rare earth metals from monazite sands, by an acidic process, for use in manufacturing industrial products such as mantles for gas lanterns. The plant also produced a variety of other materials, including lithium compounds, detergents, alkaloids, and oils. The plant stopped accepting monazite sands for extraction of thorium in 1956, but it processed stockpiled materials until 1959. Based on available historical information and knowledge of the chemical processes involved, the chemicals identified as having been used in the thorium extraction process include sulfuric acid, nitric acid, ammonium hydroxide, and ammonium oxalate. Oxalic acid was also used at the site in the production of higher-grade thorium.

A detailed discussion of the site history is given in the GEPP (USACE 1999) and the reader is directed to the GEPP for follow-up.

1.3 PROJECT DESCRIPTION

Each task-specific Work Plan provides a description of the work that will be performed in order to provide an overall picture of how the project will resolve the problem or questions described in Section 1.2.1 (Problem Definition). A general description of the sampling will be included. Anticipated task start and completion dates will be included in addition to the following:

- Measurements that are expected during the course of the task and the approach that will be used.
- Applicable technical, regulatory, or program-specific quality standards, criteria, or objectives if they differ from those in this CDQMP.
- Any special personnel and equipment requirements that may indicate the complexity of the project.
- Assessment tools that will be employed for the task (program technical reviews, peer reviews, surveillance, technical audits, etc.).
- Project schedule or a sequence of milestones and their expected durations. If individual sampling plans will be developed for discrete task plans, their preparation schedule will be included.

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2.0 DATA QUALITY OBJECTIVES (DQO)

Data Quality Objectives (DQOs) are qualitative and quantitative statements that specify the quality of data required to support decisions made during investigation activities, and are based on the end uses of the data being collected. Detailed, site-specific DQOs shall be provided in the task-specific Work Plans and shall clearly describe what data are needed and how that data will be used to satisfy project DQOs.

For radiological samples, analytical test methods will be selected that have Minimum Detectable Activities (MDA) that meet the DQOs for the project. Similarly, for chemical analyses, methods shall be chosen that have Practical Quantitation Limits (PQLs) lower than the established Data Quality Objectives to the greatest extent practicable. Such test method pre-selection provides the highest probability that generated data is useful in making project decisions.

The DQO process is designed to provide a means to determine what type of data need to be collected, as well as to ensure that the data collected are scientifically sound, legally defensible, and of known, documented quality. The DQO process used for this remedial action follows the method outlined in MARSSIM (EPA 2000b) and the *Guidance for the Data Quality Objectives Process* (EPA 2000c) and in EM-200-1-2, *Technical Project Planning Process* (USACE 1998). The DQO process was chosen because it is an established process that identifies quality of data required for decisions.

An analytical DQO summary for these investigations is presented in the form of quality control limits for precision and accuracy in Appendix B. Any deviations or exceptions will be detailed in the task-specific Work Plan. All QC parameters stated in the specific SW-846 methods (i.e., percent recoveries) will be adhered to for each chemical listed.

Laboratories are required to comply with all methods as written. Laboratories selected will be required to submit all lab method SOPs and references, and the actual method detection limits (MDLs) to be achieved in all chemical analyses to Shaw and the USACE. For radiological parameters in soil, Shaw and the USACE will set the MDA to comply with the project requirements and the selected laboratory will be required to meet these limits.

In accordance with EPA guidance (EPA 2000c) and USACE guidance (USACE 1997), a combination of Screening Level and Definitive Level data will be required for each project. Definitive data is typically data generated under laboratory conditions using EPA-approved procedures. Data of this type, both qualitative and quantitative, are used for determination of source, extent, or characterization and to support evaluation of remedial technologies and preliminary assessment memorandum. The elements in the DQO process are as follows:

- Statement of the problem / Data Uses
- Identification of the decisions
- Data needed to meet objectives
- Definition of study boundaries
- Determination of decision rules
- Placement of limits on decision errors
- Optimization of design

The ability of a data generation process to meet the DQOs is provided through the establishment of data quality criteria, which include precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS) parameters. DQOs are also met by meeting certain goals for the PQL concentrations. Laboratory and field sampling activity documentation will be used to assess the PARCCS parameters. To provide for reliability of field sampling procedures and materials, QC samples will be collected or prepared at a defined frequency for each medium sampled, sample shipment, and each sampling event.

In addition to the collection of QC samples, QA samples will be collected at a frequency of five percent of the field samples collected for FSS samples and environmental monitoring samples only. There are no QA split samples collected for air, excavation control, and document control samples. QA split samples will be submitted to a separate USACE QA lab. The QA laboratory will be assigned by the USACE KCD.

The following subsections present the development of the DQOs for the FMSS investigations, remedial designs, and remedial actions.

2.1 STATEMENT OF THE PROBLEM / DATA USES

The FMSS vicinity property soils have been impacted primarily by radionuclides, specifically ^{226}Ra, ^{232}Th, and ^{238}U. If certain FMSS property soils and debris are contaminated with these radionuclides, or any other parameters listed in the final Record of Decision (ROD), at concentrations that exceed acceptable risk levels, they will be removed and transported off-site for disposal. Additionally, it will be necessary to show that remedial activities do not result in contaminant concentrations in the air, surface, and/or groundwater that exceed regulatory limits for on-site or off-site impact to workers, members of the public, and the environment.

The problem is to identify the types, quality, and quantity of data that will be used to support the remedial action within the planned project schedule.

The remainder of chapter two addresses DQOs for soil and groundwater remediation.

2.2 IDENTIFICATION OF DECISIONS

There are four key decisions that must be made to support project objectives. The key questions are:

1. **Work Area Remediation**—Do post-remedial site soil concentrations meet the appropriate cleanup criteria?
2. **Verification of Remedial Action**—Are there sufficient data to demonstrate that the FMSS vicinity properties have been remediated as specified in the ROD?
3. **Groundwater Remedial Investigation**—Have enough groundwater sample data been generated to adequately characterize groundwater contamination and thus allow for informed groundwater treatment decisions to be made? Is there enough data to allow us to assert that wastewater collected during remediation activities and treated on-site are below the discharge limits established by the Bergen County POTW?
4. **Transportation/Disposal—**Are the concentrations of contaminants of concern below the maximum concentrations allowed by a given soil disposal facility?

Associated with each of the key decisions are intermediate or follow-on decisions termed decision elements. The key decisions and decision elements are discussed in the following sections.

2.2.1 Work Area Remediation

The primary decision for work area remediation is whether soil concentrations for radionuclides and selected metals are reduced to levels that are less than the appropriate cleanup criteria. Decision elements are associated with individual soil excavation areas within each of the identified work areas. The decision as to whether all contaminated soils have been removed, and therefore that remaining soil analyte concentrations meet cleanup action levels, will be made for each excavation. The following are actions that would be taken to help answer the study questions:

- The excavation area is backfilled
- Additional soils are excavated

Inputs to this decision are discussed in Section 2.3.

The key decision for the demonstration of clean closure is whether there is sufficient site data to demonstrate that all accessible contaminated soils have been removed. The following are actions that would be taken to help answer the study questions:

- The FMSS properties are qualified as remediated via the radioisotopic results of a final status survey (FSS).
- Additional excavation of soil is required for successful remediation.

Sampling activities described in this document are used to support preparation of excavations for clean closure. Final verification surveys and verification sampling will be described in property-specific final status survey work plans.

2.2.2 Groundwater Remedial Investigation

The key question concerning the adequacy of groundwater sampling is whether groundwater characterization is sufficient to determine whether groundwater contaminant concentrations exceed action levels, and whether the exceedances can be attributed to historical site operations, or other off-site sources. To some extent, the answers to these questions will depend on the accuracy of groundwater modeling in predicting contaminant distribution. This will likely be an iterative process, in which initial sampling guidance, which may be provided by numerical models, will be succeeded by follow up sampling events. The actions that could be taken to help answer the study questions are that:

- Groundwater has been adequately characterized to determine:
  - Whether remediation is required, and if required, to develop preliminary remediation goals by evaluating the feasibility of remedial alternatives.
  - Whether contamination can be attributed to historical operations, or to off-site sources.
- More samples are needed.
- The model needs to be revised or a new model employed.

In addition, as part of the groundwater program, wastewater (excavation water, storm water runoff, etc.) shall be tested periodically. The accuracy of this data relative to Publicly Owned Water Treatment facility (POTW) requirements shall be considered in deciding whether to discharge these waters to the POTW.

2.2.3 Transportation and Disposal

The key question concerning the adequacy of sampling of soils destined for off-site disposal depends on the following:

- Whether sampled soils are representative of the soil quantity being shipped.
- The accuracy and precision of test data relative to the landfill disposal criteria and permitting requirements for contaminant concentrations.
- Possible changes in the concentration of contaminants over time.

The actions that may result are:

- Additional soil samples are collected from the disposal pile.
- Soil is shipped to the off-site disposal facility.

2.3 DATA NEEDED TO MEET OBJECTIVES

One major input decision is assurance that an individual work area has been remediated. This will be demonstrated through the use of field screening methods, in situ field measurements, and laboratory analytical methods for measurement of radiological constituents, which are stored in the EDMS (see Section 4.7). Inorganic and organic concentrations have been and will continue to be determined by laboratory analysis. These measurements will be used in nonparametric statistical tests as part of the final status surveys to demonstrate successful remediation for all contaminants of concern at the FMSS properties (^{238}U, ^{226}Ra, and ^{232}Th, plus any other contaminants listed in the ROD) or that may be discovered during a given site investigation.

A second major input decision is the conclusion that groundwater has been characterized adequately enough to determine the source of the contamination and the feasibility of treatment. PQLs (see Section 2.8.3 for definition of PQLs, also known as reporting limits [RLs]) for groundwater testing, must be lower than the proposed Maximum Contaminant Levels (MCLs) and New Jersey Groundwater Quality Criteria for chemicals and the National Primary Drinking Water Regulations for radionuclides. The groundwater program has adequately characterized the nature and extent of all chemical and radiological contamination in groundwater. Several groundwater plumes within the MISS, notably a benzene, lithium, and arsenic plume have been delineated. The remedial investigation determined that tetrachloroethene, trichloroethene, and dichloroethene plumes in Rochelle Park are derived from an offsite source; i.e., they are not associated with waste derived from the MCW. A baseline risk assessment is presently being prepared to determine the risk to various receptors within the FMSS due to contaminants present in groundwater, surface water, and sediment. Additionally, initial stages of the Feasibility Study have been initiated. Monitored Natural Attenuation (MNA) is being evaluated in conjunction with groundwater modeling efforts to determine if a reduction of benzene to below cleanup standards is likely due to the presence of aerobic and anaerobic bacteria present in the groundwater system. Two other chemicals, lithium and arsenic, exhibit concentrations well above cleanup action levels. The source of these two chemicals is believed to be the retention ponds on the MISS. No treatment schemes have been proposed yet for these chemicals.

2.4 DEFINITION OF STUDY BOUNDARIES

The study boundaries for the FMSS vicinity properties are defined in the ROD (USACE 2003d). The FMSS consists of properties in the boroughs of Maywood and Lodi and the township of Rochelle Park, New Jersey that became contaminated by thorium processing operations at the former MCW. The ROD

states that these remedial actions are limited to hazardous substances released during the aforementioned thorium processing operations. More specifically, the Federal Facilities Agreement (FFA) states that USACE is responsible for FUSRAP waste, defined as:

- All radioactive and chemically impacted materials, whether mixed together or not, occurring on MISS.
- All radioactive impacted materials from past thorium processing at the MCW site above action levels on any nearby property.
- Any chemically impacted material on nearby properties that is mixed with radioactivity above cleanup criteria.
- Impacted material that originated at MISS or was associated with specific thorium manufacturing or processing at MCW.

The remedial actions are to remove and dispose of all accessible soils that are above the cleanup criteria, and to treat and discharge groundwater and excavation water that is contaminated with radionuclides of concern or chemicals above acceptance criteria.

2.5 DEVELOPMENT OF DECISION RULES

2.5.1 Work Area Remediation

The cleanup criteria for radionuclides, SVOCs, VOCs, metals, etc. are contained in Appendix A of this CDQMP.

During excavation activities, a combination of exposure rate monitoring and remedial support soil sampling will be conducted to determine if radiological contaminants have been removed to a level below established clean-up goals. When remedial support data suggests that the appropriate cleanup level has been attained, final status survey measurements will be collected and evaluated against defined clean-up criteria. These will consist of soil samples collected and analyzed by a state-certified radioanalytical laboratory (gamma/alpha spectroscopy) and collection of gamma walkover survey data. Section 2.1.3 of the FSP discusses the final status surveys to be performed. FSS and associated clearance evaluations are conducted based on guidance provided in NUREG 1575 (MARSSIM, EPA 2000b) and according to the requirements of the Master Final Status Survey (FSS) Plan (USACE 2001a).

2.5.2 Groundwater Remediation

For the groundwater program, the upper 95% confidence limit of the mean of each chemical and radiological contaminant data set shall be compared to the most stringent (lowest) groundwater and soil action levels. The action levels used for this project are the MCL and New Jersey Groundwater Quality Criteria for water and the soil impact to groundwater and New Jersey direct contact residential criteria for soils. If the upper 95% confidence limit is less than the action level, no cleanup action will be required. If the upper 95% confidence limit is greater than the action level, a treatment scheme shall be developed. The radiological cleanup levels for groundwater and surface water are as follows:

Table 2-1
Radiological Cleanup Levels for Groundwater and Surface Water

Ra-226 plus Ra-228	5 pCi/L
Total uranium	30 μg/L
Gross alpha	15 pCi/L (excluding uranium and radon)
Gross beta	50 pCi/L

As stated earlier, the cleanup criteria for chemical parameters are listed in Appendix A of this CDQMP.

2.6 SPECIFY THE LIMITS ON DECISION ERRORS

Because decisions pertaining to remediation will be based on analytical data, an attempt is made to define, and if possible, limit decision errors that may result from the limitations of the sampling and analyses. To limit decision errors, analytical method data indicator objectives have been established and are presented in Section 2.8.

Limits on decision errors will be controlled through development of a sampling and analytical methodology to demonstrate that sufficient data have been generated for a decision. Methodology described in MARSSIM (EPA 2000b) will be followed to determine the number of measurements needed for final status surveys. This methodology consists of a statistical determination of the number of required sampling points. Statistical determination of the number of sampling points will also be used for the groundwater and material transportation and disposal programs. Determination of the number of samples depends on:

- The difference between the mean value of a contaminant of concern and the cleanup level.
- The precision of the mean values for a given parameter as determined by the standard deviation of the mean.
- The distribution of past and more recent data (e.g., normal, lognormal, non-parametric, etc.).
- Values established for decision errors.

Analysis of soil samples could potentially result in the incorrect reporting of the concentration of a contaminant. The two types of decision errors that could result are the reporting of false positives (Type I) and the reporting of false negatives (Type II). False positives and false negative decision errors are defined in the context of hypothesis testing, where the terms are defined with respect to a null hypothesis. The null hypothesis states that the concentration of a given contaminant of concern is above the cleanup action level. A false positive decision error occurs when the null hypothesis is rejected when it is true and corresponds with an analytical false negative (or more accurately, the analytical result is biased so low that the incorrect decision is made that the contaminant concentration is below the cleanup action level). A false negative decision occurs when the null hypothesis is not rejected when it is false and corresponds with an analytical false positive (the analytical result is biased so high that the incorrect decision is made that the contaminant concentration is above the cleanup action level).

Potential consequences of an analytical false positive (for establishment of soil remediation design limits and remedial support sampling decisions) are as follows:

- Unnecessary excavation and disposal of soils that meet cleanup criteria.
- Incorrect identification of additional areas as exceeding cleanup criteria when in reality they meet cleanup criteria.

Potential consequences of an analytical false negative (for establishment of soil remediation design limits and remedial support sampling decisions) are as follows:

- Failure to remove soils that exceed the cleanup criteria.
- Failure to identify additional areas within the FMSS properties that require remediation.

- Verifying that the property under consideration is remediated when in fact accessible soils exceeding the cleanup criteria remain.

Potential consequences of an analytical false negative (for FSS) are as follows:

- Failure to remove soils that exceed the cleanup criteria.

Potential consequences of an analytical false positive (for FSS) are as follows:

- Unnecessary excavation and disposal of soils that meet cleanup criteria.

Potential consequences of an analytical false positive (for the groundwater treatment decision) are:

- Unnecessary treatment of FMSS groundwater that is below cleanup standards.
- Possible incorrect interpretation that contaminated groundwater is migrating off-site.

Potential consequences of an analytical false negative (for the groundwater treatment decision) are:

- Failure to treat groundwater that is contaminated above specific parameter action levels.
- Failure to notify adjacent property owners that groundwater migrating onto their property is contaminated.

Potential consequences of an analytical false positive (for the soil disposal decision) are:

- Unnecessary shipment of below cleanup criteria soils to the soil disposal facility.

Potential consequences of an analytical false negative (for the soil disposal decision) are:

- Failure to ship soils that are contaminated above cleanup criteria to a disposal facility.

Definitive data are required for supporting project decisions. It is assumed that if the precision, accuracy, and completeness requirements specified in this section are met, and the minimum number of samples are collected in accordance with appropriate statistical tests, then definitive data will be obtained and can be used for performing remedial actions and monitoring. The limits on the magnitudes of decision errors selected for the FMSS site radiological data will be 5% for false positive (α) decision errors (corresponding to an analytical false negative; see consequences on previous page) and 10% for false negative (β) decision errors (corresponding to an analytical false positive; see consequences on previous page. Decision error rates may be set lower in coordination with USACE. A decision level will be established for each sample count and/or count protocol so that there is 5% probability of a false positive result. This decision level is defined as the Critical Level, or L_c. The count result shall be reported as the sample activity where the sample counts are greater than the L_c. The Minimum Detectable Activity (MDA) will be reported in place of the sample activity for those sample results that are less than the L_c - except where unbiased results are permitted. The MDA shall be equal to or less than the DQO for those cases where the count results are less than the L_c, - except where it is permitted that the DQO be exceeded.

For chemical data, the decision error limits shall be 5% for false positive (α) and 15% for false negative (β) decision errors.

2.7 OPTIMIZATION OF THE DESIGN

As a result of the DQO process, the optimum sampling design is derived for this remedial action. While all of the properties have been sampled, the quality and quantity of existing data do not enable completion of accurate designs. Two types of survey data will be collected to optimize the design. Characterization data for radionuclides will be collected at all accessible FMSS properties for which the quality and quantity of existing data do not enable completion of accurate designs. Remedial support survey data will be collected to guide the excavations such that all soils containing radionuclide concentrations that exceed the cleanup criteria are removed.

To optimize the design for the groundwater characterization effort, additional data shall be collected from areas of known contamination to better define contamination plumes and sources.

2.8 STANDARDS / CONTROLS TO ENSURE OBJECTIVES ARE MET

The analytical data used as inputs to the DQO process must be of known and sufficient quality to support the end use of the data. Analytical data of known and acceptable quality for the intended use are generated by the implementation of carefully chosen QA/QC protocols, both in the field and in the laboratory. QA/QC goals are set for:

- Each single measurement.
- The entire data set of which the single measurement is a part.

Each individual measurement should be precise, accurate, representative, comparable, and part of a complete data set. Precision, accuracy, representativeness, comparability, and completeness are often referred to by the acronym PARCC, and are known as the PARCC parameters. The PARCC parameters of precision and accuracy can be quantified for a single measurement and for a complete data set. Representativeness and comparability are not as quantifiable as precision and accuracy, although there is necessarily some overlap between the parameters of representativeness, precision, and accuracy. Analytical completeness is assessed by comparing the total number of analytical results expected for a data set (based on the number of samples collected) with the total number of usable (i.e., not qualified R, or rejected) analytical results. The test measurement method must be sensitive enough to ensure that method detection limits are less than project cleanup criteria. The count time for radiological samples will be set so that the Minimum Detectable Activity (MDA) for a typical sample type meets the DQOs for the project. Similarly, for chemical parameters, the method chosen will be, to the greatest extent practicable, the one that achieves reporting limits that are below cleanup levels. Methods may require modifications to achieve project DQOs.

The goal for analytical precision and accuracy is that each measurement should be associated with laboratory QC that is within limits. QC limits for both chemical and radiological parameters are those required by the requested analytical method. This CDQMP sets forth the QC limits (see Appendix A) required for the FMSS properties remediation for radiological and chemical analyses. Matrix samples including matrix spike (MS) and matrix spike duplicate (MSD) samples (MS/MSD for organics and MS/MD (matrix duplicate) for inorganics), will be used to assess the effect of matrix on the measurement process. Laboratory control samples (LCS), or blank spikes, will be used to assess the accuracy and precision of the measurement process in the absence of effects from field samples. Method blanks will be used to assess possible laboratory contamination, and field blanks – such as trip blanks and equipment rinseate blanks – will be used to determine sources of contamination from the sampling location, the sample container, the sampling equipment, or sample transport.

Requirements for precision and accuracy to meet data quality goals are identified in Appendix B. Requirements for completeness are noted in Section 2.8.4.

Data quality indicators are percent differences between replicate or duplicate sample (precision), percent recoveries of blank or matrix spike results (accuracy), and MDLs or MDAs, and PQLs (sensitivity). Data indicator objectives are established to ensure the quality of the analytical data produced by the laboratory. A general description of each of the data indicator objectives is given below along with the data assessment procedures. All data must meet or exceed limits for precision and accuracy stated in the individual analytical methods.

2.8.1 Precision

Precision is the degree to which the measurement is reproducible and is frequently determined by comparison of laboratory designated duplicates or designated laboratory MS/MSDs. Precision is important because it represents the ability of the laboratory to produce consistent results. Precision of analyte concentrations in field samples is typically measured by the collection and testing of field duplicate samples. In that case, precision is calculated by the percent difference (%D) between the field duplicate results. That is:

$$\%D = (A - B)/[(A + B)/2] \times 100$$

where: A = *first sample result*
B = *second sample result*

Standard deviation (S) is calculated as follows:

$$S = \left(\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1} \right)^{1/2}$$

x_i = *measured value of the* i^{th} *replicate*
$\bar{x}$ = *average of replicate measurements*
n = *number of replicates*

If more than two samples are collected at the same location and at the same time, precision will be calculated as % relative standard deviation (%RSD). %RSD may be calculated as follows:

$$\%RSD = \frac{S}{\bar{X}} \times 100\%$$

$\bar{X}$ = *average of replicate measurements*
S = *standard deviation*

For radiological laboratory replicate and field duplicate results, the absolute difference $|X_1 - X_2|$, provides an indication of precision if the average value of the two replicates is less than the action level. If the average value of the two replicates is greater than the action level, the relative percent difference (RPD), 100 x $|X_1 - X_2| / \overline{X}$ provides an indication of precision

See Appendix D of this QAPP, USACE Radionuclide Data Quality Evaluation Guidance for additional details on acceptance criteria for laboratory replicate and field duplicate results.

2.8.2 Accuracy

For chemical parameters, accuracy is reported as the percent recovery (%R) of a parameter from a laboratory or field sample spiked with a known value of the parameter for a given analytical procedure. Accuracy is important because it is a measure of the true concentration of a parameter for a given analytical procedure. The determination of the accuracy of a measurement requires knowledge of the true or accepted value for the parameter being measured and the value of the parameter for the unspiked sample. Accuracy is monitored for each matrix type. The %R may be calculated as follows:

$$\%R = \frac{X_s - X_u}{K} x\ 100\%$$

where: X_s = *measured value for spiked sample*
X_u = *measured value of unspiked sample*
K = *known value of the spike in the sample*

For radiological parameters, the percent difference (%D) is used to assess the accuracy of laboratory control sample (LCS), or blank spike results, and the Z score (EPA 2004) is used to assess the accuracy of matrix spiked sample results. Tracers, which are known spikes of either an isotope of the same element as the isotope of interest, or an element that is chemically very similar to the isotope of interest, are added to all field samples and batch QC samples and so provide a recovery value for each sample which is indicative of any losses or method anomalies that might have affected the isotope of interest. The %D is defined as:

$$\%D = \frac{SSR - SA}{SA} x100$$

Where:

%D is the percent difference
SSR is the measured result (spiked result)
SA is the spike activity (or concentration) added.

For matrix spike results, the Z score statistic is defined as follows:

$$\text{Z-Score} = \frac{SSR - SR - SA}{\phi_{MR}\sqrt{SSR^2 + \max(SR, UBGR)^2}}$$

Where:
max (x,y) denotes the maximum of x and y
φ_{MR} is the maximum allowable (relative) standard deviation at the UBGR
SSR is the spiked sample result
SR is the sample result

SA is the activity spiked into the sample

The terms φ_{MR} and UBGR are defined within Appendix D of this QAPP. Accuracy may also be impacted by blank contamination. The potential impacts of LCS, matrix spike, and blank results on sample results are evaluated within Appendix D of this QAPP.

2.8.3 Method Detection Limits and Reporting Limits

RLs will be based on MDLs, except that the RLs for samples analyzed under the Toxicity Characteristic Leachate Procedure (TCLP) will be the regulatory limits for individual compounds as listed in 40 CFR, Part 261.24, Table 1. The RL is often called the PQL.

MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from the analyses of seven blanks, each spiked in an identical fashion with the analytes of interest, so that the final concentration of the spiked solution is approximately two to five times the expected method detection limit. Following analyses, the mean and standard deviation of the seven results is calculated. The MDL may be calculated as follows:

$$MDL = t_{(n-1,\ \alpha = 0.99)} \times S$$

where: S = *standard deviation of the replicate analyses*
$t_{(n-1,\alpha=0.99)}$ = *one-sided 99% t-statistic*
n = *number of measurements of analyte*

Typical RLs are provided in Appendix A of this QAPP. They are typically 2 to 10 times the MDL.

It should be recognized that MDLs and RLs are sample matrix dependent and may be raised due to matrix interferences and/or dilution factors.

Several parameters unique to radiochemical analyses are used to describe the sensitivity of the detection systems. These parameters are lifted directly out of the NUREG/MARSSIM guidance (EPA 2000b). They include the critical level (L_c), detection limit (L_d), and MDA.

L_c is the net response level (in counts) at which the detector output can be considered above background. It may be calculated as follows:

$$L_c = k\sqrt{2B} = 2.33\sqrt{B} \quad \text{for } \alpha, \beta = 0.05$$

L_d is the net response level (in counts) that can be expected to be seen with a detector with a fixed level of certainty. It may be calculated as follows:

$$L_d = k^2 + 2k\sqrt{2B} = 3 + 4.65\sqrt{B} \quad \text{for } \alpha, \beta = 0.05$$

where: k = *Poisson probability sum for* α *and* β *(assuming* α *and* β *are equal)*
B = *number of background counts that are expected to occur while performing an actual measurement*

The MDA is the a priori net activity level above the L_c that an instrument can be expected to detect 95% of the time. It may be calculated as follows:

$$MDA = C \times (3 + 4.65\sqrt{B})$$

where: *C = factor to convert from counts to concentration*
B = number of background counts that are expected to occur while performing an actual measurement

2.8.4 Data Completeness

Completeness refers to the amount of valid data obtainable (by the specific method the laboratory used with the instrument to be employed) from a measurement system compared to the expected amount of data, and is usually expressed as a percentage. Completeness may be calculated as follows:

$$Completeness = \frac{amount\ of\ valid\ data}{expected\ amount\ of\ data}\ X\ 100\ \%$$

Valid data can be defined as either acceptable data or quality data. Quality data are data that passed all QC indicators. Acceptable data are data that are either quality data or data for which corrective actions have been performed. The minimum completeness for acceptable data required for this project is 95%. The minimum completeness is 98% for each of the analytical methods employed in the task-specific Sampling and Analysis Plans (SAPs). Completeness for quality data shall be 80%.

Analytical data will be divided into two categories:

- Non-critical measurements
- Critical measurements

Non-critical measurements are defined as organic and wet chemistry (e.g., anions, alkalinity, Total Kjeldahl Nitrogen (TKN), etc.) soil and water quality parameters, while critical measurements are defined as radiological constituents, metals, and TCLP. Non-attainment of QA objectives for non-critical measurements will have a minor impact on project objectives. The most important objective for critical measurements is completeness because it is based on data validity and directly impacts project decisions. Non-attainment of completeness may result in the need for resampling at specific locations. Water quality parameters may be critical if one is considering discharge of groundwater, storm water, or decontamination water.

3.0 DOCUMENTATION AND RECORDS

3.1 DATA REDUCTION, VALIDATION, AND DOCUMENTATION

3.1.1 Calculations

All FMSS samples requiring radiological testing, including waters, soils, air filters and smears are routinely analyzed by UFML, except for USACE QA split samples, which are analyzed by Test America Laboratories in Earth City, MO. The analyses of water and soil samples, as well as smears that are used as equipment blanks, are described below. The air filters and all other smear analyses are discussed in the Radiation Protection Plan, a component of the Site Safety & Health Plan (USACE 2006a).

Soils

The UFML method to be used for routine detection of ^{232}Th, ^{226}Ra and ^{238}U in soils is gamma spectrometry. The method is based upon the HASL-300 Method Ga-01-R, Gamma Radioassay (HASL-300, 28th Ed., Feb. 1997, US DOE Environmental Measurements Laboratory).

Soil loadout soil samples are analyzed "as is" (i.e., without drying and grinding) since knowing the exact radionuclide activity in these samples is not as critical as other types of samples. For FSS, document control, and backfill samples, the samples are dried 4 to 10 hours (or overnight) in a 105°C oven. Each dried sample is placed in a pulverizer and pulverized, then transferred to a Marinelli or tuna can container for counting using gamma spectrometry. Excavation control samples are also dried, but are sometimes first counted wet. Such measurements quantify the ^{232}Th, ^{226}Ra and ^{238}U activities by counting the gamma-emitting decay products ^{228}Ac, ^{214}Pb, and ^{234}Th, respectively. Since in each case the two radionuclides are assumed to be in equilibrium, the activity of the parent radionuclide equals the activity for the daughter radionuclide. Correction factors for wet-dry analysis (i.e., to account for the presence of moisture in soil sample undergoing gamma spectrometry) have been developed for the project. An additional correction factor has been developed for Ra-226 gamma spectrometry analyses (applicable to dried soil samples that have had insufficient time to allow for the in-growth of the photon emitting daughters in the Ra-226 decay chain.

The equation for calculation of the activity of each isotope in picoCuries (pCi) per gram (pCi/g) is:

$$C\ (pCi/g) = \frac{CF \times (Cpm\ of\ sample\ peak - Cpm\ background\ peak)}{(2.22\ dpm/pCi) \times D \times W}$$

where: *CF=Applicable correction factor(s)*
D = efficiency of counting for the gamma spectrometer (cpm/dpm)
W = weight of solid (grams)

Isotopic uranium, isotopic thorium, Ra-226, and Ra-228 in soil can be measured by the onsite laboratory. The equations for calculation of the activities of these isotopes are discussed in the Waters Section below.

Waters

Wastewater samples are collected and analyzed in accordance with the requirements established by the Bergen County POTW. Currently, wastewater samples are collected after 125,000 gallons have been processed. The sample collected after 125,000 gallons of wastewater have been processed is analyzed for gross alpha (GA) and gross beta (GB). After every 500,000 gallons have been processed, a sample is

collected and analyzed for not only GA and GB, but also iso-thorium, iso-uranium, Ra-226, and Ra-228. The GA method used depends upon the amount of total solids (dissolved plus suspended) in the sample. If there are less than 500 parts-per-million (ppm) of total solids, EPA Method 900.0, Gross Alpha and Gross Beta radioactivity in Drinking Water is used. If the total solids is greater than 500 ppm, Method 7110C (Standard Methods Ref.), Coprecipitation Method for Gross Alpha Radioactivity in Drinking Water, is utilized. EPA Method 900.0 is always used for GB.

Measurement of iso-thorium, iso-uranium, and Ra-226, utilizes an isotopic tracer spike followed by acid digestion. Measurement of Ra-228 relies upon barium sulfate carrier recovery to estimate the Ra-228 recovery. The SOPs for these methods are equivalent to Eichrom methods ACW02, Revision 1.3 for iso-uranium and ACW10, Revision 1.0 for iso-thorium (Horwitz 1993); EPA 903.0, Alpha-Emitting Radium Isotopes in Drinking Water (modified)(EPA 1980) and HASL-300 method Se-02, Isotopic Uranium, Isotopic Thorium, and Radium-226 (modified) for Ra-226 (DOE 1997); and EPA Method 9320 (modified), Ra-228 in Drinking Water, for Ra-228 (EPA 1997). These SOPs are located in the EDMS (see Section 4.7). For iso-uranium and iso-thorium, an aliquot of a homogenous sample is digested with an acid mixture. Uranium-232 and thorium-229, man-made isotopes, are added to the samples, as required, in known quantities as tracers. The solution is subsequently passed through an ion exchange resin column that separates the elements of interest, each of which are subsequently coprecipitated as tetrafluorides with neodymium fluoride. The activity of each thorium isotope, C (pCi/l), is calculated from the alpha spectrometry count as follows:

$$C\ (pCi/l) = \frac{\text{Cpm of sample (thorium isotope peak) - Cpm background (thorium isotope peak)}}{(2.22\ dpm/pCi) \times D \times V \times Y}$$

where: D = *efficiency of counting for the alpha spectrometer (cpm/dpm)*
V = *volume of water (liters)*
Y = *fractional recovery of the Th-229 (^{229}Th) tracer.*

The conversion value of 2.22 disintegrations per minute (dpm) per picocurie (pCi) is based on the standard value for 1 curie of 3.700E10 disintegrations per second (dps) (CRC 1974-75). 3.7E10 dps/curie X 60 sec/min X (1 curie / 10^{12} pCi) = 2.22 dpm/pCi.

The activity of a given uranium isotope in a water sample, F (pCi/L), is calculated from the alpha spectrometry count as follows:

$$F\ (pCi/L) = \frac{\text{cpm of sample (^{238}U peak) - cpm background (^{238}U peak)}}{(2.22\ dpm/pCi) \times D \times V \times Y}$$

where: D = *efficiency of counting for the alpha spectrometer (cpm/dpm)*
V = *volume of water (liters)*
Y = *fractional recovery of the U-232 (^{232}U) tracer*

For ^{226}Ra, the method coprecipitates radium with barium and lead sulfate, and purifies it by re-precipitation from EDTA solution. Barium-133 (Ba-133) tracer is added to the sample during the initial sample preparation. Citric acid is added to the sample to ensure that complete interchange occurs before the first precipitation step. The final $BaSO_4$ precipitate, which includes Ba-133, Ra-226, radium-224 (Ra-224), and radium-223 (Ra-223) is counted by alpha spectroscopy for Ra-226. The activity of Ra-226, A (pCi/L) is calculated from the alpha spectrometry count as follows:

$$A\ (pCi/L) = \frac{\text{cpm of sample (^{226}Ra peak) - cpm background (^{226}Ra peak)}}{(2.22\ dpm/pCi) \times E \times V \times R)}$$

Where:
E = predetermined counter efficiency for Ra-226 in $BaSO_4$
V = volume of sample aliquot in liters
R = fractional chemical yield (Ba-133 activity recovered / Ba-133 added)

For Ra-228, radium in the sample is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from an EDTA solution. After an in-growth of 36 hours, equal to approximately 6 half-lives of Ac-228 and allowing for the transient equilibrium of the Ra-228 to Ac-228, the actinium is coprecipitated with yttrium oxalate, purified, and beta counted. The initial chemical separation process isolates radium from potential beta emitters such as cesium, strontium, and lead. The actinium yttrium oxalate is counted in a gas proportional counter for gross beta. Since the Ac-228 was in equilibrium with Ra-228 at the time it was precipitated as the oxalate, the gross beta count equals the Ra-228 activity. The activity of Ra-228, D (pCi/L) is calculated from the gas proportional detector count as follows:

$$D = \frac{C}{2.22 * E * V * R} \; X \; \frac{\lambda * t_2}{\left(1 - e^{-\lambda t_2}\right)} \; X \; \frac{1}{\left(1 - e^{-\lambda t_3}\right)} \; X \; \frac{1}{e^{-\lambda t_1}}$$

where:
C = average net count rate, cpm
E = efficiency of detector, for Ac-228 or comparable average beta energy nuclide
V = volume of the sample in mL or g
R = fractional chemical yield of the yttrium carrier (R_Y) X fractional chemical yield of the barium carrier (R_{BaSO4})
λ = decay constant for Ac-228 = 0.001884 min^{-1}
t_1 = time interval between first Yttrium Hydroxide step (11.80) and start of counting time
t_2 = time interval of the count of the sample = 30 minutes
t_3 = the in-growth time of the actinium in minutes measured from the last barium precipitation

The fractional chemical yield of the yttrium carrier, R_Y, is determined from the weight of yttrium oxalate recovered and the mass of yttrium added (step 11.59). The mass of yttrium oxalate precipitate is converted to mass of yttrium by multiplying by the ratio of yttrium in one mole of $Y_2(C_2O_4)_3\ H_2O$.

$$R_Y = \frac{\left(M_{YOx}\right)\left(\frac{2 * Z_Y}{MW_{YOx}}\right)}{M_Y}$$

where:
M_{YOx} = mass of yttrium oxalate recovered
M_Y = mass of yttrium added
Z_Y = atomic weight of yttrium
MW_{YOx} = molecular weight of yttrium oxalate ($Y_2(C_2O_4)_3\ H_2O$)
The atomic weight of yttrium is multiplied by two because there are two moles of yttrium in one mole of yttrium oxalate.

The fractional chemical yield of the barium carrier R_{BaSO4}, is determined by weighing the $BaSO_4$ precipitate, converting that weight to the weight of barium, and dividing it by the weight of barium added.

For SW-846 methods, the procedures to be used for calculation of the concentration of organics can be found in Sections 7.7 of both Method 8260B and 8270C for volatile and semivolatile organics, respectively, Sections 7.5.6 and 7.6 of Method 8081A for pesticides, and Sections 7.8 and 7.9 of Method 8082 for PCBs. For metals by Method 6010B, there is no calculation for aqueous samples; that is, the instrument response, which is based on a method acceptable calibration, provides the analyte concentration. If a dilution is required, the instrument response must be multiplied by the dilution factor to obtain the analyte concentration in the original sample. For metals in soils by 6010B, the dilution factor incurred by sample preparation is approximately 100 (depends on actual sample weight and percent moisture). The instrument response is then multiplied by the dilution factor to obtain the analyte concentration in the sample. For solid samples, the result is also divided by the weight fraction of dry solids in the sample to obtain the final result.

3.1.2 Procedures to Ensure Data Integrity

The principal criteria to assure data integrity during collection and reporting shall include the following:

- For collection, the number of samples to be collected will be statistically determined to provide the highest probability that the data quality objectives outlined in this CDQMP will be met.
- For testing, both field and laboratory QC samples will be analyzed in order to evaluate potential blank contamination, analyte recovery from the sample matrix, laboratory and field sample testing precision, and proper instrument calibration. The laboratory will be instructed how to proceed when recoveries are outside of established QC limits, blank contamination is present, or other unforeseen problems arise. These instructions, entitled Guiding Principles, are contained within the first two pages of Appendix E of this QAPP.

3.1.3 Treatment of Outliers

Outliers are extreme high or low measurements that are set apart from most of the data. They may arise from matrix interferences, errors in transcription, sample preparation, analytical method, or regional variations in the background geochemistry. Apparent outliers may also represent areas with unusually high concentrations.

Outliers that are obvious mistakes should be corrected, otherwise they will disproportionately affect the statistical descriptors of the data set. Outlier statistical tests, however, should only be used to identify potential outliers that require further evaluation (EPA 2000a). EPA 2000a recommends 1 of 4 types of statistical tests: Dixon's Extreme Value test (when sample size is less than or equal to 25), Discordance test, Walsh's test (non-parametric test), or Rosner's test. After identification as a potential outlier, consideration should be given to the magnitude of the observation with respect to the assumed distribution for the data set. It is important to note that no datum should be discarded as an outlier based solely upon the results of these statistical tests. The chosen statistical test should be performed on the original data set and the truncated data set.

Decisions on the use or rejection of outlier data will be aided by the laboratory supplying information justifying an extreme result, especially when associated with QC results that exceed criteria.

3.1.4 Data Management

The laboratory will employ a three-phase review. First, the analyst reviews the data, then the analyst's supervisor reviews the data, and finally a QA person checks for proper QA/QC protocol as well as any results that appear unusual.

3.1.5 Data Archive

Sample data is saved electronically within the laboratory database, project database, and project shared hard drive. Hardcopies are retained for 6 months in file cabinets within the laboratory building. After the 6-month period, data is stored in boxes in a different location onsite or disposed as directed by USACE. Electronic data packages and data validation reports received by the FMSS Project Chemist or Sample Coordinator are scanned and the scanned files moved into Documentum, an electronic data and document repository for the FMSS project. Hardcopy data will be stored for the duration of the project.

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4.0 MEASUREMENT / DATA ACQUISITION

4.1 SAMPLING PROCESS DESIGN

Systematic evaluation of the objectives of the investigation, the use of the data to be collected, and an evaluation of the data quality requirements form a methodology for designing an adequate and appropriate sampling plan. The following discussion presents three approaches to defining the sampling requirements: the Observational Approach, which focuses on the data needed to define and evaluate site conditions based on source / pathway / receptor evaluation; Technical Project Planning, which breaks down project planning into distinct phases; and EPA's DQO process, which focuses on a need/ decision/ action evaluation for the site. Each of these planning methodologies is used to define the minimum acceptable and necessary data set for each investigative area or media type. Once the minimum data set is defined, refinements and additions are made to fulfill all identified and anticipated data requirements, and to resolve or constrain uncertainty. These approaches require systematic identification of the end use of the data. If there is no identifiable action to be taken or decision to be made based on a given proposed data set, then these data are deleted from the sampling plan. The systematic evaluation of collected data and the decision / action process result in collecting only needed data in a cost-effective and expedited manner.

This Section describes the approach that will be employed in the task-specific Work Plans for defining sampling requirements. Shaw shall follow EM 200-1-2, Technical Project Planning Guidance for HTRW Data Quality Design, for defining data needs and data quality objectives for FMSS project tasks in those Work Plans.

4.1.1 Observational Approach

The Observational Approach assesses the site's "probable conditions" based on the available data. It is intended that the "probable conditions" be understood to the extent necessary to meet the sampling objectives (i.e., evaluate potential risks and resolve data gaps).

As part of the approach, a detailed conceptual model is developed based on the current understanding of site conditions including:

- Primary Sources.
- Primary release mechanisms.
- Secondary sources.
- Secondary release mechanisms.
- Pathway of migration.
- Exposure routes.
- Potential receptors.

The primary release mechanisms for the primary contaminants of concern (PCOCs) are:

- Erosion.
- Wind-blown dust.
- Surface water runoff.
- Operation activities / construction disturbances.
- Infiltration / percolation to adjacent and underlying soils.

- Solubility or suspension in ground water.
- Ground-water infiltration / discharge to surface water.

Secondary sources of PCOCs include surface water and features receiving surface water such as drainageways and sediments, groundwater, soils surrounding and underlying storage and disposal areas, and on-site and off-site sediments. Secondary sources may also include receptors, which consume contaminated biotic or abiotic matrices.

Secondary release mechanisms include:

- Channel flow / surface water transport
- Sediment deposition (in-channel and over-bank)
- Sediment traps
- Dredging of sediments from drainageways
- Overland flow / storm water runoff
- Infiltration to subsurface soil
- Fugitive dust
- Potential ground-water movement from source areas

Potential contaminant of concern (COC) exposure routes for human and ecological receptors include:

- Inhalation of dust
- Ingestion of soil, surface water, ground water, contaminated fish, plants, or animals
- External exposure
- Dermal contact with soil, surface water, sediments, or ground water

The Observational Approach uses "decision rules" (as does the DQO process) for the purpose of linking data needs and uses. This approach helps to focus the sampling plan and sampling strategies by developing a conceptual model that identifies sources, pathways, and potential receptors. To augment the conceptual model, a DQO discussion that follows EPA's guidance is presented in Section 2.0.

4.1.2 Technical Project Planning

The Technical Project Planning approach (USACE 1998) occurs in several phases. In Phase I, the team identifies the site approach, including site objectives, regulator and stakeholder perspectives; and then prepares a Phase I Memorandum for Record to document the team's findings and decisions during Phase I.

In Phase II, one defines and documents data needs by determining the role of the data user, and evaluating the use of existing data.

In Phase III, one plans the sampling and analysis approach, including various data collection options.

In Phase IV, the description of the data collection program is finalized. This includes communicating with the customer and the regulators, encouraging participation by all stakeholders, preparing a Final Scope of Work or Work Plan, and preparing a cost estimate.

Phase V is the actual implementation of the data collection program. During and after the program, the project team will assess the data collection effort, including whether or not project data quality objectives have been attained. It will use this information to guide and plan future data collection efforts.

4.1.3 Data Quality Objective Process

The DQO process is discussed in Section 2.0.

4.1.4 Sampling Network

For soils, the line transect method will be used to locate areas of contamination. The types of samples required will include all matrices known or having the potential to be contaminated including surface and subsurface soils, concrete, building interior and exterior surfaces, groundwater, surface water, sediments, and storm water.

4.2 SAMPLING METHODS REQUIREMENTS

Field screening and sampling covers all sampling activities at the FMSS properties including sampling of soils, building materials, backfill materials, air, groundwater, surface water, sediments, and wastewater. Additionally, it covers radiological background determination (downhole logging, gamma walkover surveys, soil gas surveys for VOC screening, meteorological monitoring, and air monitoring for industrial hygiene requirements). Section 2.0 of the FSP describes the methods and techniques to be used for sampling / monitoring all applicable media and parameters. Sampling protocols will follow USACE Environmental Sampling Instructions (EM-200-1-3). The task-specific Work Plans will describe specific soil sampling activities for the various tasks such as pre-design investigation, remedial confirmation / final status surveys, groundwater remedial investigation, wastewater treatment, and materials handling in preparation for transport and disposal. In the FSP, **Tables 3-1** and **3-2** provide bottle requirements, preservation, and holding times to extraction and/or analysis for all analytical parameters and matrices. Support facilities will be required and will include:

1. Area where hand-held field surveying equipment can be properly calibrated and kept periodically charged.
2. Decontamination area for cleaning of sampling equipment, including drill bits and sampling tools.
3. Area for storing / stocking sampling supplies such as tape, foil, solvents, bailers, paper towels, etc.
4. Clean area for sample management.

4.2.1 Corrective Actions

Technical staff and project personnel will be responsible for reporting all suspected technical and QA nonconformances or suspected deficiencies of any activity or issued document by reporting the situation to the Project Manager or his / her designee and the CQCSM. The Project Manager will be responsible for assessing the suspected problems in consultation with the CQCSM and Sampling Coordinator to make a decision based on the potential for the situation to impact the quality of the data. When it is determined that the situation warrants a reportable nonconformance and corrective action, then the CQCSM will initiate a NCR, or Corrective Action Report (CAR) in accordance with the CQCP (USACE 2005). The CQCSM will be responsible for ensuring that corrective actions for nonconformances are initiated by:

- Evaluating all reported nonconformances
- Controlling additional work on nonconforming items
- Determining disposition or action to be taken
- Maintaining a log of nonconformances
- Reviewing NCRs and corrective actions taken

- Ensuring that NCRs are included in the final site documentation project files

If appropriate, the CQCSM will ensure that no additional work dependent on the nonconforming activity is performed until the corrective actions are completed.

Corrective action for field measurements may include:

- Repeating the measurement to check the error
- Checking for all proper adjustments for ambient conditions such as temperature
- Checking the batteries
- Re-calibrating equipment
- Checking the calibration
- Modifying the analytical method including documentation and notification (e.g., standard additions)
- Replacing the instrument or measurement devices
- Stopping work (if necessary)

The Project Manager or designee is responsible for all site activities. In this role, the Project Manager may at times be required to adjust the site activities to accommodate activity-specific needs. When it becomes necessary to modify an activity, the responsible person notifies the Project Manager of the anticipated change and implements the necessary changes after obtaining the approval of the Project Manager and the USACE Task / Technical Lead, as required. All such changes will be documented on USACE Field Change Request Form (FCRF, see **Figure 4-1**) that will be signed by the initiators and the Project Manager and USACE Task / Technical Lead. The FCRF for each document will be numbered serially as required. The FCRF will be attached to the file copy of the affected document. The Project Manager must approve the change in writing or verbally before field implementation. If unacceptable, the action taken during the period of deviation will be evaluated in order to determine the significance of any departure from established program practices and action taken.

The Project Manager for the site is responsible for controlling, tracking, and implementing the identified changes. Reports on all changes will be distributed to all affected parties, including the USACE Task / Technical Lead. USACE will be notified whenever significant program changes in the field are made.

Shaw® Shaw Environmental, Inc.

Field Change Request (FCR)

Section 1 through 4 to be filled out by Shaw Environmental (Shaw), Section 5 to be filled out by USACE

PROJECT:	OFS No:	Field Change Request:
FUSRAP Maywood Superfund Site		**FCR #** **Rev #**

To: _____ Dept: _____ Location _____ Date _____

Re: ☐ Drawing No. _____ Title _____
☐ Spec. No. _____ Title _____
☐ Other _____

1. DESCRIPTION (Items involved, submit sketch if applicable) _____

2. REASONS FOR CHANGE (If from disposition of nonconformance report, list report number) _____

3. RECOMMENDED DISPOSITION
☐ Technical Clarification (COR approval required)
☐ Out of Scope (COR/ACOR approval required)
☐ Cost of Growth
☐ ROM Estimate (If Applicable) **$** _____
☐ Schedule Impact _____

Shaw Initiator (Signature/Title):	Date

4. Shaw Project Manager (Signature)	Date	Site Manager Concurrence (Signature)	Date

5. USACE DISPOSITION
☐ Approved per recommended disposition
☐ Not approved (give reason)
☐ Approved with modification(s) [describe below]

Technical Mgr. (Signature)	Date

COR Concurrence (Signature)	Date	ACOR Concurrence (Signature if required)	Date

COR Approval (Signature	Date	ACOR Approval (Signature if required)	Date

Engineer signs and transmits to Project Engineer with copies to:

_____	Project Manager	Project Engineer	_____
_____	Contract Manager	Cost (WVN & ATP)	_____
_____	Quality Control Representative	Doc Control File:Q1.5.1	_____

Figure 4-1
Field Change Request Form

4.3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Once the samples have been received, the sample custodian must inspect the samples against the chain of custody and any other documentation for nonconformances. Any discrepancies are documented on the sample receipt verification form and communicated to the laboratory project manager immediately, in the case of the offsite laboratory. The laboratory project manager shall contact the Project Chemist to resolve the issue. Once the paperwork from the sample receipt is completed and reviewed, it is given to the laboratory project manager for log-in to the Laboratory Information Management System (LIMS) computer system. For UFML, any discrepancies are resolved immediately with the field person delivering the samples to the lab, or the Maywood Task Manager for the activity pertaining to the collected sample(s). The sample information from the hardcopy COC is entered into the UFML database by one of the laboratory technicians.

4.4 ANALYTICAL METHODS REQUIREMENTS

4.4.1 Analytical Procedures

The following text provides detailed information on analytical procedures. The task-specific Work Plans shall contain tabular summaries of analyses required for each site or project. These summaries shall contain the number of samples to be collected for each method including field and laboratory QC samples. The actual quality assurance methods and procedures employed in the subcontractor laboratories' daily activities are provided in EDMS (see Section 4.7).

4.4.1.1 Laboratory Analytical Procedures

All samples shall be prepared and analyzed in accordance with laboratory test methods, copies of which are stored in EDMS (see Section 4.7). These procedures contain detailed descriptions of the sample preparation and analyte detection steps, including instrumentation and other laboratory apparatus, reagent and standards preparation, and calibration. It also includes discussions of interferences, sample collection (including containers and preservation), QC samples, calculations, and reporting of results. Each individual task Work Plan shall reference one or more of these analytical methods. Use of alternate procedures or modified procedures must be pre-approved by the Contracting Officer (CO), or designee.

4.4.1.2 Field Measurement Methods

Initial field measurements may consist of geophysical surveys, gamma walkover surveys, building surveys, soil gas surveys, organic screening or inorganic screening.

The geophysical survey will be used primarily to define subsurface features to be considered during the remedial work. Geophysical screening techniques are presented within the 200 series SOPs in EDMS (see Section 4.7).

Radiological testing of soils by gamma spectrometry is employed using UFML (see description in Section 1.1.2.6).

Soil gas surveys will be conducted as appropriate. The SOP for conducting soil gas surveys is SOP 105, a copy of which is found in EDMS (see Section 4.7).

Data collected from these field reconnaissance activities has been used to establish the boundaries, soil sample locations, and well locations for site investigations and remedial actions.

Organic and inorganic screening methods including hand-held monitors or real time soil analyses by an on-site laboratory may be utilized to help determine extent and location of non-radiological contaminants.

4.4.2 Analytical / Statistical / Control Parameters

Section 5.3.5 of the DOD Quality System Manual (DOD 2000) discusses when laboratories must implement corrective actions. Refer to the Guiding Principles, contained within Appendix E of this QAPP (the Guidance), for specific corrective actions to be taken when QC control limits are exceeded.

4.4.2.1 Accuracy - Organics

Accuracy shall be evaluated by requiring the laboratory to treat no less than 10% of all FMSS samples (per matrix) as MS/MSD pairs, to analyze at least one blank spike (or LCS) with the entire analyte list for a given method (analyte lists are shown in **Table A-1** of Appendix A for the FMSS project) per matrix per sample batch (a sample batch contains a maximum of 20 environmental samples), to add surrogate spikes to all samples as required by the method, and to analyze method blanks every 12 hours of analysis time or every batch, whichever is more frequent. The field sample coordinator will clearly identify the sample chosen for matrix spiking and the equipment rinsate blanks on the sample chain of custody. Under no circumstances will trip blanks or equipment rinsate blanks be analyzed as MS/MSD pairs. The sample designated for MS/MSD analyses will have approximately triple the volume of a normal sample. Triple volume is required for aqueous samples, not soil samples. For FMSS, it is practical to batch samples and assign MS/MSDs per investigation or remediation site. Obviously, for large sites multiple batches may be necessary. MS/MSD samples should be spiked by the laboratory with those compounds that have been detected in FMSS property soils most frequently. Lists of MS/MSD compounds for the various test methods are provided in **Table B-1** of Appendix B of this QAPP. Both the MS and MSD samples must be reanalyzed if the recoveries are outside of laboratory-derived acceptable recovery ranges listed in **Table B-1** of Appendix B. Specific off-site laboratory corrective action guidelines are provided in Appendix E.

If analysis results show surrogate recoveries outside laboratory-derived acceptable ranges (in-house limits established as per SW-846 guidance [Method 8000, section 8.7]) the laboratory shall take corrective action in accordance with the Guiding Principles, contained within Appendix E of this QAPP. If method blanks are consistently out of control (see Chapter One of SW-846) for one or more analytes, the laboratory will be required to stop analysis of field samples and find and eliminate the source of contamination. If the source of contamination cannot be found in a timely fashion, Shaw shall procure another laboratory subcontractor for those analyses.

LCS samples are clean matrices, such as organic-free water or high purity sodium sulfate spiked with all of the analytes for a given method as listed in **Table A-1** of Appendix A. LCS samples will be analyzed with each batch. If there are aqueous and solid samples within the same batch, the laboratory must run an aqueous LCS for the aqueous samples and a solid LCS for the solid samples. The LCS provides method performance data for samples free from interferences. As such, they serve as a warning for laboratory methods that are out of control. Like surrogate spikes, control limits must be established for LCS results using SW-846 Method 8000, Section 8.7. If an LCS result falls outside QC recovery limits, the LCS should be reanalyzed in real time with respect to sample analyses, to see if the failure represents a transient instrumental condition. A second failure indicates a fundamental problem that must be corrected before sample analysis can restart. All of the sample results associated with that LCS (only for those analytes that failed LCS recovery) must be reanalyzed after the method performance problem has been corrected. The corrective actions taken by the laboratory must follow the corrective action procedures described in the Guiding Principles (Appendix E). If a laboratory is in the process of implementing a new GC/MS method, and LCS recovery limits have not yet been established, the temporary percent recovery

limits shall be 80 to 120% for water and 70 to 130% for solids. For Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), and Total Recoverable Petroleum Hydrocarbons (TRPH) (413.2, 418.1, and/or 1664) methods, QC limits may be established by the laboratory for surrogate, LCS, and MS/MSD recoveries, as appropriate. If not, a default recovery range of 65-135% may be used.

In all cases, construction of control charts or QC limit ranges should eliminate outliers, which are defined as those exceeding the mean plus or minus three standard deviations. In addition, reanalysis as a result of QC recovery exceedances as described here, may not be required if the spike signal is obscured by gross contamination. In such cases, the laboratory **must** substantiate its case for not reanalyzing or following the Guidance by providing the proper chromatograms or other pertinent raw data. The final decision as to the acceptability of a laboratory deviating from the requirements of this CDQMP will be made by the USACE CO.

4.4.2.2 Accuracy - Inorganics (non-radiological) and General Chemistry

Accuracy shall be evaluated by requiring the laboratory to treat no less than 5% of all FMSS samples (per matrix or per batch) as a MS sample, to analyze LCSs with the entire analyte list for a given method, and to analyze method blanks as required by the selected analytical method. Shaw will coordinate field sample collection with the laboratory so that batch size is maximized and the frequency of MS sample designation is not too high. The sample chosen for matrix spiking should be similar to other samples in the batch. The field sample coordinator will clearly identify the sample chosen for matrix spiking and the equipment rinsate blanks on the sample chain of custody. Under no circumstances will equipment rinsate blanks be analyzed as MS/MD pairs. The sample designated for MS/MD analyses will have approximately triple the volume of a normal sample. Triple volume is required for aqueous samples, not soil samples. For FMSS, it is practical to batch samples and assign MS samples per investigation or remediation site.

MS inorganic samples should be spiked with the complete analyte target list for a given method at a concentration per analyte of about 3 to 5 times the expected background. The percent recovery of the spiked compounds will provide a measure of accuracy. The MS must be reanalyzed if any of the analyte recoveries are outside of acceptable recovery ranges. The default QC recovery range typically used for inorganics and general chemistry parameters is 75 to 125%. Prior to any redigestion / reanalysis, sample preparation and test data must be reviewed to see if the cause of the spike recovery exceedance can be determined. If an out-of-control condition is discovered in this process, it must be corrected prior to the redigestion / reanalysis.

Similar to organics, the LCS should be performed for each sample batch up to a maximum of 20 samples per batch. If there are aqueous and solid samples within the same batch, the laboratory must run an aqueous LCS for the aqueous samples and a solid LCS for the solid samples. If the LCS recovery falls outside of the QC criteria (default range is 80 to 120%), the LCS must be reanalyzed for the analyte(s) falling outside criteria. If the LCS recovery fails a second time, corrective action must be taken to improve test measurement performance for the analyte(s) of concern. All samples associated with the faulty LCS must be reanalyzed (only for those analytes that failed LCS recovery) after the problem has been corrected.

The post-digestion spike sample recovery test described in Section 8.5 of Method 6010B of SW-846 must be performed on one representative sample from a given analytical batch whenever new or unusual matrices are encountered. It is the responsibility of the analyst to look at the samples prior to digestion and select the representative sample in a conservative manner, such that in his or her judgment, the selected sample is the one most likely to contribute interference. If the results of the interference tests are outside the QC limits provided in Section 8.5, these results must be discussed in the case narrative. For

SW-846 Series 7000 methods, spiked samples may be analyzed as described in Section 8.6.2. If the results are outside of the QC limits stipulated in Section 8.6.2, the method of standard additions (Section 8.7) must be employed.

QC criteria for metals analysis will conform to the requirements of SW-846 and Appendix B of this CDQMP QAPP.

4.4.2.3 Accuracy - Radionuclides

The accuracy described here applies to isotopic radium, thorium, uranium, and gross alpha and beta. Accuracy shall be evaluated by requiring the laboratory to analyze a method blank and LCS at a minimum frequency of 5% of field samples per matrix or per sample preparation batch, whichever is more frequent. For alpha spectroscopy, isotopic tracers shall be added to every sample to evaluate matrix effects. Shaw will coordinate field sample collection with the laboratory so that batch size is maximized. In addition, a field duplicate shall be collected at a minimum frequency of 10% for FSS and environmental monitoring field samples. The field sample coordinator will clearly identify the sample chosen for the equipment wipe sample blank on the sample chain of custody.

The LCS should be performed for each sample batch up to a maximum of 20 samples per batch. If there are aqueous and solid samples within the same batch, the laboratory must run an aqueous LCS for the aqueous samples and a solid LCS for the solid samples. If any of the LCS or isotopic tracer analyte recoveries fall outside of the current control limits established by the laboratory (default limits are 80 to 120% for aqueous samples and 70 to 130% for solid samples, and should only be used if laboratory-established limits are not available), the LCS and/or tracer spike solution must be reprepared and reanalyzed for the analyte(s) falling outside criteria (see the Guidance in Appendix D of this QAPP). All samples associated with a faulty LCS must be reanalyzed (only for those analytes that failed LCS recovery) after the problem has been corrected. The LCS should mimic the nominal activity of samples of interest. Recommended LCS activity levels for the radionuclides of interest in soils are 2 to 3 pCi/g each of ^{226}Ra and ^{232}Th, and 5 to 15 pCi/g for ^{238}U. Recommended LCS activity levels for the radionuclides of interest in waters are 10 to 15 pCi/L for GA, 35 to 50 pCi/L for GB, 3-6 for Ra-226, 3-6 for Ra-228, 5-10 each for U-234 and U-238, and 3-6 for Th-230.

For alpha spectrometry measurements, chemical separation specificity shall be verified. The observed peak energy of each radionuclide shall be within 40 keV of the actual radionuclide energy.

For gamma spectroscopy measurements, a target radionuclide list must be provided. It must contain an example calculation plus uncertainties for all quantitated radionuclides. Positive identification shall be achieved by the following:

1. The observed peak energy is within 2 keV of the target energy.
2. There are no radionuclide gamma peaks interfering with the radionuclide of interest. If an interference is present, the peak for the radionuclide of interest must be corrected to remove the contribution from the interferent.
3. Calibration standards will have been run at the frequency specified in the approved SOP.

4.4.2.4 Sensitivity

The offsite laboratory will have developed MDLs in accordance with 40 CFR 136 Appendix B. The PQL, also known as the reporting limit, shall be set at 3 to 5 times the MDL. It is understood that PQLs are subject to approval by the USACE Contracting Officer. MDLs should be consistent with the MDLs shown in SW-846. **Table A-1** of Appendix A contains the most current Contract Laboratory PQLs for all

analyses. All results for dilution runs must be provided. A discussion as to which values are to be reported must also be provided in the Case Narrative.

For UFML, radionuclide quantitation must be calculated according to project-approved SOPs. Minimum Detectable Activities (MDAs) specified in the SOPs and in Appendix A of this QAPP must be met. Analytical uncertainties shall be reported with all results, including all uncertainties associated with the analyses.

Matrix effects caused by highly contaminated samples will be reviewed to assess the laboratory's ability to meet sensitivity requirements. A detailed analysis of all failures to meet sensitivity requirements must be provided in the Case Narrative.

4.4.2.5 Precision

Precision is defined in DQOs Section 2.8.1 of this QAPP. It is represented by the Percent Difference (%D) between duplicate sample results, and the relative standard deviation for more than two results. The results of many laboratory control sample (LCS) results can be used to determine the mean precision (from the relative standard deviation of the average percent recovery) and accuracy (from the average percent recovery) for a given analyte since there are no matrix effects. For metals and radionuclides, laboratory duplicates (replicates of 1 field sample) will be analyzed at a rate of at least 1 in 20 or 1 per batch, whichever frequency is greater. Laboratory duplicates not meeting QC criteria must be reextracted / reanalyzed once. For organics, precision may be calculated from spiked and unspiked (if present) analyte results obtained from analysis of MS/MSD samples. Field duplicate results are used for both metals and organics to provide a measure of precision. Field duplicate samples are collected at a frequency of 5% for organic and inorganic, and 10% for radiological of the total number of samples of a given matrix or site, or one per batch, whichever is more frequent.

4.4.2.6 Laboratory Internal QC Checks

1. The analytical batch is defined by the group of samples that are prepared (extracted, digested, etc.) together and analyzed sequentially on a single instrument.
2. The Laboratory shall analyze internal QC samples at a frequency consistent with a given method. These shall include method blanks, MS/MSD (MS and laboratory duplicates for inorganic analyses) and LCS. The matrix used for LCS samples will be reagent grade water for aqueous samples and reagent sand for soils and sediments. Failure to analyze a matrix spike, LCS, or method blank will result in rejection of data.
3. One method blank will be analyzed per analytical batch. At a minimum, a method blank must be analyzed for every 12 hours analysis time for GC / mass spectrometry analyses. Chronic blank contamination from one or more analytes shall result in reselection of the Laboratory Subcontractor.
4. Second column confirmation will be required for all GC analyses except when results are between the MDL and PQL. The results obtained from the two columns should be less than 40% different.
5. The Laboratory should have control charts for surrogate recoveries and LCS at a minimum. These charts should be updated at least quarterly. The Laboratory Quality Assurance Plan must have detailed procedures describing corrective actions to be taken if QC criteria are exceeded for LCS, method blanks, surrogate recoveries, etc. for each method and matrix. It must also describe changes made to laboratory protocols or operations to prevent such exceedances from reoccurring.

4.5 ANALYTICAL QUALITY CONTROL REQUIREMENTS

4.5.1 Completeness

Completeness shall be evaluated both qualitatively and quantitatively. The project goals for completeness, expressed in percent, are provided in DQO Section 2.8.4 of this CDQMP. The qualitative determination will be a function of sample handling (in the field and in the lab), labeling, shipping, etc. The quantitative description will depend on the number of sample results that are rejected due to gross exceedances of QC criteria.

The completeness requirement for holding times is 95%. Samples exceeding holding times must be resampled and reanalyzed. Results from samples with proven matrix effects will not be used in calculating completeness.

4.5.2 Representativeness

Shaw accepts responsibility for ensuring that all field samples, including blind duplicates and QA splits, are representative of field conditions and are properly preserved. Samples with results that are rejected due to lack of preservation must be resampled and reanalyzed.

Laboratory procedures must detail the steps taken to ensure that the sample aliquot collected for analysis is representative of the whole sample.

4.5.3 Data Comparability

To ensure data comparability, laboratory procedures shall include, but not be limited to the following:

- Use of standard approved methodologies
- Methodologies for quantitation within test procedures, as appropriate
- Use of standard units and report format
- Use of standard measures of accuracy and precision for QC samples

Samples collected as QA split samples should be analyzed by the same or equivalent analytical methods with comparable MDLs/PQLs.

All final solid sample results shall be reported on a dry weight basis, and the percent moisture will be reported. If QA split samples sent to an independent laboratory yield results that are significantly different from the Contract Laboratory results, Shaw will investigate the discrepancies. If errors in sampling or testing are discovered, samples will be resampled / reanalyzed.

4.5.4 Preventive Maintenance

4.5.4.1 Field Instruments and Equipment

The field equipment for this project may include temperature probes, pH meters, conductivity meters, turbidimeter, platinum Eh electrode, dissolved oxygen meter, alpha / beta and gamma survey meters, organic vapor detectors (flame or photoionization detector), and geophysical equipment. Specific preventative maintenance procedures to be followed for field equipment are those recommended by the manufacturers. These procedures are included in the technical procedures governing the use of these instruments.

Field instruments will be checked and/or calibrated before they are shipped or carried to the field. Each field instrument will be checked for good condition and operability prior to use. Items such as frayed cords, loose components, or cracked casings shall be cause for not using the instrument. Operational checks against a traceable standard or reference with a known value shall be performed prior to use to ensure that the instrument is in proper calibration. Reference standards used in the field for calibration checks should be labeled with an expiration date and recorded in the log. Instruments found to be out of calibration or improperly responding to instrument checks will be recalibrated before use in the field. If the instrument cannot be calibrated, it will be returned to the supplier or manufacturer for recalibration, and a backup instrument will be used in its place. Calibration checks and calibrations will be documented on the Field Meter / Calibration Log Sheets in the Equipment Logbook. Any maintenance conducted on field equipment must be documented in the Equipment Logbook and the process documented, including the results of the check / calibration and any adjustments required. Any significant adjustment shall be cause for recalibration by the manufacturer or approved calibration facility.

Critical spare parts such as tapes, papers, pH probes, electrodes, and batteries will be kept on site to minimize down time of malfunctioning instruments. Backup instruments and equipment should be available on site or within one day shipment to avoid delays in the field schedules.

4.5.4.2 Laboratory Instruments

As part of their QA/QC Program, a routine preventive maintenance program will be conducted by all investigation-associated laboratories to minimize the occurrence of instrument failure and other system malfunctions. All laboratory instruments will be maintained in accordance with manufacturers' specifications and the requirements of the specific method employed. This maintenance will be carried out on a regular, scheduled basis and will be documented in the laboratory instrument service logbook for each instrument. The laboratory shall maintain an inventory of expendable parts and supplies to minimize downtime. Emergency repair or scheduled manufacturer's maintenance should be provided under a repair and maintenance contract with the manufacturer or authorized factory representatives.

4.5.5 Performance Evaluation Samples

Testing of performance evaluation (PE) samples by USACE laboratories may be part of a laboratory performance audit. The performance evaluation program may also include a maximum of two blind PE samples (provided by the USACE) for each matrix and analysis. PE samples provide an ongoing assessment of laboratory precision and accuracy. The analytical results of the analysis of performance evaluation samples are evaluated by USACE Kansas City District to ensure that laboratories maintain an acceptable performance.

Radiological PEs will be identified and supplied as required by the NJDEP pertinent to the regulations set forth in NJAC 7:18. These PEs may consist of EPA regulated PEs for Drinking Water analysis and US DOE PEs for Solid Hazardous Waste.

4.6 INSTRUMENT CALIBRATION AND FREQUENCY

This section describes procedures for maintaining the accuracy of all the instruments and measuring equipment used for conducting field tests and laboratory analyses. These instruments and equipment shall be calibrated before each use or on a scheduled, periodic basis according to manufacturer instructions using certified equipment or standards traceable to nationally recognized standards (as applicable).

4.6.1 Field Instruments / Equipment

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated with sufficient frequency (and at least annually) and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications. All field instruments for this purpose will have unique identifiers and each instrument will be entered into the Equipment Logbook before use in the field. The SSHO, Project Environmental Sampler, designee, or other assigned responsible individual will be responsible for performing and documenting daily calibration / checkout records for instruments used in the field.

Equipment to be used during the field sampling will be examined to certify that it is in operating condition. This will include checking the manufacturer's operating manual and instructions for each instrument to ensure that all maintenance requirements are being observed. Field notes from previous sampling trips will be reviewed so that the notation on any prior equipment problems will not be overlooked, and all necessary repairs to equipment will be carried out. Spare parts or duplication of equipment will be available to the sampling effort.

Calibration of field instruments is governed by the specific SOP for the applicable field analysis method, and it will be performed at the intervals specified in the SOP. If no SOP is available, calibration of field instruments will be performed at intervals specified by the manufacturer or more frequently as conditions dictate. Calibration procedures and frequency will be recorded in a field logbook.

Field instruments may include a pH meter; temperature probe; specific conductivity meter; respirable dust meter; turbidimeter; platinum Eh electrode; dissolved oxygen meter; hand held scintillation, Geiger-Muller, or proportional detectors for radioactivity screening levels; photoionization and flame ionization detectors for organic vapor detection; low/high volume air samplers; geophysical equipment, etc. If an internally calibrated field instrument fails to meet calibration / checkout procedures, it will be returned to the manufacturer for service and a back-up instrument will be calibrated and used in its place. Field instrument uses, detection levels, and calibration are summarized in **Table 4-1**.

Table 4-1
Field Instrument Uses, Detection Limits, and Calibration

Instrument	Uses	Detection Limits	Calibration	Comments
Total organic vapor meters	Sample screening for VOCs	PID - 0.2 ppm benzene or	1 point - PID benzene daily	Action level must be stated in Health and Safety Plan
	Health and safety screening	FID - 1.0 ppm methane	1 point - FID methane daily	Instrument cannot differentiate naturally occurring compounds from contaminants
			Verification check every 20 samples	PID cannot detect compounds with ionization potentials > 11 eV
Radiological monitoring	Monitoring of beta-gamma surface, gross gamma, alpha surface contamination levels	Daily calibration check varies by equipment	Daily source check per manufacturer	Action level must be stated in Health and Safety Plan
pH meters	Field screening of waters	N/A	2 point with standards at pH 7.0 and 4.0 or pH 7.0 and 10.0 daily	Accuracy is to within 0.5 pH units
Temperature	Determining water	N/A	To manufacturer	

(in-line)	temperature		instructions	
Conductivity meter	Determining conductivity of water	N/A	1 point in KCL solution	Calculations and acceptance criteria must be available in the field
Membrane electrode meter	Determining dissolved oxygen levels	N/A	1 point using calculated value for water at ATP at least once every 3 hours	Accuracy is to within 0.01 ppm
Gamma Spectroscopy System	Analysis of soil samples for general isotopic conditions	≤ 0.2 pCi/g for ROIs	Yearly at a minimum using a multi-gamma source from 60 - 1840 keV	Requires a low-background condition to enable proper detection conditions

Notes:
PID = photoionization detector
FID = flame ionization detector
N/A = not applicable
ATP = Ambient temperature and pressure
ROI = radionuclides of interest

4.6.1.1 pH Meter Calibration

The pH meter will be calibrated according to SOP 409, Onsite Water Quality Testing (see UFML SOPs in EDMS; see Section 4.7)

4.6.1.2 Temperature Calibration

Temperature measurement will be calibrated according to SOP 409, Onsite Water Quality Testing (see UFML SOPs in EDMS; see Section 4.7).

4.6.1.3 Conductivity Meter Calibration

A specific conductivity meter will be calibrated according to SOP 409, Onsite Water Quality Testing (see UFML SOPs in EDMS; see Section 4.7).

4.6.1.4 Organic Vapor Detection

Organic vapor detectors will be checked according to SOP 401, Operation of the MultiRAE Plus Multi-Gas Monitor and SOP 402, Operation of the TVA-1000 Photoionization / Flame Ionization Detectors.

4.6.1.5 Radiation Testing

Several types of radiation detection instrumentation will be used by Radiation Protection Technicians (RPTs) during the course of the project activities. They include sodium iodide (NaI) detectors used to monitor exposure rates and collect downhole gross gamma logging data, Geiger Muller detectors used for screening measurements, and scintillation detectors used to quantify levels of surface radioactivity on miscellaneous materials. Proper use of these instruments includes a series of QC measurements that will be reviewed as part of the data validation process. These are described below.

Each detector / meter combination will be calibrated no less than annually at a licensed calibration facility. At a minimum of once per day during use, each instrument utilized in the field will undergo the

following: source check, battery check, voltage check, and background check. Results will be recorded in a dedicated notebook in the form of a QC log. Instruments found to be operationally deficient will be tagged "out of service" and sent to an appropriate facility for repair and recalibration. Procedures for the operation and management of portable radiation survey instruments are established in the Radiation Protection Program (*Site Safety & Health Plan*, Appendix C, USACE 2006a).

4.6.2 Laboratory Instruments

Calibration of laboratory equipment will be based on approved written procedures. Records of calibration, repairs, or replacement will be filed and maintained by laboratory personnel performing QC activities. These records will be filed at the location where the work is performed and will be subject to QA audit. Procedures and records of calibration will follow USACE and Shaw-reviewed laboratory-specific QA Plans.

In all cases where analyses are conducted according to the EPA Region 2 or SW-846 protocols, the calibration procedures and frequencies specified in the applicable EPA Region 2 SOPs or SW-846 methods shall be followed, or be more stringent. For analyses governed by SOPs, refer to the appropriate SOP for the required calibration procedures and frequencies.

Records of calibration will be kept as follows:

- Each instrument will have a record of calibration with an assigned record number.
- A label will be affixed to each instrument showing identification numbers, manufacturer, model numbers, date of last calibration, signature of calibrating analyst, and due date of next calibration. Reports and compensation or correction figures will be maintained traceable to the instrument.
- A written step-wise calibration procedure will be available for each piece of test and measurement equipment.
- Any instrument that is not calibrated to the manufacturer's original specification or equivalent procedure shall be tagged out of service and not utilized for this project.

4.7 ELECTRONIC DOCUMENT MANAGEMENT SYSTEM (EDMS)

4.7.1 EDMS in use at FMSS

Two electronic systems are used by the Maywood Project to capture the permanent project record: an electronic document control system, Documentum, and the Maywood Site Sample Database (MSSDB). A quality program with strict controls is in place to ensure quality (USACE 2005).

Documentum is the integrated, computer-based document and information control system. It is used as the repository for records including the base contract, contract modifications, cost and schedule reports, QA/QC records, minutes of meetings, and reports and deliverables submitted to the client. Records are entered as files and sub-files under broad functional categories called "cabinets" which include Correspondence, Contract Management, Engineering, Construction, Procurement, Historic and Background Records, Community Relations, and Quality Control. Documentum provides multiple attribute search capabilities and is accessible to project members on site as well as from remote locations. Ultimately, at the conclusion of the project, the Documentum electronic record will be submitted to our client in accordance with the terms of our contract.

The MSSDB (based upon Microsoft™ Access) is used to capture field investigation and laboratory data and provides the capability to query and prepare data tables. Specific information captured includes field

related sampling and monitoring data including final status survey results, waste soil load out information that includes rail car number and verification sample results, and occupational training records. The field data includes descriptions of sampling locations, such as coordinates of sample locations, GW well development and purge data, and environmental monitoring data. The database also generates sequential sample labels /numbers prior to sampling events and incorporates sample tracking from collection through laboratory analytical result reporting and validation. Select USEPA and NJDEP regulatory criteria are loaded in the database, thereby permitting comparison of analytical results against the criteria. Data in the Access database can be linked to associated reports captured in Documentum.

4.7.2 Responsible Personnel

An on-site document control administrator is responsible for entering records and assisting users in retrieving records. This person is supported on an as-needed basis by Shaw corporate IT and Documentum specialists. The Maywood Project technical staff are responsible for identification of work products to be captured in Documentum, and determining the applicable attributes. Documentum is accessible by project personnel and the Documentum administrator.

An off-site Database Manager, who enters electronic laboratory data, administers the Access database. Field personnel enter field-related data directly. The database is also accessible by project personnel, the database manager, and the client.

4.7.3 Documented Procedures for use of EDMS

An electronic project record is a requirement of the prime contract. Documentum use is described in the Contract Management Procedures CMP 2, Management Information System as well as the Maywood Project Procedures PP 6-1-0 Project File Index; PP 6-2-0 Task File Maintenance; PP 6-4-0 Project Records Management Plan; and PP 7-5-0 Document Control.

The Access Database system use is described in the Database Documentation Manual, which includes a User's Guide.

4.7.4 Advantages and Limitations of the System

Documentum is a searchable, multi-attribute electronic project record, and will be a highly usable system to the USACE, USEPA, and DOJ when delivered following project conclusion. This advantage was emphasized to the USACE when attempts were made to take the earlier FUSRAP microfilm project records consisting of more than 7 million records and assign basis attributes to enable query and sorting capabilities. Documentum is available to project employees and the use of the system is easily learned.

Similarly, the MSSDB is available to designated Shaw employees and can be accessed from any location in the United States. This system is searchable, user friendly, and holds capability for USACE connection via a DSL line. Furthermore, the relational database permits preparation of project reports relating to sample information.

An advantage of the MSSDB is that it manages sample number assignment (automated) and tracking. There is a semi-automated process for importing electronic data deliverables from laboratories, minimizing data entry errors.

The MSSDB has a built in quality control in that the database enforces preferential integrity. Sample results must be linked to a specific sampling location, sampling number, and any other field related to that specific sample, or else it flags the entry. This provides a check against error in laboratory data reports.

As the MSSDB is MS-Access based and easily copied, it can be provided to the client in a usable format. It will be an end product deliverable as part of the project record.

Both Documentum and the MSSDB are secured by password protection and differing levels of authorized access, data entry, editing, changes, and utilization of data. Disadvantages of both systems are that they require administrators with an associated cost, and they require training for users.

4.7.5 Purpose of EDMS

Documentum contains some historical reports relating to the Maywood site. Further, the administrative record is contained on the Maywood project website and is linked to Documentum.

The MSSDB is used for historical measurement data. Shaw has integrated certain amounts of historical soil and water data from Bechtel as well as other investigations, into the MSSDB. This historical data helps us characterize areas with greater time depth. Note that the data entered are not comprehensive because of the labor-intensive effort required to manually enter it.

4.7.6 System Backup

Documentum is run on a dedicated Maywood project server. The server records are backed up daily on tapes. Additionally, monthly backup tapes are made and permanently stored.

The MSSDB is run on a Shaw corporate network system. This system is backed up daily by the secure Shaw corporate network.

4.7.7 Description of Quality Program

The MSSDB has built in quality controls designed to ensure data quality by employing cross-checks of relational attributes. The data is also frequently being used and reviewed by the Project Chemist, project engineers, and the Database Manager.

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5.0 ASSESSMENT / OVERSIGHT

Shaw will maintain an aggressive oversight program and implement a three-phase inspection process. These programs are addressed in detail in the CQCP (USACE 2005). The task-specific Work Plans shall describe the specific three-phase control procedures with particular emphasis on execution of field operations relating to sampling and analysis. Checklists to be used for implementation of three-phase control shall also be included in the task-specific Work Plans.

5.1 ASSESSMENTS AND RESPONSE ACTIONS

Performance and system audits of both field and laboratory activities will be conducted to verify that sampling and analysis activities are performed in accordance with the procedures established in the CDQMP and task-specific Work Plans. Audits of laboratory activities will include both internal and external audits. Field audits are described in the CQCP (USACE 2005).

5.1.1 Laboratory Audits

Laboratories that possess the appropriate State certification, are compliant with the most recently published version of the DOD Quality Systems Manual (QSM) (including the NELAC Standard Chapter 5 and Appendix requirements), and that successfully test performance evaluation samples (performance audits) are qualified to perform USACE environmental analysis (USACE 2001b).

Internal performance and system audits of laboratories will be conducted by the Laboratory QA Officer as directed in the laboratory QA Management Plan (see copies of the UFML and offsite laboratory Plans within EDMS). System audits are conducted annually by the laboratory or corporate QA manager and shall include examination of laboratory documentation of sample receiving, sample log-in, sample storage, chain-of-custody procedures, sample preparation and analysis, and instrument operating records. Internal performance audits are also conducted at a minimum frequency of twice per year. The UFML participates annually, and the offsite laboratory twice per year in PE studies conducted by outside agencies. The double blind format ensures that samples are introduced into the laboratory without their knowledge. Criteria for success of laboratory audits will be compliance with the QC requirements outlined in this QAPP.

Shaw is not contracted to perform laboratory audits; however, additional audits of laboratories may be planned and budgeted within specific USACE task scopes. These project-specific laboratory performance review audits would be conducted by Shaw on an as-needed basis to ensure laboratory compliance.

External audits may be conducted in conjunction with or at the direction of EPA Region 2 or the State of New Jersey Department of Environmental Protection.

5.2 REPORTS TO MANAGEMENT

5.2.1 Daily Quality Control Reports

During the field investigation activities performed for this project, Shaw will prepare DQCRs as delineated in the CQCP (USACE 2005).

5.2.2 Quality Control Summary Reports (QCSRs)

At the conclusion of field investigation activities and laboratory analysis for each major task, Shaw, in addition to any review conducted by the laboratory, will prepare a QCSR, which will be included as an appendix to the final report. This report will be submitted to the USACE Task/Technical Lead as determined by the project schedule and included in any regulatory deliverables. The contents of the QCSR will include data validation documentation and discussion of all data that may have been compromised or influenced by aberrations in the sampling and analytical processes. Both field and laboratory sampling and analysis QC activities will be summarized, and relevant DQCR information will be consolidated. Problems encountered, corrective actions taken, and their impact on project DQOs will be discussed.

Specific elements to be addressed within the QCSR include the following. Note that only deviations from these elements, as described in the CDQMP or the task-specific Work Plan, are included in the QCSR. The effect of deviations on the data and the rationale for occurrence of the deviations should also be provided.

- Data collection – This will include deviations from sampling procedures, sample handling and custody, equipment calibration and maintenance procedures, and analytical procedures. If new methods or modified standard methods were used, but not described in the QAPP, they should be described in the QCSR. The description of the modified analytical method must include method applicability; detection limit; the presence of interferences and attempts to minimize them; and changes in instrumentation, operating parameters, calibration standard type and concentration, and procedures.
- Data Analysis and Validation – This will include a discussion of how data was analyzed. Typically this will be done according to Section 6.0 of this QAPP. This Section will discuss deviations from the guidance provided in Section 6.0. Treatment of outliers shall be discussed. The typical process for treatment of outliers is described in Section 3.1.3 of this QAPP.
- Chemical Analytical and QA/QC Problems Encountered – This Section will summarize those instances for which project DQOs were not met. A discussion of how the problem was discovered, and how/if it was resolved, should be included. Examples include but are not limited to the following:
    1. Unexpected Tentatively Identified Compounds (TICs) that were detected
    2. Compounds that should have been included on a method analyte list, but were not
    3. Analytical methods that were inadequate or that required modification to satisfy project DQOs
    4. Safety problems that might have been avoided if the chemistry of a sample preparation or other test method procedure had been better understood
    5. Higher than expected data variability and their cause, such as erratic instrument performance
    6. Improved strategies for the type, number, or frequency of QC sample testing

5.2.3 Non-Routine Occurrences Reports

Shaw will send the USACE CO, or designee, written reports of all significant non-routine occurrences within 48 hours of the event. These shall include non-routine events in both the laboratory and the field relative to data quality. The reports shall describe the occurrence, corrective action(s) taken, and if

available, any instructions provided by the USACE CO to resolve the problem. Significant events are defined as those that adversely impact project cost or schedule, or the quality of the analytical data.

5.2.4 Data Report to the QA Laboratory

Shaw will provide the KCD Project Chemist with a copy of QA/QC results summaries. The primary and QA samples of each split sample pair shall be identified. Depending on the absolute difference or relative absolute difference between split sample results, Shaw and the Laboratory Subcontractor may be asked to resample and reanalyze at the direction of the USACE Project Chemist and the CO. The data report shall be sent to:

David Evans
601 E. 12th Street
Room 610, EC-EF
Kansas City, MO 64106
Ph: (816) 389-3857

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6.0 DATA VALIDATION AND USABILITY

6.1 DATA REVIEW, VALIDATION, AND VERIFICATION REQUIREMENTS

A systematic process for data verification and validation will be performed to ensure that the precision and accuracy of the analytical data are adequate for their intended use. The greatest uncertainty in a measurement is often a result of the sampling process and inherent variability in the environmental media rather than the analytical measurement. Therefore, analytical data validation will be performed only to the level necessary to minimize the potential of using false positive or false negative results in the decision-making process (i.e., to ensure accurate identification of detected versus non-detected compounds). This approach is consistent with the DQOs for the project, with the analytical methods, and for determining contaminants of concern and calculating risk.

Samples will be analyzed through implementation of definitive analytical methods. Definitive data will be reported consistent with the deliverables identified in the Subcontractor laboratories contracts and shown in **Tables 6-1** and **6-2**. This report content typically contains data forms including laboratory QC and calibration information. These definitive data will then be validated through the review process presented here. DQOs identified in Section 2.0 and certain method-specified criteria will be validated. Data from groundwater, environmental monitoring, final status survey, and backfill material to be added to excavated areas shall be validated. Currently, there are no plans to validate sample results associated with soil transportation & disposal, wastewater treatment, remedial support surveys, or document control sampling activities. Comprehensive analytical information will be retained by the subcontract laboratories.

Laboratories will prepare and submit analytical and QC data reports to USACE and the contractor in accordance with the requirements of this CDQMP and the task-specific Work Plans, including data forms listed in **Table 6-1**. An electronic copy of data will be provided in Microsoft® Access format and complying with the New Jersey DEP EDD requirements and **Table 6-2** for entry into the database.

Table 6-1
Summary of Analytical Hard-copy Data Deliverables

Method Requirements	Deliverables
Requirements for all methods:	
Holding time and preservation information	Signed chain-of-custody forms; Run logs and sample prep. Sheets with dates and times; Sample receipt log with temperature and pH
Discussion of laboratory analysis, including any laboratory problems	Case narratives
Percent solids calculation for soil/sediments	Appropriate calculation
Organics: GC / Mass Spectrometry analysis	
Sample results and reporting limits	CLP Form 1 or equivalent
Surrogate recoveries	CLP Form 2 or equivalent
Matrix spike/spike duplicate and blank spike data	CLP Form 3 or equivalent, with control criteria
Method blank data	CLP Form 4 or equivalent
GC / Mass Spectrometry initial calibration data	CLP Form 6 or equivalent
GC / Mass Spectrometry continuing calibration data	CLP Form 7 or equivalent
Organics: GC analysis	
Sample results and reporting limits	CLP Form 1 or equivalent
Surrogate recoveries	CLP Form 2 or equivalent
Matrix spike/spike duplicate and blank spike data	CLP Form 3 or equivalent
Method blank data	CLP Form 4 or equivalent
Initial calibration and continuing calibration data	CLP Form 6 or equivalent
If calibration factors are used	A form listing each analyte, the concentration of each standard, the relative calibration factor, the mean calibration factor, and %RSD
Calibration curve if used	Calibration curve and correlation coefficient
Analytical test sequence	CLP Form 8 or equivalent
Positive identification (second column confirmation; Only if mentioned as a problem in the Case Narrative)	CLP Form 10 or equivalent
Metals	
Sample results and reporting limits	CLP Form 1 or equivalent
Initial and continuing calibration	CLP Forms 2A and 2B or equivalent, dates of analysis and calibration curve, and the correlation coefficient factor
Method blanks	CLP Form 3 or equivalent and dates of analyses
Spike sample recovery	CLP Form 5A or equivalent
Post digestion spike sample recovery for ICP metals	CLP Form 5B or equivalent
Lab Duplicates	CLP Form 6 or equivalent
LCS	CLP Form 7 or equivalent that includes acceptable range or window
Method of Standard additions (when implemented)	CLP Form 8 or equivalent
Serial Dilution (required when analyte concentration is > 25 times the MDL)	CLP Form 9 or equivalent
Holding times (prep. and analysis run logs)	CLP Forms 13 and 14 or equivalent
Wet Chemistry	
Sample results and reporting limits	Report result and reporting limits
Matrix spike recovery	%Recovery
Matrix spike duplicate or duplicate	%Recovery and %RPD
Method blank	Report results
Initial calibration	Calibration curve and correlation coefficient

Method Requirements	Deliverables
Continuing calibration check	Recovery and % difference
LCS	LCS result and control criteria
Run log	Copy of run log
Radiochemical Analysis	
Sample results	Report results with uncertainties (errors)
Initial calibration (submitted annually, typically near the beginning of the calendar year, to the data validator)	Energy, Efficiency & Activity determination (alpha spec); Full Energy and Shape Cal., Peak-to-Compton Ratio & Efficiency Cal. (gamma spec); average activities and standard deviations on control charts (gas proportional detectors)
Continuing Calibration	Daily pulser and monthly calibration checks (alpha spec); daily calibration checks (gamma spec and gas proportional detectors)
Blanks and Background determinations	Report results with uncertainties, plus mean ± 3σ control limits for daily blanks and backgrounds; and mean ± 3μ control limits for method blanks.
Sample Specific Chemical Tracer recovery Matrix Spike Z score results	Report results, spike concentration added, and %recovery (alpha spec for iso-U and iso-Th tracers; Ba-133 by gamma spec for Ra-226 method; $BaSO_4$ [gravimetric] for Ra-228, and matrix spike Z score for GA/GB) as well as mean ± 3σ control limits for tracer percent recoveries, and the Z score control limits of ±3 for matrix spike results
Duplicate results	Report results and either the absolute difference between the results (if they are < action level) or the relative difference between the results (if they are > action level) as well as lab-derived control limits
LCS	LCS results and percent differences (%Ds) as well as a control chart or a range of acceptable values based upon the mean %D and the warning limits of ±3φ
Sample Tracking Form (STF) Run Logs	Copies of STF Run Logs
Minimum detectable activity (MDA)	MDA value for each radionuclide for each sample specific result
Radionuclide energies	Theoretical (target) and observed peak energies
Matrix density variability	Densities (or weights and volumes) of calibration standards and samples (gamma spec only)

Notes:

CLP	contract laboratory program	LCS	laboratory control sample
GC	gas chromatography	RPD	relative percent difference
ICP	inductively coupled plasma	RSD	relative standard deviation

Refer to Appendix D of this QAPP, Radionuclide Data Evaluation Guidance for definitions of required method uncertainty, μ , relative method uncertainty, φ, and Z score.

Table 6-2a
Standardized Electronic Data Deliverables for Chemical Analyses

Field No.	Field Name	Data Type	Field Length/Type	Comments
1	S&W Sample ID	Text	11	Shaw Sample ID - Format exactly as follows: 12B-079999: No additional characters
2	Date of Sample Collection	Date/Time	Short Date	Date of Sample Collection (MM/DD/YY)
3	Time of Sample Collection	Date/Time	Short Time	Time of Sample Collection (HH:MM military format)
4	Lab Batch Number	Text	12	Laboratory Analytical Batch/Sample Delivery Group (SDG) Number
5	Sample Matrix	Text	8	Sample Matrix, e.g., Soil, Water, etc.
6	Lab Sample ID Number	Text	20	Laboratory Sample Identification Number
7	Extraction/Prep Date	Date/Time	Short Date	Sample Preparation/Extraction Date (MM/DD/YY)
8	Sample Analysis Date	Date/Time	Short Date	Sample Analysis Date (MM/DD/YY)
9	Sample Analysis Time	Date/Time	Short Time	Sample Analysis Time (HH:MM military format)
10	Result Type	Text	10	REG = Regular Analysis; DUP = Duplicate; DIL = Dilution; REN = Re-analysis
11	CAS Number	Text	12	Chemical Abstract Services (CAS) Number
12	Analyte	Text	40	Chemical Name
13	Analysis Method*	Text	25	Analysis Method (Method numbers shall be the EPA, SW-846, NIOSH, etc. method number)
14	Result	Number	Single	Results (Report PQL if not detected)
15	Result Qualifier	Text	5	Result Qualifier (U, J, etc.)
16	Unit of Measure	Text	12	Unit of Measure
17	PQL**	Text	10	Practical Quantitation Limit
18	Percent Solids	Text	5	Percent Solids (Report “0” for water matrices)
19	Sample Weight/Volume	Text	10	Sample Weight/Volume
20	Sample Weight/Volume Unit	Text	5	Sample Weight/Volume Units
21	Dilution	Text	10	Dilution factor
22	LABNAME	Text	20	Laboratory name performing the analysis
23	RESULTTYPE	Text	1	“A” for Analyte; “P” for Parameter; “T” for Tentatively Identified Compound
24	NJDLABCERT	Text	5	New Jersey Laboratory Certification Number
25	FILTUNFILT	Text	1	“F” for Filtered; “U” for Unfiltered

*If test method follows TCLP leaching procedure, method used should read, 1311/8260B, 1311/8270C, etc.

**For metals, the IDL or MDL shall be substituted for the PQL

Table 6-2b
Standardized Electronic Data Deliverables for Radiological Analyses

Field No.	Field Name	Data Type	Field Length/Type	Comments
1	S&W Sample ID	Text	11	Shaw Sample ID - Format exactly as follows: 12B-079999: No additional characters
2	Date of Sample Collection	Date/Time	Short Date	Date of Sample Collection (MM/DD/YY
3	Sample Analysis Date	Date/Time	Short Date	Sample Analysis Date (MM/DD/YY)
4	Lab Batch Number	Text	12	Laboratory Analytical Batch/Sample Delivery Group (SDG) Number
5	Lab Sample ID Number	Text	12	Laboratory Sample Identification Number
6	Sample Volume	Number	Single	Sample Volume
7	W/D	Text	4	"Wet" = analysis on wet sample or "Dry" = analysis on dried sample
8	Sample Type	Text	10	REG = Regular Analysis; DUP = Duplicate; DIL = Dilution; REN = Re-analysis
9	CAS Number	Text	12	Chemical Abstract Services (CAS) Number
10	Analyte	Text	40	Chemical Name
11	Result	Number	Single	Results (Report reporting limit if not detected)
12	Error	Number	Single	Total measurement error[1]
13	Unit of Measure	Text	12	Unit of Measure
14	Result Qualifier	Text	5	Result Qualifier (U, J, etc.)
15	Analysis Method	Text	25	Analysis Method
16	MDA	Text	10	Minimum Detectable Activity
17	Reporting Limit	Number	Single	Reporting Limit is typically 3 to 5 times the MDA
18	Sample Matrix	Text	8	Sample Matrix, e.g., Soil, Water, etc.
19	FILTUNFILT	Text	1	"F" for Filtered; "U" for Unfiltered sample
20	TOP_DEPTH	Number	Single	Top of sample depth, ft
21	BOT_DEPTH	Number	Single	Bottom of sample depth, ft
22	LABNAME	Text	20	Laboratory name performing the analysis
23	RESULTTYPE	Text	1	"A" for Analyte; "P" for Parameter; "T" for Tentatively Identified Compound
24	NJDLABCERT	Text	5	New Jersey Laboratory Certification Number
25	Date Received	Date/Time	Short Date	Date sample was received by laboratory (MM/DD/YY)

[1]Prior to receiving FMSS samples, the Subcontractor must provide the Contractor with a description of what is included in the total measurement error.

The laboratory will be required to confirm sample receipt and log-in information. The laboratory will return a copy of the completed chain-of-custody and confirmation of the laboratory's analytical log-in to the contractor on a daily basis (see Section 3.2.3 of the FSP).

The subcontract analytical laboratories will prepare and retain full analytical and QC documentation. Such retained documentation will include all data, both QC summaries and raw data, in hardcopy or electronic form. As needed, the subcontract analytical laboratories will make available all retained analytical data information.

Validation will be accomplished by comparing the contents of the data packages and QA/QC results to requirements contained in the requested analytical methods. Validation support staff will be responsible for these activities. For final status survey results, the protocol for organic and inorganic analyte data validation is presented in the EPA Region 2 SOPs for data review of specific organic and inorganic parameters.

For all other organic and inorganic analyte data, the DOD Quality System Manual shall be used.

There are no Contract Laboratory Program (CLP) protocols for radiological data. Radiological data validation will be performed on data collected during final status surveys according to the USACE Radionuclide Data Quality Evaluation Guidance (USACE 2009; see Appendix D).

Validation support staff will conduct a systematic review of chemical data for compliance with the established QC criteria based on the following categories:

- Holding times and preservation
- Method (or preparation) blanks, trip blanks, equipment rinseate blanks, and initial / continuing calibration blanks
- LCS
- Surrogate recovery (organic methods)
- MS/MSD and MS/MD percent recoveries and RPDs; MS Z scores for radiological data
- Field Duplicates and Lab Replicates
- Calibration
- Pulser checks (alpha spectroscopy only)
- Second column confirmation (only if mentioned as a problem in the Case Narrative)
- Postdigestion spike sample recovery for ICP metals (inorganic only)
- Interference check sample and CRDL standard recoveries (metals only)
- Method of standard additions (inorganic only, when implemented)
- Sample specific chemical recoveries (radionuclides)
- Chemical separation specificity (tracer recovery; radionuclides only)
- Target radionuclide list
- Peak energies (alpha spectroscopy only)
- Run log
- Minimum detectable activity (MDA) and/or analyte / instrument MDLS
- Radionuclide energies (gamma spectroscopy only)
- Matrix density variability (gamma spectroscopy only)
- Laboratory case narrative
- GC/MS tuning
- Percent moisture

Consistent with the data quality requirements as defined in the DQOs, all project data and associated QC will be evaluated on these categories and qualified as per the outcome of the review. Data validation reports will be completed and presented with the QCSR.

6.2 VALIDATION AND VERIFICATION METHODS

The QC items in the following Region 2 SOPs will be reviewed as part of the data validation task for chemical data. For radiological data, the QC items described within the Radionuclide Data Evaluation Guidance (see Appendix D of this QAPP) will be reviewed as part of the data validation task. These QC items apply to all sample types unless noted otherwise:

Table 6-3
EPA Region 2 SOPs

SOP No.	Title	Date
SOP HW-2 Rev.13, ILM05.3	Evaluation of Metals Data for the CLP Program	September 2006
SOP HW-6 Revision 14	CLP Organic Data Review and Preliminary Review	September 2006
SOP HW-13 Rev. 3, OLC03.2	Organic Data Review for Low Concentration Water	September 2006
SOP HW-17 Revision 2	Validating Chlorinated Herbicides by GC	September 2006
SOP HW-22 Revision 3	Validating Semivolatile Organic Compounds by SW-846 Method 8270	October 2006
SOP HW-24 Revision 2	Validating Volatile Organic Compounds by SW-846 Method 8260B	October 2006
SOP HW-44 Revision 1	Data Validation SOP of Organochlorine Pesticides by Gas Chromatography SW-846 Method 8081B	October 2006
SOP HW-45 Revision 1	Data Validation SOP of Organic Analysis of PCBs by Gas Chromatography SW-846 Method 8082A	October 2006

In addition, checks will be made of how results were obtained from the raw data (only for those data being validated using Region 2 protocols) to verify proper calculation and transcription of results (EPA 1999 and 2002). Data review will verify PQLs to be the same as those agreed upon in the CDQMP (see references EPA 1999 and 2002 for data review guidelines; PQLs shall be obtained from the current subcontract laboratory and compared to the Project Action levels in Appendix A).

The data validation will review field notes to confirm that correct sampling and excavation decisions were made based on screening and on-site testing data.

Shaw will perform statistical treatment tests to determine the degree of attainment of DQOs and potential elimination of outliers as per Section 3.1.3.

6.3 RECONCILIATION WITH DATA QUALITY OBJECTIVES

The primary criterion for satisfying DQOs is to maximize the number of analyte PQLs that are below applicable cleanup action levels. This will give us confidence that we can detect contaminants of concern below the action levels. Cleanup levels for radiological contaminants are discussed in Section 2.3. Standard laboratory radiochemical techniques and in situ gamma spectroscopy can easily attain minimum detectable levels, which are significantly less than the cleanup criteria. Screening levels for chemical contaminants of concern are taken from the New Jersey cleanup criteria in Appendix A. If standard methods cannot produce PQLs that are less than screening levels, the methods may need to be modified or non-standard methods should be utilized if possible. Even using modified or substitute methods, there may be analytes with screening levels that fall between the PQL and MDL, or below the MDL. These analytes are indicated in footnotes at the end of **Table A-1** of Appendix A. For these analytes, there will likely be negotiations with stakeholders and regulators to agree upon a satisfactory approach to test for these analytes.

For each task (Field Demonstration, groundwater remedial investigation, remediation of a given property, etc.), sample results will be grouped according to matrix and action level cleanup categories. For example, if the soil cleanup action levels differ depending on depth, separate groupings of sample results will be made according to depth. All test results for samples within a given category will be compared to the appropriate action level. If the results are all below the action level, no further action will be required. If one or more results are above the action level, the mean and standard deviation of the sample grouping will be calculated and compared to the analogous background results. If the comparison, using an appropriate statistical technique, indicates that the two sample populations are indistinguishable, then no further action will be required. If the comparison indicates that the sample grouping is higher than the background population, then remedial action will be undertaken. For Final Status Surveys of property soils, MARSSIM (EPA 2000b) will be employed.

7.0 REFERENCES

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APPENDIX A
COMPARISON OF ACTION LEVELS WITH TYPICAL METHOD DETECTION LIMITS

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Table A-1
Analytical Parameters, Action Levels, and Laboratory PQLs for the FUSRAP Maywood Superfund Site Investigation [(a)]

Parameters	Water Action Level (µg/l, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/l, unless noted otherwise)		Soil [b] Action Level (µg/kg, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/kg, unless noted otherwise)	
Volatile Organic Compounds (VOC) (g)						
Acetone	6000	10		100,000	20	
Benzene	1.0	1		1000	5	
Bromochloromethane	NA	1		NA	5	
Bromodichloromethane	1.0	1		1000	5	
Bromoform	4.0	1		1000	5	
Bromomethane	10	1		1000	5	
2-Butanone	300	10		50,000	20	
Carbon disulfide	700	1		620	5	
Carbon tetrachloride	1.0	1		1000	5	
Chlorobenzene	50	1		1000	5	
Chloroethane	NA	1		NA	5	
Chloroform	70	1		1000	5	
Chloromethane	NA	1		10,000	5	
Cyclohexane	NA	1		NA	5	
Dibromochloromethane	1.0	1		1000	5	
1,2-Dibromo-3-chloropropane	0.02	2		NA	10	
1,2-Dibromoethane	0.03	1		NA	5	
1,2-dichlorobenzene	600	1		50000	5	
1,3-dichlorobenzene	600	1		100000	5	
1,4-dichlorobenzene	75	1		100000	5	
Dichlorodifluoromethane	1000	1		NA	5	
1,1-Dichloroethane	50	1		10,000	5	
1,2-Dichloroethane	2	1		1000	5	
1,1-Dichloroethene	1	1		8000	5	
cis-1,2-dichloroethene	70	1		1000	5	
trans-1,2-dichloroethene	100	1		50,000	5	
1,2-Dichloropropane	1.0	1		10,000	5	
cis-1,3-dichloropropene	1.0	1		1000	5	
trans-1,3-dichloropropene	1.0	1		1000	5	
1,4-dioxane	NA	200		NA	200	
Ethylbenzene	700	1		100,000	5	
2-hexanone	NA	10		NA	20	

Table A-1
Analytical Parameters, Action Levels, and Laboratory PQLs for the FUSRAP Maywood Superfund Site Investigation [(a)]

Parameters	Water Action Level (µg/l, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/l, unless noted otherwise)		Soil [b] Action Level (µg/kg, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/kg, unless noted otherwise)	
Isopropylbenzene	NA	1		NA	5	
Methyl Acetate	7000	NA		NA	NA	
Methylene Chloride (dichloromethane)	3	1		1,000	5	
Methylcyclohexane	NA	NA		NA	NA	
4-methyl-2-pentanone	NA	10		50,000	20	
Methyl tert-butyl ether	70	1		NA	5	
Styrene	100	1		23,000	5	
1,1,2,2-Tetrachloroethane	1	1		1000	5	
Tetrachloroethene	1	1		1000	5	
Toluene	1,000	1		500,000	5	
1,2,3-trichlorobenzene	NA	1		NA	5	
1,2,4-trichlorobenzene	9	1		68000	5	
1,1,1-Trichloroethane	30	1		50,000	5	
1,1,2-Trichloroethane	3	1		1000	5	
Trichloroethene	1	1		1000	5	
Trichlorofluoromethane	2000	1		NA	5	
1,1,2-Trichloro-1,2,2-trifluoroethane	NA	1		NA	5	
Vinyl chloride	1	1		2000	5	
o-xylene	1000	1		67,000	5	
m,p- xylenes	1000	1		67,000	5	
Semivolatile Organic Compounds [c] (SVOCs)						
Acenaphthene	400	10		100,000	333.3	
Acenaphthylene	NA	10		NA	333.3	
Acetophenone	700	10		NA	333.3	
Anthracene	2000	10		100,000	333.3	
Atrazine	3	10		NA	333.3	
Benzaldehyde	NA	10		NA	333.3	
Benzo(a)anthracene	0.1	10		900	333.3	
Benzo(a)pyrene	0.1	10		660	333.3	
Benzo(b)fluoranthene	0.2	10		900	333.3	
Benzo(k)fluoranthen	0.5	10		900	333.3	
Benzo(g,h,i) perylene	NA	10		NA	333.3	
1,1'-Biphenyl	400	10		NA	333.3	

Table A-1
Analytical Parameters, Action Levels, and Laboratory PQLs for the FUSRAP Maywood Superfund Site Investigation [(a)]

Parameters	Water Action Level (µg/l, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/l, unless noted otherwise)		Soil [b] Action Level (µg/kg, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/kg, unless noted otherwise)	
Bis(2-chloroethoxy)methane	NA	10		NA	333.3	
Bis(2-chloroethyl) ether	7	10		660	333.3	
Bis(2-ethylhexyl) phthalate	3	10		49,000	333.3	
4-Bromophenyl-phenylether	NA	10		NA	333.3	
Butylbenzylphthalate	100	10		100,000	333.3	
Caprolactam	NA	10		NA	333.3	
Carbazole	NA	10		NA	333.3	
4-Chloroaniline	30	10		230,000	333.3	
4-Chloro-3-methylphenol	NA	10		100,000	333.3	
2-Chloronaphthalene	600	10		NA	333.3	
2-Chlorophenol	40	10		10,000	333.3	
4-Chlorophenyl-phenyl ether	NA	10		NA	333.3	
Chrysene	5	10		9000	333.3	
Dibenz(a,h)anthracene	0.3	10		660	333.3	
Dibenzofuran	NA	10		NA	333.3	
3,3'-dichlorobenzidine	30	10		2000	333.3	
2,4-Dichlorophenol	20	10		10,000	333.3	
Diethylphthalate	6000	10		50,000	333.3	
2,4-Dimethylphenol	100	10		10,000	333.3	
Dimethylphthalate	NA	10		50,000	333.3	
Di-n-butylphthalate	700	10		100,000	333.3	
4,6-Dinitro-2-methylphenol	NA	20		NA	666.6	
2,4-Dinitrophenol	40	20		10,000	666.6	
2,4-Dinitrotoluene	10	10		1000	333.3	
2,6-Dinitrotoluene	10	10		1000	333.3	
Di-n-octylphthalate	100	10		100,000	333.3	
Fluoranthene	300	10		100,000	333.3	
Fluorene	300	10		100,000	333.3	
Hexachlorobenzene	0.02	10		660	333.3	
Hexachlorobutadiene	1	10		1000	333.3	
Hexachlorocyclopentadiene	40	10		100,000	333.3	
Hexachloroethane	7	10		6000	333.3	
Indeno(1,2,3-cd)pyrene	0.2	10		900	333.3	

Table A-1
Analytical Parameters, Action Levels, and Laboratory PQLs for the FUSRAP Maywood Superfund Site Investigation [(a)]

Parameters	Water Action Level (µg/l, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/l, unless noted otherwise)		Soil [b] Action Level (µg/kg, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/kg, unless noted otherwise)	
Isophorone	40	10		50,000	333.3	
2-Methylnaphthalene	NA	10		NA	333.3	
2-Methylphenol	NA	10		2,800,000	333.3	
4-Methylphenol	NA	10		2,800,000	333.3	
Naphthalene	300	10		100,000	333.3	
2-Nitroaniline	NA	20		NA	666.6	
3-Nitroaniline	NA	20		NA	666.6	
4-Nitroaniline	NA	20		NA	666.6	
Nitrobenzene	6	10		10,000	333.3	
2-Nitrophenol	NA	10		NA	333.3	
4-Nitrophenol	NA	20		NA	666.6	
N-nitroso-di-n-propylamine	10	10		660	333.3	
N-nitroso-diphenylamine	10	10		100,000	333.3	
2,2'-Oxybis(1-chloropropane)	NA	NA		NA	NA	
Pentachlorophenol]	0.3	20		6000	666.6	
Phenanthrene	NA	10		NA	333.3	
Phenol	2000	10		50,000	333.3	
Pyrene	200	10		100,000	333.3	
1,2,4,5-Tetrachlorobenzene	NA	10		NA	333.3	
2,3,4,6-Tetrachlorophenol	200	10		NA	333.3	
2,4,5-Trichlorophenol	700	10		50,000	333.3	
2,4,6-Trichlorophenol	20	10		10,000	333.3	
Pesticides [c]						
Aldrin	0.04	0.05		40	1.67	
Alpha-BHC	0.02	0.05		NA	1.67	
Alpha-Chlordane	0.5	0.05		NA	1.67	
Beta-BHC	0.04	0.05		NA	1.67	
4,4'-DDD	0.1	0.05		3000	1.67	
4,4'-DDE	0.1	0.05		2000	1.67	
4,4'-DDT	0.1	0.05		2000	1.67	
Delta-BHC	NA	0.05		NA	1.67	
Dieldrin	0.03	0.05		42	1.67	

Table A-1
Analytical Parameters, Action Levels, and Laboratory PQLs for the FUSRAP Maywood Superfund Site Investigation [(a)]

Parameters	Water Action Level (µg/l, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/l, unless noted otherwise)		Soil [b] Action Level (µg/kg, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/kg, unless noted otherwise)	
Endosulfan I	40	0.05		50,000	1.67	
Endosulfan II	40	0.05		50,000	1.67	
Endosulfan sulfate	40	0.05		NA	1.67	
Endrin	2	0.05		17,000	1.67	
Endrin aldehyde	NA	0.05		NA	1.67	
Endrin ketone	NA	0.05		NA	1.67	
Gamma-BHC	0.03	0.05		520	1.67	
Gamma-Chlordane	0.5	0.05		NA	1.67	
Heptachlor	0.05	0.05		150	1.67	
Heptachlor epoxide	0.2	0.05		NA	1.67	
Methoxychlor	40	0.25		50,000	8.33	
Toxaphene	2	2.5		100	83.33	
PCBs (d)						
Aroclor-1016	0.5	0.5		490	1.67	
Aroclor-1221	0.5	0.5		490	1.67	
Aroclor-1232	0.5	0.5		490	1.67	
Aroclor-1242	0.5	0.5		490	1.67	
Aroclor-1248	0.5	0.5		490	1.67	
Aroclor-1254	0.5	0.5		490	1.67	
Aroclor-1260	0.5	0.5		490	1.67	
Aroclor-1262	0.5	0.5		NA	1.67	
Aroclor-1268	0.5	0.5		NA	1.67	
Herbicides (TCLP only)	Action Level (mg/l in leachate)			Action Level (mg/l in leachate)		
2,4-D	70	50		10	50	
2,4,5-TP (Silvex)	60	5		1	5	
Metals						
Aluminum, Total	200	200		NA	20 mg/kg	
Antimony, Total	6	8		14 mg/kg	2 mg/kg	
Arsenic, Total	3	5		20 mg/kg	1 mg/kg	
Barium, Total	2,000	100		700 mg/kg	10 mg/kg	

Table A-1
Analytical Parameters, Action Levels, and Laboratory PQLs for the FUSRAP Maywood Superfund Site Investigation [(a)]

Parameters	Water Action Level (µg/l, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/l, unless noted otherwise)		Soil [b] Action Level (µg/kg, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/kg, unless noted otherwise)	
Beryllium, Total	1	5		2 mg/kg	0.5 mg/kg	
Boron, total [j]	NA	100		NA	10 mg/kg	
Cadmium, Total	4	4		39 mg/kg	0.5 mg/kg	
Calcium, total	NA	1000		NA	100 mg/kg	
Chromium, total	70	10		NA	1 mg/kg	
Cobalt, total	NA	10		NA	1 mg/kg	
Copper, Total	1,300	10		600 mg/kg	1 mg/kg	
Iron, Total	300	100		NA	10 mg/kg	
Lead, Total	5	3		400 mg/kg	0.3 mg/kg	
Lithium, Total [j]	NA	10		NA	1 mg/kg	
Magnesium, total	NA	1000		NA	100 mg/kg	
Manganese, Total	50	10		NA	1 mg/kg	
Nickel, Total	100 (soluble salts)	20		250 mg/kg	12 mg/kg	
Potassium, total	NA	1000		NA	100 mg/kg	
Selenium, Total	40	5		63 mg/kg	0.5 mg/kg	
Silver, Total	40	10		110 mg/kg	1 mg/kg	
Sodium, Total	50,000	1000		NA	100 mg/kg	
Thallium, Total [j]	2	5		2 mg/kg	1 mg/kg	
Vanadium, total	NA	10		370	1 mg/kg	
Zinc, Total	2000	20		1,500 mg/kg	2 mg/kg	
Mercury, Total	2	0.2		14 mg/kg	0.033 mg/kg	
Miscellaneous Analytes						
Amenable Cyanide	100	10		1100 mg/kg	0.5 mg/kg	
Methane, dissolved	NA	1		NA	NA	
Sulfate	250,000	1000		NA	10,000	
Sulfide	NA	5,000		NA	50,000	
Ammonia Nitrogen	NA	100		NA	1,000	
Nitrate, nitrogen	10,000	10		NA	0.1 mg/kg	
Phosphorous, ortho	NA	200		NA	0.5 mg/kg	
Grain Size	NA	Na		NA		
Total Suspended Solids (T.S.S.)	See Table A-2	20,000		NA	NA	
Total organic carbon	NA	1,000		NA	250 mg/kg	

Table A-1
Analytical Parameters, Action Levels, and Laboratory PQLs for the FUSRAP Maywood Superfund Site Investigation [(a)]

Parameters	Water Action Level (µg/l, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/l, unless noted otherwise)		Soil [b] Action Level (µg/kg, unless noted otherwise)	Paragon PQLs (or UFML MDA) (i) (µg/kg, unless noted otherwise)	
Total Recoverable Phenolics	See Table A-2	NA		(e)	NA	
Total Recoverable Petroleum Hydrocarbons (TRPH)	See Table A-2	NA		(e)	NA	
BOD-5	See Table A-2	NA		(e)	NA	
Oil & Grease	See Table A-2	1250000		(e)	NA	
Reactivity	NA	NA		NA	NA	
Corrosivity (pH)	For TCLP test, > 2 and < 12; for water treatment samples, see Table A-2	NA		NA	NA	
Ignitability	NA	NA		NA	NA	
Radiochemical Parameters [f]						
Gamma Emitters	(e)	10 for Cs-137		See Ra-226 and Uranium isotope entries	1.0 for Cs-137	
Thorium 228, 230, 232	none	0.2		see Ra-226	0.1	
Uranium 234, 235, 238	Total Uranium 50 pCi/L	0.2		50 pCi/g U-238; 100 pCi/g total U	0.1	
Gross Alpha and gross beta	15 pCi/L for alpha; 50 pCi/L for beta	3 for gross alpha 4 for gross beta		NA	3 for gross alpha 4 for gross beta	
Radium 228	See Ra-226	1.0		NA	1.0 by Gamma	
Radium 226	5 pCi/L (w/ Ra-228)	1.0		5 pCi/g	1.0 by Gamma	

Notes:

NA = Not Available for this Constituent, if shown in an Action level column; Not Applicable if shown in a PQL column since samples do not need to be analyzed for this parameter, or the parameter does not have a PQL, such as Grain Size

TBP = To be provided

a. Soil chemical action levels are the most stringent (lowest) of the 3 soil action levels; namely, nonresidential direct contact, residential direct contact, and soil impact to groundwater cleanup criteria from the NJDEP proposed rule, Cleanup Standards for Contaminated Sites, N.J.A.C. 7:26D, dated February 3, 1992, last revised May 12, 1999. Parameter specific notes shall be added to these footnotes. Water action levels are the more stringent of the NJ Groundwater Quality Criteria and the Maximum Contaminant Level (MCL) for groundwater as taken from the NJDEP Ground Water Quality Standards, N.J.A.C. 7:9-6. These values are provided for comparison to detection and quantitation limits. Additional ARAPS are discussed in the Environmental Protection Plan (Stone & Webster 1999)

b. All solids will be reported on a dry weight basis, with the associated sample percent moisture reported separately.

c. Soxhlet extraction must be used during the sample preparation step on clay or clay-like soils.

d. PCB action level is for total PCBs.

e. Samples do not need to be analyzed for this parameter for the matrix indicated.

f. Present soil action level is 5 pCi/g for combined Ra-226 plus Th-232; and 50 pCi/g for U-238. Instead of PQLs, the radionuclide minimum detectable activities (MDAs) for low level activity samples are provided in pCi/g for soil and pCi/L for water.

g. Volatile organic analyses for aqueous samples is performed using a 25 ml purge

h.These compounds have action levels that are lower than their corresponding PQLs. In all cases, however, except for ADD COMPOUND LIST, the corresponding MDLs were lower than the action levels.

i. Paragon PQLs apply to all chemical parameters; UFML MDAs apply to radiological parameters only.

This table does not cover wastewater parameters, the limits for which are provided in Table A-2.

j. Lithium, thallium and boron (soil) are analyzed by ICP/MS, Method 6020B which has lower reporting limits and can therefore meet the regulatory action levels for water. All other metals except mercury are analyzed by Method 6010B. Mercury is analyzed by 7470A and 7471A for water and soil samples, respectively.

Table A-2
Analytical Parameters, and Action Levels for Water Treatment Samples

Parameters	**Paragon PQLs (mg/l)**		**Project Action Levels** [a] Water Discharge Limit (mg/L)
Volatile Organic Compounds (VOC)			
Acetone	0.01		---
Acrolein	0.01		0.3
Acrylonitrile	0.01		8.4
Benzene	0.001		0.85
Bromodichloromethane	0.001		---
Bromoform	0.001		1
Bromomethane	0.001		---
2-Butanone	0.01		---
Carbon disulfide	0.001		---
Carbon tetrachloride	0.001		0.15
Chlorobenzene	0.001		10.6
Chloroethane	0.001		21.5
Chloroform	0.001		1.75
Chloromethane	0.001		---
Dibromochloromethane	0.001		---
1,1-Dichloroethane	0.001		19.4
1,2-Dichloroethane	0.001		4.5
1,1-Dichloroethene	0.001		0.14
cis1,2-Dichloroethene	0.001		---
Trans1,2-Dichloroethene	0.001		17
1,2-dichlorobenzene	0.001		21.6
1,4-dichlorobenzene	0.001		26.3
1,2-Dichloropropane	0.001		21.2
Cis-1,3-dichloropropene	0.001		---
Trans-1,3-dichloropropene	0.001		---
Ethylbenzene	0.001		9.3
2-Hexanone	0.01		---
4-Methyl-2-pentanone	0.01		---
Methylene Chloride (dichloromethane)	0.001		17
Styrene	0.001		---
1,1,2,2-Tetrachloroethane	0.001		3.85
Tetrachloroethene	0.001		1.8

Table A-2
Analytical Parameters, and Action Levels for Water Treatment Samples

Parameters	**Paragon PQLs (mg/l)**		**Project Action Levels** [a] Water Discharge Limit (mg/L)
Toluene	0.001		8.1
1,1,1-Trichloroethane	0.001		65
1,1,2-Trichloroethane	0.001		8.6
Trichloroethene	0.001		3.3
Trichlorofluoromethane	0.001		6.25
Vinyl chloride	0.001		0.005
TAL Metals			
Aluminum	0.2		---
Antimony	0.02		---
Arsenic	0.01		---
Barium	0.1		---
Beryllium	0.005		---
Cadmium	0.005		---
Calcium	1		---
Chromium	0.01		---
Cobalt	0.01		---
Copper	0.01		1
Iron	0.01		---
Lead	0.003		---
Magnesium	1		---
Manganese	0.01		---
Mercury	0.0002		---
Nickel	0.02		---
Potassium	1		---
Selenium	0.005		---
Silver	0.01		---
Sodium	1		---
Thallium	0.01		---
Vanadium	0.01		---
Zinc	0.02		---
Cyanide	0.01		0.5
Miscellaneous Analytes			
BOD-5 day	NA		350
Total Recoverable Phenolics			0.771

Table A-2
Analytical Parameters, and Action Levels for Water Treatment Samples

Parameters	**Paragon PQLs (mg/l)**		**Project Action Levels** [a] Water Discharge Limit (mg/L)
Total Recoverable Petroleum Hydrocarbons (TRPH)	NA		100
Total Suspended Solids	20		350
Corrosivity (pH)	0.1		5.5 – 9.5
Oil & Grease (petrol. origin)	1250		100 ppm (monthly average): 150 ppm (single sample)
Oil & Grease (nonpetrol. origin)	1250		200 ppm daily maximum

Notes:
--- = Not Applicable
NA – Not Available
a. Discharge limits are from the Bergen County Publicly owned treatment works (POTW) discharge permit

APPENDIX B
DATA QUALITY OBJECTIVES

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Table B-1
Required Precision and Accuracy

QC Parameter	Spiking Compounds	Paragon Laboratory			
		Accuracy (%R)		Precision (RPD)	
		Water	Soil	Water	Soil
SW8260B Volatile Organic Compounds (10 ml purge for water)					
Surrogate Spike	Dibromofluoromethane	80-124	61-134	--	--
	4-Bromofluorobenzene	78-129	52-151	--	--
	Toluene-d8	81-119	57-135	--	--
MS/MSD[1]	1,2-dichlorobenzene [1]	82-128	74-119	20	30
	1,1-dichloroethene	75-126	65-136	20	30
	acrylonitrile [1]	NE	NE	20	30
	Benzene	82-122	73-126	20	30
	Chlorobenzene	82-121	75-123	20	30
	Toluene	83-121	71-127	20	30
	Trichloroethene	82-121	77-124	20	30
LCS	Acetone	50-150	19-158	--	--
	Acrolein [2]	NE	NE	--	--
	Acrylonitrile [2]	NE	NE	--	--
	Benzene	82-122	73-126	--	--
	Bromochloromethane	85-126	71-127		
	Bromodichloromethane	82-120	72-128	--	--
	Bromoform	79-118	56-137	--	--
	Bromomethane	76-133	31-159	--	--
	2-Butanone	50-150	29-159	--	--
	Carbon disulfide	68-129	47-159	--	--
	Carbon tetrachloride	83-135	67-133	--	--
	Chlorobenzene	82-121	75-123	--	--
	Chloroethane	81-130	39-157	--	--
	Chloroform	84-125	72-124	--	--
	Chloromethane	62-141	51-129	--	--
	Cyclohexane	NE	NE		
	Dibromochloromethane	80-123	66-130	--	--
	1,2-dibromo-3-chloropropane	64-134	40-135		
	1,2-dibromoethane	85-124	70-124		
	1,2-dichlorobenzene	82-128	74-119		
	1,3-dichlorobenzene	79-126	72-124		
	1,4-dichlorobenzene	81-125	72-125		
	Dichlorodifluoromethane	38-131	84-134		
	1,1-Dichloroethane	72-131	73-125	--	--
	1,2-Dichloroethane	84-126	72-137	--	--
	1,1-Dichloroethene	75-126	65-136	--	--
	cis1,2-Dichloroethene	81-121	67-135	--	--
	Trans1,2-Dichloroethene	76-135	66-134	--	--
	1,2-Dichloropropane	81-121	71-119	--	--
	Cis-1,3-dichloropropene	79-120	72-126	--	--
	Trans-1,3-dichloropropene	78-113	65-127	--	--
	Ethylbenzene	83-126	74-127	--	--
	2-Hexanone	50-150	47-146	--	--
	Isopropylbenzene	75-132	77-129		
	Methyl acetate	NE	NE		
	Methyl cyclohexane	NE	NE		
	Methylene Chloride (dichloromethane)	22-146	54-141		
	4-Methyl-2-pentanone	30-150	47-147	--	--

Table B-1
Required Precision and Accuracy

QC Parameter	Spiking Compounds	Paragon Laboratory			
		Accuracy (%R)		Precision (RPD)	
		Water	Soil	Water	Soil
	Methyl tert-butyl ether	75-125	50-125	--	--
	Styrene	82-123	74-128	--	--
	1,1,2,2-Tetrachloroethane	74-130	54-131	--	--
	Tetrachloroethene	79-136	67-139	--	--
	Toluene	83-121	71-127	--	--
	1,2,3-trichlorobenzene	77-128	62-133		
	1,2,4-trichlorobenzene	80-128	65-131		
	1,1,1-Trichloroethane	82-129	63-133	--	--
	1,1,2-Trichloroethane	82-122	62-127	--	--
	Trichloroethene	82-121	77-124	--	--
	Trichlorofluoromethane	84-146	25-186	--	--
	1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)	71-144	50-150		
	Vinyl chloride	77-124	58-126	--	--
	o-xylene	87-132	77-125		
	m,p-xylenes	82-129	79-127		
SW8270C Semivolatile Organics					
Surrogate Spike	Nitrobenzene-d5	34-111	28-113	--	--
	2-Fluorobiphenyl	21-106	41-106	--	--
	Terphenyl-d14	33-111	25-147	--	--
	2-Fluorophenol	21-100	32-98	--	--
	Phenol-d5	15-104	38-98	--	--
	2,4,6-Tribromophenol	23-100	33-107	--	--
MS/MSD	1,2,4-trichlorobenzene	37-107	44-111	30	30
	Acenaphthene	47-108	46-108	30	30
	2,4-dinitrotoluene	51-118	48-116	30	30
	pyrene	49-128	46-123	30	30
	1,4-dichlorobenzene	32-98	35-103	30	30
	N-Nitroso-di-n-propylamine	34-128	40-114	30	30
	Pentachlorophenol	38-117	25-119	30	30
	Phenol	49-101	39-100	30	30
	2-chlorophenol	37-106	44-106	30	30
	4-chloro-3-methylphenol	47-111	46-113	30	30
	4-nitrophenol	21-119	17-138	30	30
LCS	Acenaphthene	47-108	46-108		
	Acenaphthylene	50-107	44-107		
	Acetophenone	NE	NE		
	Anthracene	54-112	53-107		
	Atrazine	NE	NE		
	Benzaldehyde	NE	NE		
	Benzo(a)anthracene	56-109	52-111		
	Benzo(a)pyrene	53-110	50-111	--	--
	Benzo(b)fluoranthene	45-118	45-114	--	--
	Benzo(k)fluoranthene	45-124	45-123	--	--
	Benzo(g,h,i)perylene	38-123	38-126		
	1,1'-biphenyl	NE	NE		
	Bis(2-chloroethoxy) methane	46-107	43-108		
	Bis(2-chloroethyl)ether	37-110	38-105		
	Bis(2-ethylhexyl) phthalate	42-126	47-127	--	--
	4-Bromophenyl-phenylether	52-113	43-117		

Table B-1
Required Precision and Accuracy

QC Parameter	Spiking Compounds	Paragon Laboratory			
		Accuracy (%R)		Precision (RPD)	
		Water	Soil	Water	Soil
	Butylbenzylphthalate	46-116	49-123		
	Caprolactam	NE	NE		
	Carbazole	48-117	44-117		
	4-Chloroaniline	15-109	25-125		
	4-Chloro-3-methylphenol	47-111	46-113		
	2-Chloronaphthalene	36-137	45-105		
	2-Chlorophenol	37-106	44-106		
	4-Chlorophenyl-phenyl ether	50-111	47-112		
	Chrysene	55-109	53-112	--	--
	Dibenz(a,h)anthracene	42-127	47-112	--	--
	Dibenzofuran	54-107	51-103		
	3,3'-dichlorobenzidine	19-111	25-125		
	2,4-Dichlorophenol	48-105	45-110		
	Diethylphthalate	41-118	50-114		
	2,4-Dimethylphenol	28-109	32-103		
	Dimethylphthalate	25-127	49-110		
	Di-n-butylphthalate	54-116	56-110		
	4,6-Dinitro-2-methylphenol	40-130	29-137		
	2,4-Dinitrophenol	14-138	13-132		
	2,4-Dinitrotoluene	51-118	48-116		
	2,6-Dinitrotoluene	49-117	48-112		
	Di-n-octylphthalate	37-137	41-132		
	1,4-dioxane				
	Fluoranthene	54-116	54-114		
	Fluorene	60-112	49-108		
	Hexachlorobenzene	52-112	47-118		
	Hexachlorobutadiene	27-103	40-117		
	Hexachlorocyclopentadiene	10-125	10-125		
	Hexachloroethane	28-94	34-110		
	Indeno(1,2,3-cd)pyrene	43-125	38-121	--	--
	Isophorone	50-112	42-111		
	2-Methylnaphthalene	46-104	47-107		
	2-Methylphenol	38-109	40-104		
	4-Methylphenol	32-110	41-107		
	Naphthalene	39-102	40-107		
	2-Nitroaniline	48-115	44-118		
	3-Nitroaniline	19-126	27-110		
	4-Nitroaniline	36-118	34-113		
	Nitrobenzene	44-109	41-113		
	2-Nitrophenol	39-113	42-111		
	4-Nitrophenol	21-119	17-138		
	N-nitroso-di-n-propylamine	34-128	40-114	--	--
	N-nitroso-diphenylamine	48-111	49-116	--	--
	2,2'-Oxybis(1-chloropropane)	26-131	21-115		
	Pentachlorophenol	38-117	25-119	--	--
	Phenanthrene	51-117	50-110		
	Phenol	49-101	39-100		
	Pyrene	10-108	46-123		
	1,2,4,5-Tetrachlorobenzene	NE	NE		
	2,3,4,6-Tetrachlorophenol	23-112	11-120		

Table B-1
Required Precision and Accuracy

QC Parameter	Spiking Compounds	Paragon Laboratory			
		Accuracy (%R)		Precision (RPD)	
		Water	Soil	Water	Soil
	2,4,5-Trichlorophenol	49-111	49-111		
	2,4,6-Trichlorophenol	49-113	45-105		
SW8081A/8082 Pesticides/PCBs					
Surrogate Spike	DCB	20-110	50-120	--	--
	TCX	40-131	51-114	--	--
MS/MSD	Aldrin	70-1300	56-128	30	30
	4,4'-DDT	70-130	55-127	30	30
	Dieldrin	70-130	61-126	30	30
	Endrin	55-135	60-135	30	30
	Gamma-BHC	70-130	60-123	30	30
	Heptachlor	70-130	57-130	30	30
	Aroclor 1260	30-145	60-130	30	50
LCS	Aldrin	70-130	56-128	--	--
	Alpha-BHC	60-130	51-129		
	alpha-Chlordane	65-125	57-129	--	--
	Beta-BHC	65-125	50-130		
	4,4'-DDD	70-130	48-138		
	4,4'-DDE	70-130	56-141		
	4,4'-DDT	70-130	55-127		
	Delta-BHC	61-119	41-130	--	--
	Dieldrin	70-130	61-126	--	--
	Endosulfan I	31-111	15-135		
	Endosulfan II	41-120	29-1226		
	Endosulfan sulfate	67-123	60-123		
	Endrin	55-135	60-135		
	Endrin aldehyde	55-135	31-139		
	Endrin ketone	72-133	54-143		
	Gamma-BHC	70-130	60-123		
	Gamma-chlordane	60-125	56-130		
	Heptachlor	70-130	57-130	--	--
	Heptachlor epoxide	60-130	57-131	--	--
	Arochlor-1016	25-145	40-140	--	--
	Arochlor-1260	25-145	60-130		
SW8151A – Herbicides (TCLP only)					
Surrogate Spike	DCAA	56-140	57-126		
MS/MSD	2,4-D	60-135	44-140	30	50
	2,4,5-TP (Silvex)	72-135	61-136	30	50
LCS	2,4-D	60-135	44-140		
	2,4,5-TP (Silvex)	72-135	61-136		
SW6010B - Metals [3]					
MS/Replicate	Aluminum	80-120	80-120	20	20
	Antimony	80-120	80-120	20	20
	Arsenic	80-120	80-120	20	20
	Barium	80-120	80-120	20	20
	Beryllium	80-120	80-120	20	20
	Cadmium	80-120	80-120	20	20
	Calcium	80-120	80-120	20	20
	Chromium, total	80-120	80-120	20	20

Table B-1
Required Precision and Accuracy

QC Parameter	Spiking Compounds	Paragon Laboratory			
		Accuracy (%R)		Precision (RPD)	
		Water	Soil	Water	Soil
	Cobalt	80-120	80-120	20	20
	Copper	80-120	80-120	20	20
	Iron	80-120	80-120	20	20
	Lead	80-120	80-120	20	20
	Magnesium	80-120	80-120	20	20
	Manganese	80-120	80-120	20	20
	Nickel	80-120	80-120	20	20
	Potassium	80-120	80-120	20	20
	Selenium	80-120	80-120	20	20
	Silver	80-120	80-120	20	20
	Sodium	80-120	80-120	20	20
	Thallium	80-120	80-120	20	20
	Vanadium	80-120	80-120	20	20
	Zinc	80-120	80-120	20	20
LCS	Aluminum	80-120	80-120	--	--
	Antimony	80-120	80-120	--	--
	Arsenic	80-120	80-120	--	--
	Barium	80-120	80-120	--	--
	Beryllium	80-120	80-120	--	--
	Cadmium	80-120	80-120	--	--
	Calcium	80-120	80-120		
	Chromium, total	80-120	80-120	--	--
	Cobalt	80-120	80-120		
	Copper	80-120	80-120	--	--
	Iron	80-120	80-120	--	--
	Lead	80-120	80-120	--	--
	Magnesium	80-120	80-120		
	Manganese	80-120	80-120	--	--
	Nickel	80-120	80-120	--	--
	Potassium	80-120	80-120		
	Selenium	80-120	80-120	--	--
	Silver	80-120	80-120	--	--
	Sodium	80-120	80-120	--	--
	Thallium	80-120	80-120	--	--
	Vanadium	80-120	80-120		
	Zinc	80-120	80-120	--	--
SW7470A/7471A Mercury					
MS/Replicate	Mercury	80-120	80-120	20	20
LCS	Mercury	80-120	80-120	--	--
SM5220 C or D Chemical Oxygen Demand (COD)					
			--		--
			--		--
EPA 150.1 pH Electrometric					
			--	0.2	--
EPA 160.2 Total Suspended Solids					
		--	--	15	--

Table B-1
Required Precision and Accuracy

QC Parameter	Spiking Compounds	Paragon Laboratory			
		Accuracy (%R)		Precision (RPD)	
		Water	Soil	Water	Soil
EPA 335.1 Amenable Cyanide					
		85-115	--	30	--
			--		--
EPA 405.1 or SM 5210B BOD 5					
			--		--
EPA 413.1 or EPA 1664 Oil and Grease					
		78-114	--	20	--
EPA 418.1 or SW8015 mod – TRPH					
			--		
EPA 420.2 Phenolics, Total Recoverable					
			--		--
SW Chapter 7.3 Reactivity (Cyanide / Sulfides)					
		NA for cyanide;	--		--
DOE Ga -01-R Gamma Emitters in soil					
LCS/replicate		--	85-115	--	30
Method 4.5.5 (alpha spec) Isotopic Thorium (see Note 3 & 4)					
Tracer/ replicate	Th-228			20	30
	Th-230	85-121	85-121	20	30
	Th-232			20	30
DOE U-02, U-04 or EPA 00-07 or 908.1 Isotopic Uranium in water (see Note 3 & 4)					
Tracer/replicate	U-234	82-122	--	20	--
	U-235		--	20	--
	U-238	82-122	--	20	--
DOE U-02 (alpha spec) or U-04 (fluorometry) Isotopic Uranium in Soil (see Note3 & 4)					
Tracer/replicate	U-234	--	82-122	--	30
	U-235	--		--	30
	U-238	--	82-122	--	30
EPA 900, 00-01, or 00-02 Gross alpha and gross beta activity in water (Note 3 & 4)					
MS/replicate		70-130	--	20	--
LANL MLR-100 modif or equiv or SW9310 - Gross alpha and gross beta activity in soil (Note 3 & 4)					
MS/replicate		--	70-130	--	30
Modified EPA 903.1 or 903.0 or Ra-04 or Ra-03 - Ra-226 in water (Note 3 & 4)					
Tracer/ replicate	Ra-226	903.0---75-125 903.0---67-120	--	20	--
EPA Ra-04 or 903.1 Ra-226 in soil (Note 3 & 4)					
Tracer/ replicate	Ra-226		57-126	--	30
Modified EPA 904.0 or Ra-05 Ra-228 in water (Note 3& 4)					
Tracer/ replicate	Ra-228	70-130	--	20	--

Table B-1
Required Precision and Accuracy

QC Parameter	Spiking Compounds	Paragon Laboratory			
		Accuracy (%R)		Precision (RPD)	
		Water	Soil	Water	Soil
SW9320 Ra-228 in soil (Note 3 & 4)					
Tracer/ replicate	Ra-228	--	70-130	--	30

Notes:

1. For Maywood wastewater samples, only the compounds acrylonitrile and 1,2-dichlorobenzene are required as MS/MSD analytes.
2. These compounds are not on the VOC TCL list, but are part of the select list of VOCs for which Maywood wastewater samples are analyzed.
3. For metals and Rad parameters, the acceptance criterion for precision of aqueous replicate pairs is a RPD of less than 20% when sample results are greater than 5 times the PQL; when one or both results are less than 5 times the PQL, the absolute difference between the two replicate results must be less than the PQL
4. MS and LCS limits are the same.

NA – not applicable; NE – not established

APPENDIX C
FORMS

Note: The Sample Receipt Checklist shown in this Appendix is typical of an off-site lab checklist. The USACE FUSRAP Maywood laboratory has a Sample Receiving Log shown as Attachment 22.1 of SOP 641.

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USACE FUSRAP MAYWOOD RADIOCHEMISTRY LABORATORY

CHAIN OF CUSTODY

COC#

100 West Hunter Ave
Maywood NJ 07607

Task Description:

Reviewed:

Entered:

Job number:

Page ____ of ____

Sample ID	Location[1]	Interval (Feet) **OR** Volume (Liters)	Collection		Matrix[2]	Type[3]	Analysis Requested[4]								Lab ID (Lab Entry ONLY)
			Date	Time			GS	GA	GB	U	Th	Ra226	Ra228	U Mass	

1 - Location – Enter the field grid location, the FSS sample location, the Northing and Easting, the railcar number, which ever is appropriate for each task
2 - Matrix – Enter the Initials relating to the sample - Soil (SO), Smear (SM), Air Filter (AF), Ground Water (GW), Drinking Water (DW), Solid (S), Bioassay (BA)
3 - Type – Enter the Initials relating to the sample - Grab (G), Core (C), Volumetric (V)
4 - Analysis Requested – Check the box relating to the sample - GS (Gamma Spec) indicate wet(W) or dry(D) analysis, GA (Gross Alpha), GB (Gross Beta), Th (Isotopic Thorium), U (Isotopic Uranium), Ra226 (Radium 226), Ra228 (Radium 228), U Mass (KPA analysis)

Comments:

Relinquished By (signature)	Date	Time	Received By (signature)	Date	Time

PARAGON ANALYTICS

ALS Paragon

225 Commerce Drive, Fort Collins, CO 80524

TF: 800-443-1511 **PH**: 970-490-1511 **FX**: 970-490-1522

ALS Laboratory Group
ANALYTICAL CHEMISTRY & TESTING SERVICES

Chain-of-Custody

Lab ID

Date

Page of

Project Name/No.		**Sampler(s)**		**Turnaround**	**Standard** or (Due)	**Disposal**	**By Lab** or **Return to Client**

REPORT TO:	
PHONE:	
FAX:	
E-MAIL:	
COMPANY:	
ADDRESS:	

Provide additional information as needed in comments section.

Circle Analytical Method Above

Sample ID	**Date**	**Time ***	**Lab ID**	**Matrix**	**No. of Containers**	**TPH** SW8015B GRO DRO	**VOCs** SW8260B	**BTEX (only)** SW8260B SW8021B	**SVOCs** SW8270C	**OC Pesticides** SW8081A	**PCBs** SW8082	**Herbicides** SW8151A	**Explosives** SW8330 SW8321 by LC/MS/MS	**TCLP Organics** SW1311 SW8260B SW8270D SW8081A SW8151A	**TCLP Metals** SW1311 SW6010B SW7470A	**Total Metals** (ICP) or **Hg** SW6010B 7470A/7471A E200.7 E245.1	**Dissolved Metals** (ICP) or **Hg** SW6010B 7470A/7471A E200.7 E245.1	**Total Metals** (ICP-MS) SW6020A E200.8	**Dissolved Metals** (ICP-MS) SW6020A E200.8	**Hexavalent Chromium** SW7196A Alkaline Digestion? Y / N	**Inorganic Anions** SW9056 E300.0 (specify in comments)	**Solids:** **TDS:**E160.1 **TSS:**E160.2 **Total:E**160.3	**pH** SW9040B SW9045C E150.1		

Circle Analytical Method Above

Actinides Am / Cm / Pu / Th / U	**Gamma Isotopes** E901.1	**Gross Alpha / Beta** SW9310 E900.0	**Total Alpha-Emitting Radium** SW9315 E903.0	**Radium 226** E903.1	**Radium 228** SW9320 E904.0	**Strontium 90** (Total RadioSr) D5811	**Tritium** E906.0	**Radon 222** SM7500Rn		

*** Time Zone:** EST CST MST PST **Matrix Key:** O = oil, S = soil, NS = non-soil solid, W = water, L = liquid, E = extract, F = filter

Comments:

Originator: Retain a photocopy after transfer!

Relinquished By: (1)
Signature _____
Printed Name _____
Date _____ Time _____
Company _____

Relinquished By: (2)
Signature _____
Printed Name _____
Date _____ Time _____
Company _____

Received By: (1)
Signature _____
Printed Name _____
Date _____ Time _____
Company _____

Received By: (2)
Signature _____
Printed Name _____
Date _____ Time _____
Company _____

SHAW ENVIRONMENTAL, INC.

Field Change Notification (FCN)

Section 1 through 4 to be filled out by Shaw E&I, Section 5 to be filled out by USACE

Contract No. DACW41-99-D-9001 Task Order 05

PROJECT:	TASK/WAD 05/15	Change Request Form :
FUSRAP, Maywood, NJ		FCN # Rev # **0**

To: Michael Johnson COR Dept: **USACE** Location **Maywood, NJ** Date

Re: ☐ Drawing No. Title

☐ Spec. No. Title

☒ Other

1. DESCRIPTION (Items involved, submit sketch if applicable)

2. REASONS FOR CHANGE (If from disposition of nonconformance report, list report number)

3. RECOMMENDED DISPOSITION

☐ Technical Clarification (COR approval required)
☐ Out of Scope (COR/ACOR approval required)
☐ Cost of Growth
☒ ROM Estimate (If Applicable)
☐ Schedule Impact

TOTAL

4. Shaw Environmental Initiator (Signature/Title): Project Engineer			

4. Shaw Environmental Project Manager (Signature)	Date	Project Superintendent Concurrence (Signature)	Date

5. USACE DISPOSITION

☐ Approved per recommended disposition
☐ Not approved (give reason)
☐ Approved with modification(s) [describe below]

Project Engineer Concurrence (Signature)	Date	ACOR Concurrence (Signature if required)	Date

Contracting Officer Representative (COR) Approval (Signature)	ACOR Approval (Signature if required)	Date

Engineer signs and transmits to Project Engineer with copies to:

Andy Mills	Project Manager	Others as Required	
Don Ellis	Construction Manager	File: Q1.5.1	Denise Smith
Maurice Hanashy	Quality Control	Cost (WVN & ATP)	

APPENDIX D
USACE RADIONUCLIDE DATA QUALITY EVALUATION GUIDANCE AND EPA REGION 2 STANDARD OPERATING PROCEDURES

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Final - May 2009

US Army Corps
of Engineers ®
Kansas City District

RADIONUCLIDE DATA QUALITY EVALUATION GUIDANCE

U.S. Army Corps of Engineers
Kansas City District

Final May 2009

RADIONUCLIDE DATA QUALITY EVALUATION GUIDANCE

Table of Contents

Subject Page

List of Tables

Table **Page**

Chapter 1
Introduction

This document is designed to offer guidance in laboratory data quality evaluation of radiological data and is based, in part, on the Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP, 2004). The MARLAP Manual addresses the need for a nationally consistent approach to producing radioanalytical laboratory data that meet a project's or program's data requirements. MARLAP was developed collaboratively by the following federal agencies; the Environmental Protection Agency (EPA), the Department of Energy (DOE), the Department of Homeland Security (DHS), the Nuclear Regulatory Commission (NRC), the Department of Defense (DOD), the National Institute of Standards and Technology (NIST), the United States Geological Survey (USGS), and the Food and Drug Administration (FDA).

MARLAP provides guidance for the planning, implementation, and assessment phases of those projects that require the laboratory analysis of radionuclides and is both scientifically rigorous and flexible enough to be applied to a diversity of projects and programs. The MARLAP manual is divided into two main parts. Part I is primarily for project planners and managers and provides guidance on project planning with emphasis on analytical planning issues and analytical data requirements. Part II is intended for laboratory personnel and provides guidance in the relevant areas of radioanalytical laboratory work. This document is limited to the application of MARLAP Chapters 1, 7, 8, and 9 and Appendix C of Part I, and Chapters 15, 16, 18, 19, and 20 of Part II.

The purpose of this document is to provide data quality guidelines to personnel involved in the testing of radiologically contaminated environmental media, and the interpretation and possible qualification of the results. The scope of the document includes discussions of the quality criteria, corrective actions, and data qualifications that should be used or applied during the data acquisition, verification and validation processes. This document shall be used by laboratory personnel to obtain guidance on how to establish quality control parameter control charts, how and when to employ corrective actions, and which laboratory qualifiers to apply under certain circumstances. It shall be used by project chemists to establish project data quality guidelines and oversight of laboratory operations. It shall also be used by independent third party validators to apply data qualifiers when necessary. This document, in conjunction with MARLAP, shall take precedence in the validation process over contracted labs QA/QC procedures

One of the most important factors considered when using the MARLAP approach is the issue of uncertainty. The term "uncertainty" refers to a lack of complete knowledge about something of interest. In this document, the term "measurement uncertainty" will often be used and is defined in the *Guide to the Expression of Uncertainty in Measurement* (GUM) (ISO 1995) as a "parameter, associated with the result of a measurement, that characterizes the dispersion of values that could reasonably be attributed to the measurand." MARLAP recommends the methods of GUM for describing, evaluating, and reporting measurement uncertainty. The uncertainty of a measured value is typically expressed as an estimated standard deviation, called a "standard uncertainty" or one-σ uncertainty. The topic of measurement uncertainty goes into greater detail in Chapter 3 of MARLAP (Attachment 3A, pg 3-29).

As per MARLAP, this document establishes method quality objectives (MQO) for method uncertainty for every appropriate analyte/matrix combination. The required method uncertainty, μ_{MR}, at the upper bound of the gray region (UBGR) is defined as:

$$\mu_{MR} = \Delta / 10$$

where Δ is the width of the gray region (UBGR – lower bound of the gray region (LBGR)). The UBGR is synonymous with the action level for those analytes that have an action level. For sample results that fall at or above the UBGR, the relative method uncertainty, φ_{MR}, is used to establish quality control parameter acceptance criteria. The quantity φ_{MR} is defined as:

$$\varphi_{MR} = \mu_{MR} / \text{UBGR}$$

The quality control parameters described within this document and employed during sample batch testing at USACE remedial investigation project sites help ensure that MQOs are met.

The validation process involves three steps; criteria, verification, and validation:

a. Criteria is the required quality control action that must be performed to be in compliance with the data quality objectives (DQO).

b. Verification assures that laboratory conditions and operations were compliant with the contractual Scope of Work (SOW) and the project plan. Verification compares the data package to these requirements (contract compliance) and checks for consistency and comparability of the data throughout the data package and completeness of the results to ensure all necessary documentation is available.

c. Validation addresses the reliability of the data, where the degree of confidence in the reported analytical data are considered. Data validation criteria and procedures should be established during the planning process and captured in the project plan documents (and SOW for the validation contractor). Data validation qualifiers may be applied based upon qualify control exceedances. A list of these qualifiers are shown in Table 14-1 (see MARLAP Section 8.3.3).

This document will cover the following quality control criteria:

- Holding Times and Preservation
- Calibration
- Blank Analysis
- Tracer Recoveries
- Laboratory Control Sample Analysis
- Matrix Spike Sample Analysis
- Standards and Reagents
- Laboratory Replicate Analysis
- Field Duplicate Analysis
- Spectrometry Resolution

- Radionuclide Quantitation and Detection Limits
- Matrix Density

This document may be used to establish quality control acceptance criteria for any radiological parameters, however specific control limits are provided for parameters of interest associated with the Formerly Utilized Sites Remedial Action Program (FUSRAP) Maywood Superfund Site in Maywood, New Jersey. Table 1-1 provides the Maywood project parameters, the results of which are validated and unvalidated, for each radioanalytical instrument type. Generally, this document covers sample matrices with analysis results for the parameters that require validation.

Table 1-1. Maywood Project Parameters

	VALIDATED PARAMETERS		
	Gamma Spectrometry	Alpha Spectrometry	Gas Proportional Detection
Surface water; groundwater	NA	Ra-226, iso-uranium, and iso-thorium	GA, GB, and Ra-228
Soils and sediments	Th-232, Ra-226, U-238 in backfill and FSS soils	None	NA
	UNVALIDATED PARAMETERS		
Wastewaters	NA	Ra-226, iso-uranium, and iso-thorium	GA, GB, and Ra-228
Air filters, wipes and smears	NA	NA	GA, GB
Soil	Th-232, Ra-226, U-238 in document control, excavation control and soil loadout samples	Ra-226, iso-thorium, and iso-uranium	NA

Chapter 2
Holding Times and Preservation

2.1 Criteria

Aqueous sample holding times for all Maywood project analytes, including Ra-226, Ra-228, isotopic uranium, isotopic thorium, gross alpha (GA) and gross beta (GB) are six months, when preserved to pH <2 in nitric or hydrochloric acid (EPA, 1997).

Due to limited information regarding the holding times for soil samples, it is left to the professional judgment of the Project Manager of the regulatory authority (New Jersey Department of Environmental Protection (NJDEP) in the case of Maywood) how to apply holding times to soil samples. For the Maywood project, soil samples are routinely analyzed for Th-232, Ra-226, and U-238 by gamma spectrometry. Long-lived radionuclides in a soil matrix should not have a holding time if they are chemically stable and stored properly. Proper storage means the sample is stored in a chemically compatible (i.e., non-reactive with the analytes of interest) container in a secure area either within the laboratory or a storage trailer.

2.2 Verification (MARLAP, Chapter 8, Radiochemical Data Verification and Validation)

Actual holding times are established by comparing the sampling date in the sampling logbook, or Chain-of-Custody (COC) with the dates of analysis found in the laboratory raw data (digestion logs and instrument run logs).

Analyte Holding Times (days) = Analysis Date - Sampling Date

For water samples, the pH is checked using pH paper (range of 0-3 pH units) to verify that samples are properly preserved to a pH of <2.

Physical characteristics and half-lives must also be considered when evaluating holding times. It is important that radionuclides with short half-lives and low action levels or relatively high MDAs be analyzed as quickly as possible. For example, suppose radionuclide X has the following characteristics:

- Method MDA: 1.5 pCi/g
- Action level: 5 pCi/g
- Activity at time of collection: 5.2 pCi/g
- Half-life: 4 days

If a sample containing X at 5 pCi/g is analyzed 8 days after collection, the activity of X will have decayed through two half-lives, and will therefore be 1.3 pCi/g. Since this activity is less than the MDA, it will most likely be qualified non-detect. Thus, a sample that exceeded the action level would be incorrectly interpreted as being less than the action level. Please note that as long as the result is not non-detect, the sample activity at the time of collection can be calculated from the decay

equation. Thus decay to less than MDA levels for radionuclides with low action levels must be avoided.

2.3 Validation

If exceptions to the holding times and preservation criteria are noted, the validator shall qualify the data corresponding to samples analyzed outside of holding time, or to samples improperly preserved estimated, J.. In cases where the improper preservation severely impacts data quality or defensibility, the validator should qualify the data rejected,R. The validator may still deem the data usable, but he or she must provide the rationale for their decision in the assessment report.

If holding times are exceeded, the reviewer shall use professional judgment to estimate the potential effects of additional storage on the sample results. The expected bias would be low.

Please note that all qualifiers are defined in Chapter 14.

Chapter 3
Calibration

3.1 Gamma Spectroscopy

3.1.1 Initial Calibration – Energies and Efficiencies (MARLAP, Chapter Sections 15.2, 15.6 and 18.5.6)

3.1.1.1 Criteria

A full energy and shape calibration, Peak-to-Compton ratio calibration, and efficiency calibration, the three of which are called an initial calibration, is performed annually and after hardware replacement or significant instrument repairs. The initial calibration must be performed with a NIST-traceable mixed gamma standard, typically a radioactive source with 8 to 10 radionuclides having gamma ray emissions at energies from approximately 60 keV to 2000 keV.

Energy Calibration

A plot of the true energy versus the observed energy (expressed as channel number) must be a straight line. The difference between the true energy and the observed energy of any radionuclide gamma emission line must be less than 1.0% ([(true energy – observed energy)/true energy] X 100 < 1%). For a 660 keV energy (Cs-137), 1% is 6.6 keV. To ensure proper resolution, the Full Width Half Maximum (FWHM) value is checked and must be less than 3% of the observed energy.

Peak-to-Compton Ratio Calibration

The Peak-to-Compton ratio, an important characteristic of the detector, shall be performed on the ^{60}Co 1332 keV peak, then compared with the manufacturer's specification. This ratio is defined as follows:

(Counts in the peak centroid channel of the full energy peak (1332 keV peak)) ÷ (Average number of counts in the Compton region)

The Compton region typically falls between 1040 keV and 1096 keV for ^{60}Co.

Efficiency Calibration

After the efficiency calibration has been performed and the parameters for the equation of the line calculated, the Delta and Fit values are observed. The Fit value is the efficiency value of the best fit line at a given energy. The Delta value, in percent, equals the difference between the Fit value and the actual efficiency, divided by the actual efficiency, all times 100.

Delta value = [(Fit Value – Actual Efficiency)/ Actual Efficiency] X 100

The actual efficiency is calculated from the activity of the standard and the counts observed. For the best fit polynomial, linear, or quadratic equation, the Delta values must each be less than 5%.

The full width tenth maximum to full width half maximum (FWTM-FWHM) ratio will also be checked quarterly. The FWTM-FWHM ratio will be determined for Co-60. The values are documented on a spreadsheet file that is kept on the laboratory shared drive. The acceptance range for this ratio will be based upon the detector specification for this ratio as well as the observed variability in the ratio over the past few years (mean ± std. deviation).

3.1.1.2 Verification

Check that the energy and efficiency determination, including calibration curves and instrument background are included in the analytical data package. Since the initial calibration is typically prepared only once per year, this documentation only must be submitted once to the validator each year; i.e., it does not have to be submitted with every data package. Typically, the initial calibration documentation is submitted to the validator at the beginning of the project, and then each time the detectors are recalibrated. If the documentation is missing, the validator shall request that the laboratory provide the missing information.

For the energy calibration, verify that a plot of the observed energies versus the channel number is a straight line. The difference between the observed energy and the true energy of any radionuclide must be less than 1.0%. If it is greater than 1% for 2 or more radionuclides, verify that the instrument gain was adjusted and the instrument recalibrated. Verify that the FWHM value for a given energy peak is less than 3% of the observed energy.

For the peak-to-Compton ratio calibration, verify that the ratio is at least as high as the following manufacturer's specifications for the three gamma spectrometer detectors:

Detector 1(30%): 58.4:1 Detector 2 (40%): 63:1 Detector 3 (40%): 64:1

For the efficiency calibration, verify that it was performed and that the delta values, as described above in 3.1.1.1, are less than 5%.

3.1.1.3 Validation

If the initial calibration data is not provided to the validator within a reasonable period of time, all data associated with the initial calibration shall be qualified rejected, R.

The data associated with the calibration shall be deemed unusable if one or more of the following criteria are exceeded:

- The energy percent difference (described above in the Energy Calibration paragraph) from the energy calibration plot is greater than 1% for two or more radionuclides (and the instrument was not recalibrated after gain adjustment);
- The efficiency calibration delta values are greater than 5% for any one radionuclide;
- The FWHM for any one energy peak is > 3%.

If only one radionuclide has an energy percent difference greater than 1%, that radionuclide can be removed and the instrument calibrated without it, unless it is Cs-137 (661.66 keV) which is a critical radionuclide.

3.1.2 Continuing Calibration (daily) – Energy and Activities

3.1.2.1 Criteria

Continuing calibrations are to be performed daily, or every day that a gamma spectroscopy detector analyzes samples and/or standards. The same NIST-traceable mixed gamma standard employed for the initial calibration, is used for continuing calibrations. The activity of each radioisotope in the calibration standard must be within 10% relative of the true, decay-corrected activity. The energy of each isotope must be within 1% of the true energy. The FWHM value will be monitored and must be less than 3% of the observed energy for one low energy, one mid-energy, and one high energy calibration radionuclide.

3.1.2.2 Verification

Check that the continuing calibration standard was analyzed on each day for which field and batch QC samples were analyzed, and that the calibration standard was analyzed before analysis of any samples. Default control limits of ± 10% (relative) and default warning limits of ± 7% (relative) of the true activity of each radionuclide must also be provided. If the control limits for one or more radionuclides, or if the warning limits for two or more radionuclides are exceeded, verify that the continuing calibration standard was reanalyzed before analysis of any samples or batch QC. Verify that the mixed gamma standard contains 8 to 10 radionuclides with energies that span the energy spectrum (approximately 60 keV to 2000 keV). Sources should provide at least 10,000 counts at each energy so counting uncertainty is less than 1%. The Full Width Half Maximum (FWHM) value will be monitored and must be less than 3% of the observed energy for one low energy, one mid-energy, and one high energy calibration radionuclide.

3.1.2.3 Validation

If any continuing calibration standard results are missing, the validator must reject all sample results generated on that day or on those days. Check all continuing calibration standard radionuclide activities to ensure they fall within ±10% relative of the true activity. If any control limits (as noted in 3.1.2.2) were exceeded and the continuing calibration standard was not reanalyzed or the reanalysis results were also unacceptable, all sample results associated with that standard (essentially all results generated on that day) shall be qualified rejected, R. Typically, the standard results are checked and it is reanalyzed if necessary. Qualify all results associated with a calibration rejected, R if one or more of the following occurs:

- The difference between the true energy and the observed energy of any radionuclide gamma emission line is > 1%;
- The FWHM value is greater than 3% of the observed energy for one low energy, one mid-energy, or one high energy calibration radionuclide, and the calibration was not reanalyzed, or if it was reanalyzed and there was still an exceedance.

3.2 Alpha Spectroscopy

3.2.1 Initial Calibration (annual) – Energy and efficiencies (MARLAP, Chapter Section 15.4)

For both initial and continuing calibrations, a pulser check must be run before the calibration on the same day of the calibration run. For the pulser check, the following QC acceptance criteria apply to each detector:

- Full Width Half Maximum (FWHM): within the mean ± 3σ; the mean and 3σ are established using 20 or more pulser check values.
- Pulser Energy Center: 5500 ± 50 keV
- Efficiency: within the mean ± 3σ; the mean and the ± 3σ control limits are established using 20 or more pulser check values

3.2.1.1 Criteria

The alpha spectrometer system is calibrated with a NIST-traceable standard containing five (5) isotopes: U-238, U-234, Th-230, Pu-239, and Am-241. The detector response created by three of these radioisotopes, U-238, Pu-239, and Am-241, are used to calibrate the instrument. The manufacturer has indicated that three radionuclides are sufficient to calibrate the alpha spectrometer detectors. An initial energy and efficiency calibration is performed annually, or whenever significant equipment changes occurs, such as replacement of a detector. The following QC acceptance criteria are established for the initial calibration for each detector.

Table 3-1. QC Acceptance Criteria Established for the Initial Calibration for each Detector

	Calibration Radioisotope		
QC CRITERION	U-238	Pu-239	Am-241
Efficiency (detector specific)	(see Note 1)	(see Note 1)	(see Note 1)
Maximum Peak Energy (keV)	4196 ± 10	5155 ± 10	5486 ± 10
Activity (%R of true value)	90-110%	90-110%	90-110%

Note 1: Average Efficiency for the 3 Radionuclides of 20.72% – 23.20%

3.2.1.2 Verification

Verify that an initial calibration has been performed within one year ± 30 days of the last initial calibration, and that the efficiency, activity (with %R values), and calibration isotope maximum peak energies have been provided in the data package. The pulser check resolution (FWHM), pulser energy center, and efficiency values must also be provided along with the acceptance criteria (mean ± 3σ for FWHM and efficiency; 5500 ± 50 for pulser energy center) for these QC parameters. Sources should provide at least 10,000 counts at each energy so counting uncertainty is less than 1%. Since the initial calibration is typically prepared only once per year, this documentation only must be submitted once to the validator each year; i.e., it does not have to be submitted with every data package.

3.2.1.3 Validation

Check the initial calibration isotope efficiency, activity and maximum peak energy values as well as pulser check acceptance criteria to see if they fall within the criteria stated in 3.2.1 and 3.2.1.1. If they do not, and the initial calibration standard was not reanalyzed or the reanalysis results were also unacceptable, all data associated with the initial calibration is deemed unusable and shall be rejected.

3.2.2 Continuing Calibration (daily) – Energy and Activities

3.2.2.1 Criteria

For alpha spectroscopy, an energy and efficiency calibration is performed monthly using the same isotopic mixture as that used for the initial calibration. For the calibration isotopes, the maximum peak energy, activity and efficiency must be within the limits provided in Table 3-1. At no time shall the maximum peak energy value vary by more than 10 keV from the theoretical peak energy.

3.2.2.2 Verification

Check that the latest (the most recent relative to the sample analyses) energy and efficiency calibrations are included in the analytical data package and that the average efficiency, maximum peak energies, and activities fall within the limits specified within Table 3-1. If the documentation is missing, the validator shall request the data from the laboratory. If the laboratory does not have a record of the continuing calibration, all data that would have been associated with the calibration is unusable, unless the lab can verify that the calibration has not shifted.

3.2.2.3 Validation

If required factors are missing, or if the QC parameter values exceed the Table 3-1 limits, the validator may elect to qualify affected data estimated J to signify an increased level of uncertainty in the measurement because of the inability to correct the measured value for efficiency. If the calibration was not supplied in the package, and the laboratory cannot verify that the calibration has not shifted, or if the results of a continuing calibration have indicated a shift has occurred, reject all data resulting from the last continuing calibration check.

3.3 Gross Alpha/Gross Beta (Gas Proportional Counter)

See Section 15.4.1.2 and 15.5 of MARLAP.

3.3.1 Initial Calibrations and Daily Calibrations

The gross alpha and gross beta initial instrument calibrations consist of 20 or more analyses each of a single paper filter gross alpha standard containing Th-230 and a single electroplated gross beta standard containing Sr/Y-90. Average activities and standard deviations are then calculated and used on control charts. These are "zero mass" standards, so that there is little or no attenuation of the alpha or beta energies. The control charts are constructed for each detector using the mean and the ±2 sigma (warning) and the ±3 sigma (control) limits. Subsequent continuing calibration standard checks are made on days of instrument operation, and checked against the control chart to ensure acceptable instrument operability prior to measurement of samples. The charts are updated periodically to reflect the most recent calibration checks.

In addition to control charts for the standards, efficiency curves are generated for gross beta and gross alpha analyses by Method 900.0 for each detector to account for self-adsorption of alpha or beta particles within the thickness of evaporated sample solids. To the greatest extent practicable, the salt used for the construction of efficiency curves should simulate the dissolved and suspended salts encountered in actual field samples. A set of standards are prepared which have varying amounts of salt but have the same activity. Each curve is a plot of mass of solids (x-axis) versus the efficiency. The efficiency is the response in counts-per-minute (cpm) divided by the known activity in disintegrations-per-minute (dpm). The efficiency for a given sample is then determined from a detector's efficiency curve by reading the efficiency that corresponds to the weight of the evaporated solids on the planchet. The efficiency taken from the curve, in conjunction with the response in cpm, are used to calculate the activity of a given sample.

The gas proportional detector is also used to measure Ac-228 in the Ra-228 analysis. Ac-228 is the daughter of Ra-228. A separate dedicated calibration is generated annually for this analysis using Sr-89, whose beta decay energy is closer to the Ac-228 decay energy than the Sr/Y-90 standard. The Sr-89 calibration is different than the gross alpha (Th-230) and gross beta (Sr/Y-90) calibrations since it uses several replicate standards instead of one standard and each replicate has a mass of solid that replicates the mass of solid generated for the Ra-228 test method. A mean efficiency is determined by calculating the efficiency of each replicate (by dividing the cpm response by the known dpm activity) and then calculating the average efficiency. It is this mean efficiency, in conjunction with a sample response, which is used to calculate the activity of a sample.

Similar to the Sr-89 calibration, a dedicated calibration is generated for gross alpha by Method 7110C, employed for water samples with high (>500 ppm) total solids. The solid used is a mixed precipitate of ferric hydroxide and barium sulfate, and the mass of the precipitate in each replicate approximates the mass of solid generated in the Method. The radionuclide standard spike is Th-230. All other aspects of the calibration are the same as the one generated with Sr-89

3.3.1.1 Criteria

For the calibration control charts, the Th-230 or Sr/Y-90 activities, which are checked on each day that a gas proportional detector will be used and are in units of cpm or percent recovery, must be within QC limits of the mean ± 3 sigma for a given detector. The calibration control charts are updated periodically, typically every six to nine months.

3.3.1.2 Verification

Verify that the daily calibration results are within the mean ± 3 sigma for a given detector. Also verify that daily calibration checks were performed on every day that a sample and/or standard was analyzed. If a daily calibration check result was outside of QC limits, verify that it was reanalyzed and that the reanalysis results were within QC limits prior to sample analysis.

3.3.1.3 Validation

If the gas proportional gross alpha or gross beta calibration checks are not within the mean ± 3 sigma, and the daily calibration was not successfully reanalyzed, all data associated with that calibration check shall be qualified rejected, R.

Chapter 4
Blanks

For all methods, blank analysis results are assessed to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all data associated with the case shall be carefully evaluated to determine whether or not there is an inherent variability in the data for the case, or if the problem is an isolated occurrence not affecting other data. (MARLAP Appendix C, Section C.4.2.3)

4.1 Gamma Spectroscopy, Alpha Spectroscopy, and Gas Proportional Counting

4.1.1 Criteria

A daily blank is analyzed on each detector on every day that samples shall be analyzed on that detector (gamma spectroscopy and gas proportional detectors only) A daily blank consists of a detector count of the same length as that of a regular sample, performed with a blank container in the shielding cave (gamma) or counting chamber (gas proportional counter). Daily blanks are not measured for alpha spectroscopy. Warning and control limits for daily blanks are established using the mean $\pm 2\sigma$, and the mean $\pm 3\sigma$, respectively. The symbol σ is the standard deviation of the mean. The mean value is calculated using at least 20 points and often many more. The mean and warning and control limits are recalculated approximately every six months.

In addition, at least one method blank must be analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. For solid samples (gamma spectroscopy only), the method blank consists of Ottawa sand, or a material with equivalent physical and radiological properties, that has been dried, ground, and stirred to homogenize in the same or similar manner as field samples. For water samples (alpha spectroscopy and gas proportional detection only), a deionized water blank is prepared or processed in the same manner as the field samples. A deionized water blank is also used as the method blank for alpha spectroscopy soil sample batches. For onsite laboratories, due to the nature of sample flow and the rapid turnaround time requirement (often less than 24 hours), the batch is defined as the samples received by the lab during a given week. Thus the method blank frequency at onsite laboratories is typically weekly, unless more than 20 samples are received in a given week, in which case a new batch is started. Warning and control limits for method blanks are established using $\pm 2\mu_{MR}$ and $\pm 3\mu_{MR}$, respectively for all parameters except Th-228, Th-230, Th-232, and U-235 in water. The variable μ_{MR} is defined in Chapter 1 of this Guidance and μ_{MR} values are taken from all detectors of a given instrument type. Since there are no regulatory action levels for Th-228, Th-230, Th-232 in water and since U-235 contributes an insignificant amount of activity to the total uranium, the control limits for these parameters come from the mean $\pm$ 3σ limits established from historical data. The warning and control limits for the thorium isotopes and U-235 are recalculated approximately every six months. The method blank warning and control limits for gamma spectroscopy, alpha spectroscopy and gas proportional detectors are provided in Table 4-1.

Background counts (12 hours each for gamma and alpha detectors, and 1000 minutes for gas proportional detectors) are conducted weekly for gamma spectrometer and gas proportional detectors and monthly for alpha spectrometer detectors. The background count rate must fall within its control

limits, which are its mean background activity ± 3σ, which is calculated for each detector. The most recent background count rate is subtracted from each sample and batch QC sample count rate. Due to the very low background count rates for alpha spectrometer detectors, an absolute total count value of six counts is used as a control limit for each detector. Six counts in 12 hours, or 720 minutes, is a count rate of 0.0083 counts per minute (cpm), which is one to two orders of magnitude less than the not-to-exceed MDA values for all alpha spectroscopy analytes. The background mean and warning and control limits are recalculated approximately every six to nine months.

The result of all blanks and backgrounds must be reported along with the sample results and must be plotted on a QC chart. Acceptable tolerances must be based on system performance and analytical requirements. The daily blank and background control charts show the mean, the warning limits (+2σ and -2σ lines), and the control limits (+3σ and -3σ lines) while the method blank control charts show the warning limits (+2μ_{MR} and -2μ_{MR} lines), and the control limits (+3μ_{MR} and -3μ_{MR} lines).

Table 4-1. Method Blank Control Limits for Maywood Analytes of Concern

Analyte	Required Method Uncertainty, μ_{MR} (pCi/g)	Warning Limit, ±2μ_{MR} (pCi/g)	Control Limit, ±3μ_{MR} (pCi/g)
	GAMMA MARINELLI		
Ac-228	0.16	0.32	0.49
Pb-214	0.11	0.22	0.33
Th-234	2.0	4.1	6.1
	GAMMA TUNACAN		
Ac-228	0.052	0.103	0.154
Pb-214	0.043	0.086	0.129
Th-234	0.246	0.492	0.738
	GAS PROPORTIONAL (units in pCi/L)		
GA (900.0)	1.44	2.88	4.32
GA (7110C)	1.115	2.23	3.34
GB (900.0)	1.395	2.79	4.18
Ra-228	0.285	0.57	0.86
	ALPHA SPECTROMETER (units in pCi/L)		
U-234	3.38	6.77	10.16
U-235 (*)	0.022	0.043	0.065
U-238	3.20	6.59	9.88
Ra-226	0.275	0.55	0.825
Th-228 (*)	0.125	0.25	0.38
Th-230 (*)	0.70	1.4	2.1
Th-232 (*)	0.10	0.20	0.30

Note: Method blank uncertainties, warning limits and control limits apply to all three detectors (gamma), all 16 detectors (gas proportional) and all 24 detectors (alpha spectrometer).
*: For Th-228, Th-230, Th-232 and U-235, the uncertainty values are the σ values from historical data.

4.1.2 Verification

If a daily blank or method blank was required but not performed, or if the required data are missing, the validator shall request the data from the lab. If the blank(s) was not generated, the field sample data generated on that day (in the case of a missing daily blank) or generated within a given batch (in the case of a missing method blank) shall not be acceptable for use. Review the blank results and

evaluate the blank control charts if available as well as the raw data for all blanks. Verify that the results were accurately reported and that tolerance limits were not exceeded.

4.1.3 Validation

If the blank result does not comply with the established criteria, that is, if a result is outside of the control limits of $\pm 3\mu$ (method blanks), or $\pm 3\sigma$ around the mean (daily blanks or backgrounds), then the qualifier B should be applied with a "+" or "-" (depending upon whether the result is above or below the control limits) to all samples in the batch in the case of method blanks, and to all samples analyzed on a given detector on a given day in the case of the daily blank. If a background activity falls outside $\pm 3\sigma$, it should be reanalyzed.

Chapter 5
Sample Specific Chemical Recovery (Tracer)

The following discussion applies to alpha spectroscopy tracers and Ba-133 measured by gamma spectroscopy. A tracer is either an isotope of the same element as the isotope of interest, or an isotope of an element different from the element of the isotope of interest, but one that behaves chemically very similar to the isotope of interest. Tracers are added to both field samples and batch QC samples prior to sample preparation. Because the tracer is chemically either identical or very similar to the isotope of interest, it provides an indication for every batch QC or field sample of any method anomalies such as sample losses due to absorption, reactivity, spillage, etc. or artifacts specific to the measurement step. Thus the percent recovery of the tracer is used to normalize the measured activity of the isotope of interest.

5.1 Alpha Spectroscopy

5.1.1 Criteria

Each sample chemical tracer percent recovery (%R) must be recorded and should be plotted on a QC chart for each radionuclide and method and fall within the prescribed limits of ±3σ of the mean recovery. There should be at least 30 points used to establish a control chart for each radionuclide and both the ±2σ warning limits and ±3σ control limits must be displayed. **Note that batch QC tracer data should not be used to establish control charts**.

The quantity of tracer material used must be adequate to provide a maximum uncertainty at the 95% confidence level in the measured recovery using the following equation (Golnick, 1994):

$$2\sigma uncertainty = \frac{1.96\sqrt{(C_s / t_s) + (C_b / t_b)}}{(E)(Vol)(R)(2.22)}$$

Where:

C_s = Sample count rate, cpm
C_b = Background count rate, cpm
t_s = Sample count time, minutes
t_b = Background count time, minutes
E = Counting efficiency
Vol = Volume of sample (liters or grams) (NOTE: This factor does not apply for the Ba-133 tracer which is measured as total activity in a centrifuge tube or on a filter disk)
R = Radiochemical recovery
2.22 = Conversion factor from dpm to pCi

5.1.2 Verification

a. Check the raw data to verify that sample specific recoveries are accurately reported. Recalculate up to 10% of the sample specific recoveries (%R) using the following equation:

$\%R = (A_{Found}/A_{True}) \times 100$

Where:
A_{Found} = activity (in pCi/L for aqueous; pCi/g for solid) of each analyte measured in the LCS.
A_{True} = activity (in pCi/L for aqueous; pCi/g for solid) of each analyte in the LCS source.

b. Check spike levels to verify that sufficient activities are used to provide adequate precision, as measured by the 2σ uncertainty equation in 5.1.1, for recovery determination.

c. Evaluate recoveries to verify that they fall within the limits specified in Section 5.1.1.

5.1.3 Validation

For sample specific recoveries, qualify results for the appropriate radionuclides in all associated samples as follows:

a. Within ±2σ of the mean recovery, data is acceptable and no qualifiers are necessary.

b. If data falls between +2σ and + 3σ, or between -2σ and -3σ, or is equal to ±2σ, qualify the data estimated, J

c. If data is greater than or equal to +3σ or less than or equal to -3σ, corrective action must be taken, typically by repreparing and reanalyzing the sample with the poor tracer recovery. If no corrective action is taken, qualify the data rejected, R. If corrective action is taken and the results are within ±3σ, qualify the data estimated, J. If corrective action is taken and the result is still greater than or equal to +3σ or less than or equal to -3σ, qualify the data rejected, R.

d. If significant errors are noted in the calculations, qualify all affected results, specific to that sample rejected, R.

Chapter 6
Laboratory Control Sample (LCS)

6.1 Gamma Spectroscopy

6.1.1 Criteria

The laboratory control sample (LCS) serves as a monitor of the overall accuracy and performance of all steps in the analysis, including the sample preparation. Please note that for the gamma spectroscopy soil LCS, there is no sample preparation. The LCS is a known radionuclide standard in an analysis geometry and containing isotopes of interest consistent with the samples undergoing analysis. For the following limits to apply, the LCS must contain greater than 10 times the radionuclide's detection limit activity. Limits are laboratory-derived using as many points as possible near the action level and must display the mean and the ±2 and $3\varphi_{MR}$ limits of the percent deviation (%D) for the LCS analysis. The statistical parameter φ_{MR} is the relative standard deviation at the UBGR (upper boundary of the gray region) and equals μ_{MR} / UBGR. LCS values must fall within the mean %D ±3 φ_{MR} limits (MARLAP Appendix C, Section C.4.2.1). For the Maywood project, the term UBGR is synonymous with the action level.

As an example, consider the action level of the sum of Th-232 and Ra-226 in soil, which is 5 pCi/g above background. Uncertainties are obtained by looking at historical data of Maywood soils with either Th-232 or Ra-226 around 5 pCi/g. The relative standard deviation values provided in Table 6-1 were calculated by dividing the mean uncertainty of a given set of USACE FUSRAP Maywood Laboratory (UFML) results with values near the action level, μ_{MR}(avg), by the action level value of 5 pCi/g, then multiplying by 100. For example, if a result and one sigma uncertainty are 4.5 and 0.7 pCi/g, respectively, the percent relative standard deviation, φ_{MR}, equals (0.7/5) x 100, or 14%. The average percent relative standard deviation (φ_{MR}) values are found to be approximately 9.75% and 6.57%, respectively for Th-232 and Ra-226 for the Marinelli geometry. For U-238, the action level is 50 pCi/g and its average percent relative standard deviation (φ_{MR}) value is 12.24% for the Marinelli geometry

Table 6-1. LCS Warning and Control Limits for Gamma Spectrometry Maywood Soil Analytes of Concern

Analyte	φMR X 100	Warning Limits (±2φMR X 100)	Control Limits (±3φMR X 100)
Marinelli Geometry			
Th-232	3.25%	6.50%	9.75%
Ra-226	2.19%	4.38%	6.57%
U-238	4.08%	8.16%	12.24%
Tunacan Geometry			
Th-232	3.88%	7.76%	11.64%
Ra-226	1.58%	3.16%	4.74%
U-238	4.08%	8.16%	12.24%

For example, if the mean LCS %D is 7.3% for Th-232 (Marinelli), the control limits are then (7.3% - 9.75%) to (7.3% + 9.75%), or -2.45% to +17.05%. So, if the activity of the Th-232 LCS is 3.3 pCi/g, the LCS limits in pCi/g are 3.22 – 3.86 pCi/g. The mean LCS activities are obtained from the (approximately) 30 most recent results using values obtained from all three gamma detectors. The mean values are updated approximately every six months.

6.1.2 Verification

At least one LCS must be analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. All aqueous and solid LCS percent deviation values, as calculated below, must be plotted on a control chart, and must fall within the control limits noted in Table 6-1. :

$$\%D = \frac{SSR - SA}{SA} x100$$

Where:

%D is the percent deviation
SSR is the measured result (spiked result)
SA is the spike activity (or concentration) added.

The control chart will contain the mean %D value and the warning and control limits shown below. The φ_{MR} x 100% values are taken from Table 6-1.
Warning limits: ± $2\varphi_{MR}$ x 100 %
Control limits: ± $3\varphi_{MR}$ x 100%

6.1.3 Validation

Review and verify that results fall within the control limits. Check the raw data (counter printout, strip charts, bench sheets, etc.) to verify the reported recoveries.

a. If any result falls outside control limits, the lab must take corrective action to ensure acceptable LCS results. The corrective action will typically be a reanalysis. If the reanalysis is unsuccessful (i.e., one or more of the LCS reanalysis results fell outside of control limits), then adjustments should be made to instrument settings. The LCS should then be reanalyzed along with any samples associated with the LCS that had already been analyzed.

b. If an acceptable LCS result (within control limits) cannot be generated, all sample results associated with the faulty LCS shall be qualified by the laboratory with an S- or S+ indicating a high or low recovery. The third party validator may apply a U, J, or R qualifier to the LCS and associated regular samples in the analytical batch based on professional judgment and the use of other quality control criteria.

c. If an LCS is not analyzed with a batch, all data associated with the batch shall be qualified rejected, R.

6.2 Alpha Spectroscopy

6.2.1 Criteria

The laboratory control sample (LCS) serves as a monitor of the overall accuracy and performance of all steps in the analysis, including the sample preparation.

6.2.2 Verification

At least one LCS must be analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. All aqueous LCS percent deviation values, as calculated using the Equation in Section 6.1.2, must be plotted on a control chart, and must fall within the control limits noted in Table 6-2. [MARLAP (C.4.2.1)].

The control limits are plotted around a mean value for the percent deviation. The mean shall be calculated using the 20-30 most recent LCS percent difference (%D) values obtained from all detectors. The mean value is updated every 12-18 months.

Control limits are determined by first calculating the relative uncertainties (φ_{MR}) of several results of a given isotope by first calculating the average uncertainty, μ_{MR}(avg), then dividing μ_{MR}(avg) by the analyte action level and multiplying the quotient by 100 to obtain the average percent relative uncertainty. If possible, the selected results should fall around the action level for that analyte. The average percent relative uncertainties are then multiplied by 3 to obtain control limits.

Isotopic thorium analytes have no action level. Since thorium-230 (Th-230) is the only thorium isotope in the LCS, the mean %D value and the control limits are derived from existing data (the mean value determines the %D, and the 3σ value is added to and subtracted from the mean %D to yield the control limits). For uranium, the action level is 20 pCi/L for total uranium and most of the contribution to total uranium activity is from U-234 and U-238, which theoretically have equal activities in any given sample. Therefore the uncertainties for U-234 and U-238 activities around 10 pCi/L were considered. There were 15 and 12 points, respectively for U-234 and U-238. Similar to the Th-230, the U-235 mean %D value and the control limits are taken from historical data. Ra-226 is another alpha spectroscopy parameter. The Ra-226 + Ra-228 action level is 5.0 pCi/L. Given these action levels for the Maywood project alpha spectrometry parameters, the mean φ_{MR} values were calculated for the following activity ranges:

- Ra-226, between 0.75 and 2.5 pCi/L.
- U-234, between 7.6 and 11.6 pCi/L.
- U-238, between 7.6 and 10.8 pCi/L

The average relative uncertainties for these parameters were used to establish the control limits shown in Table 6-2. The percent relative standard deviation (φ_{MR} x 100) values provided in Table 6-2 were calculated by dividing the mean uncertainty of a given set of UFML results, μ_{MR}(avg), by the analyte's action level, then multiplying by 100.

Table 6-2. LCS Warning and Control Limit Relative Uncertainties for Alpha Spectrometry Maywood Water Analytes of Concern

Analyte	φMR X 100	Warning Limits (±2φMR X 100)	Control Limits (±3φMR X 100)
U-238	4.42%	± 8.85%	± 13.28%
U-235	12.3%	± 24.6 %	± 36.9%
U-234	7.00%	± 14.0%	± 21.0%
Th-230	6.70%	± 13.4%	± 20.1%
Ra-226	5.50%	± 11.0%	± 16.5%

As far as control limits for soil LCS analyzed by alpha spectrometry, there have been very few samples, perhaps two to four per year, analyzed by alpha spectrometry. Therefore, there is an inadequate number of results available to establish accurate control limits for the three soil parameters with project action levels, namely Th-232, Ra-226, and U-238. Plus, UFML does not analyze a soil LCS with alpha spectrometry soil sample batches; they analyze an aqueous LCS. Therefore, the aqueous control limits provided in Table 6-2 shall also be utilized as acceptance criteria for soil LCS sample results.

6.2.3 Validation

Review and verify that results fall within the control limits. Check the raw data (counter printout, strip charts, bench sheets, etc.) to verify the reported recoveries.

a. If any result falls outside the quality control limits, the lab must take corrective action to ensure acceptable LCS results. The corrective action will typically be a reanalysis. If the reanalysis is unsuccessful, then adjustments should be made to instrument settings and/or a new LCS shall be prepared . The new LCS should then be processed through the sample preparation and analyzed along with all batch samples associated with the LCS for the failed LCS analyte.

b. If an acceptable LCS result cannot be generated, all sample results associated with the faulty LCS shall be qualified by the laboratory with an S- or S+ indicating a high or low recovery. The third party validator may apply a U, J, or R qualifier to the LCS and associated regular samples in the analytical batch based on professional judgment and the use of other quality control criteria.

c. If an LCS is not analyzed with a batch, all data associated within the batch shall be qualified rejected, R.

6.3 Gross Alpha/Gross Beta and Ra-228 (Gas Proportional Counter)

6.3.1 Criteria

The laboratory control sample (LCS) serves as one of the monitors of the overall accuracy and performance of the analysis, including the sample preparation. For the following acceptance criteria to apply, the LCS must contain greater than 10 times the radionuclide's detection limit activity.

6.3.2 Verification

At least one LCS must be analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. All aqueous LCS percent deviation values, as calculated in Section 6.1.2, must be plotted on a control chart, and must fall within the control limits noted in Table 6-3. [MARLAP Appendix C, Section C.4.2.1)]. The control limits are plotted around a mean value for the percent deviation. The mean shall be calculated using the 20-30 most recent LCS %D values from all detectors. The mean value is recalculated approximately every six months, or whenever 20 values are accumulated. The relative standard deviation values provided in Table 6-3 were calculated by dividing the average uncertainty of a set of UFML results (preferably) near the analyte's action

level, μ_{MR}(avg), by its associated action level, then multiplying by 100. Every attempt was made to use uncertainty values associated with results near the action levels of 15 pCi/L for GA and 50 pCi/L for GB. There were 37 and 29 results, respectively for GA by Method 900.0 and GA by Method 7110C. There were 33 GB results by Method 900.0 used to establish limits. The Ra-228 action level is described as 5 pCi/L for the sum of the activities of Ra-226 and Ra-228. There were 17 Ra-228 wastewater results (Method 9320) generated by UFML and they ranged from 2.1 to 7.3 pCi/L. The average relative standard deviation was calculated from these 17 values.

Table 6-3. Warning and Control Limits for Gas Proportional Detector Maywood Water Analytes of Concern

Analyte	φMR X 100	Warning Limits (±2φMR X 100)	Control Limits (±3φMR X 100)
Gross Alpha (7110C)	7.44%	± 14.9%	± 22.3%
Gross Alpha (900.0)	9.61%	± 19.2%	± 28.8%
Gross Beta	2.79%	± 5.58%	± 8.37%
Ra-228	9.10%	± 18.2%	± 27.3%

6.3.3 Validation

Review and verify that results fall within the control limits. Check the raw data (counter printout, strip charts, bench sheets, etc.) to verify the reported recoveries.

a. If any result falls outside the quality control limits, the lab must take corrective action to ensure acceptable LCS results. The corrective action will typically be a reanalysis. If the reanalysis is unsuccessful, then adjustments should be made to instrument settings and/or a new LCS shall be prepared. The new LCS should then be processed through the sample preparation and analyzed along with all batch samples associated with the LCS for the failed LCS analyte.

b. If an acceptable LCS result cannot be generated, all sample results associated with the faulty LCS shall be qualified by the laboratory with an S- or S+ indicating a high or low recovery. The third party validator may apply a U, J, or R qualifier to the and regular samples associated with the LCS in the analytical batch based on professional judgment and the use of other quality control criteria.

c. If an LCS is not analyzed with a batch, all data associated within the batch shall be qualified rejected, R.

Chapter 7
Matrix Spike Sample (MSS) Analysis

The matrix spike sample (MSS) analysis provides information about the effect of each sample matrix on the method preparation and measurement. MSS are required when sample specific chemical recoveries (tracers) are not used and the samples undergo a chemical preparation process.

MSS analysis is only performed for Gross Alpha/Gross Beta analyses. The accuracy of the matrix spike analysis is assessed using tracers for alpha spectroscopic analysis and by measuring the gravimetric yield of barium sulfate for Ra-228 measured by gross beta. For gamma spectroscopy soils, there is no matrix spike employed due to the difficulty introducing a homogenous matrix spike. Matrix spikes may also be used for water samples to be analyzed by gamma spectroscopy, although water samples are not analyzed by gamma spectroscopy on the Maywood project.

7.1 Gross Alpha/Gross Beta (Gas Proportional Counter)

7.1.1 Criteria

The acceptance criteria for matrix samples are more complicated than for LCS and method blanks due to the pre-existing activity in the unspiked sample, which must be measured and then subtracted from the activity measured after spiking. The %D warning and control limits are dependent only upon one measured value (spiked result for LCS, and blank result for the method blank), whereas the matrix spike limits are dependant upon two measured values (spiked sample result and sample result), therefore %D is not a good statistic to use for MSS. Instead, a "Z-Score" equation is employed (MARLAP Appendix C, Section C.4.2.4):

$$\text{Z-Score} = \frac{SSR - SR - SA}{\phi_{MR}\sqrt{SSR^2 + \max(SR, UBGR)^2}}$$

Where:
max (x,y) denotes the maximum of x and y,
φ_{MR} is the maximum allowable (relative) standard deviation at the UBGR
SSR is the spiked sample result
SR is the sample result
SA is the activity spiked into the sample
UBGR = 15 pCi/L for GA and 50 pCi/L for GB

A control chart shall be prepared which contains a mean Z score, obtained from 20-30 matrix spike results, as well as warning and control limits. The warning and control limits for the calculated Z-Score statistic are set as follows:

Warning limits: ±2
Control limits: ±3

If a result falls outside of control limits, the sample must be reanalyzed to confirm the exceedance.

7.1.2 Verification

At least one MSS must be analyzed for every matrix, every batch, or for every 20 samples (5% of samples), whichever is more frequent. Samples identified as field blanks must not be used for spiked sample analysis. The calculated Z-Score statistic of the matrix spike must be recorded and plotted on a QC chart and fall within the prescribed limits. Verify that the MS and its associated unspiked sample were reprepared and reanalyzed if the MS result exceeds control limits. If the sample result is > 4 times the spike level, the MSS Z-Score evaluation is not employed.

7.1.3 Validation

Verify that the calculated MSS Z-Score statistic falls within the specified control limits. A calculated Z-Score statistic that falls outside the control limits should be qualified by the laboratory with an S- or S+ indicating a high or low recovery. The third party validator may apply a U, J, or R qualifier to the MSS and associated regular samples in the analytical batch based on professional judgment and the use of other quality control criteria. Generally, if the calculated Z-Score statistic is between -2 and -3, or +2 and +3, the sample result is qualified estimated J. If the Z-Score is <-3 or >+3, the data is qualified R, rejected. Rejection of data for MSS failures requires professional judgment. If a result falls outside of control limits, corrective action may be taken by repreparing and reanalyzing the sample and its matrix spike. If the reanalysis result falls outside control limits the sample result shall be qualified rejected, R. If the reanalysis falls within control limits, the result should be qualified estimated, J.

Chapter 8
Standards and Reagents

8.1 Criteria

The traceability of standards and reference materials to be used during the analysis should be specified in the sampling and analysis plan.

8.2 Verification

Check that criteria related to traceability of reference materials and standards (completed source manufacturer and internal calibration certificates) have been addressed, and pertinent documentation is included in the analytical data package or has been verified during an audit.

8.3 Validation

The validator may factor the absence of the traceability into their evaluation of data quality and usability. At most, this should result in increasing the uncertainty of the determination and the possible assignment of an estimated "J" qualifier to the data. This would not occur normally unless one or more of the standards used in analyzing the samples was shown to be unreliable. The inability to trace a reliable standard to a sample increases the uncertainty of the data points(s).

Chapter 9
Laboratory Replicates

9.1 Criteria

Replicate analyses are indicators of laboratory precision based on each sample matrix. The variability of sample results due to analyte heterogeneity in the sample is also reflected in the replicate result. At least one replicate must be analyzed for every matrix, every batch or for every 20 samples (5% of samples) whichever is more frequent. The laboratory may not be in control of the precision, therefore, replicate results are used to evaluate reproducibility of the complete laboratory process that includes subsampling, preparation, and analytical processes (MARLAP, Appendix C, Sect. C.4.2.2).

Acceptance criteria for replicate analysis results depend on the sample concentration, which is estimated by the average $\overline{X}$ of the two measured results X1 and X2.

$$\overline{X} = \frac{X_1 + X_2}{2}$$

When the $\overline{X}$ < UBGR, the warning limit for the absolute difference $|X_1 - X_2|$ is:

$2\ u_{MR}\sqrt{2} \approx 2.83\ u_{MR}$; and the control limit is: $3\ u_{MR}\sqrt{2} \approx 4.24\ u_{MR}$

Where u_{MR} is the uncertainty at the UBGR.

When the $\overline{X}$ >= UBGR, the warning limit for the relative percent difference (RPD),

100 x $|X_1 - X_2|$ / $\overline{X}$ = 100 X 2.83 φ_{MR} ; and the control limit = 100 X 4.24 φ_{MR} (MARLAP Appendix C, Section C.4.2.2)

For the Maywood project gamma spectrometry parameters, the mean 2σ uncertainties were calculated for the following activity ranges. The mean σ uncertainty is 0.5 of the 2σ uncertainty, and equals u_{MR}:

Marinelli Geometry
Ac-228 (Th-232), between 4.4 and 5.6 pCi/g.
Pb-214 (Ra-226), between 3.9 and 6.0 pCi/g.
Th-234 (U-238), between 45.0 and 53.6 pCi/g

Tunacan Geometry
Ac-228 (Th-232), between 3.0 and 6.5 pCi/g.
Pb-214 (Ra-226), between 2.3 and 3.4 pCi/g.
Th-234 (U-238), there was no data near the action level; therefore, the Marinelli data was used as an approximation.

Table 9-1. Average 2 μ_{MR} Uncertainties, Average μ_{MR} Uncertainties and Average Relative Method Uncertainties (φ_{MR})

	No. of Points	Mean 2μ	Mean μ	φ_{MR} values
		Marinelli Geometry		
Th-232	25	0.325	0.162	3.25%
Ra-226	25	0.219	0.110	2.19%
U-238	26	4.08	2.04	4.08%
		Tunacan Geometry		
Th-232	14	0.388	0.194	3.88%
Ra-226	16	0.158	0.079	1.58%
U-238	26 (See note below)	4.08	2.04	4.08%

NOTE: For U-238 in soil, there are no values at or near the action level of 50 pCi/g for the tunacan geometry. Therefore, the μMR and φMR values for U-238 established for the Marinelli geometry were also used for the tunacan geometry.

The activity ranges for Ac-228 (Th-232) and Pb-214 (Ra-226) were chosen to represent a reasonable estimate of the uncertainty. Determination of the uncertainties for these two parameters is complicated by the fact that the action level, or UBGR, is 5 pCi/g for the sum of the activities of these two radionuclides. The author chose a group of activities around 5 pCi/g for Th-232 and for Ra-226 (if available) and around 50 pCi/g for U-238. The mean σ values are used as the u_{MR} values (see Table 9-1) to determine the warning and control limits for the gamma spectrometry parameters. The warning and control limits for laboratory replicate soils measured by gamma spectrometry are provided in Table 9-2.

Table 9-2 Warning and Control Limits for Laboratory Replicate Soil Results for Maywood Analytes Measured by Gamma Spectrometry

Table 9-2. Warning and Control Limits for Laboratory Replicate Soil Results for Maywood Analytes Measured by Gamma Spectrometry

Analyte	$\overline{X}$ < UBGR Warning Limit, 2.83 uMR	Control Limit, 4.24 uMR	$\overline{X}$ > UBGR Warning Limit, 100 X 2.83 φMR	Control Limit, 100 X 4.24 φMR
		Marinelli Geometry		
Th-232	0.460	0.689	9.20%	13.8%
Ra-226	0.310	0.464	6.20%	9.29%
U-238	5.77	8.65	11.5%	17.3%
		Tunacan Geometry		
Th-232	0.549	0.823	11.0%	16.5%
Ra-226	0.224	0.335	4.47%	6.70%
U-238	5.77 (see note below)	8.65	11.5%	17.3%

NOTE: For U-238 in soil, there are no values at or near the action level of 50 pCi/g for the tunacan geometry. Therefore, the μMR and φMR values for U-238 established for the Marinelli geometry were also used for the tunacan geometry.

For the alpha spectrometry parameters, only the Ra-226 and iso-uranium replicate limits were developed using MARLAP guidance since they are the only alpha spectrometrer parameters that are regulated. The regulatory limit for the sum of the activities of Ra-226 and Ra-228 in water is 5.0 pCi/L. The regulatory limit for total uranium is 20 pCi/L. For the purposes of this discussion, we

consider the sum of the U-234 and U-238 activities as comprising the total iso-uranium activity (U-235 is considered negligible). For the gas proportional multi-detector system (MDS), GA, GB, and Ra-228 are considered. Only GA, GB, and Ra-228 activities generated by UFML (as opposed to an outside lab) are considered and only those that meet the not-to-exceed MDA requirement of 3.0 for GA and 4.0 for GB are considered.

For the Maywood project alpha spectrometry and gas proportional detector parameters, the mean 2σ uncertainties were calculated for the following activity ranges:

- Ra-226, between 0.75 and 2.5 pCi/L.
- Ra-228, between 2.1 and 7.3 pCi/L
- U-234, between 7.6 and 11.6 pCi/L.
- U-238, between 7.6 and 10.8 pCi/L
- GA, between 9.0 and 15.5 pCi/L
- GB, between 39 and 53 pCi/L

Table 9-3. Average Required and Relative Uncertainties for Alpha Spectrometry and Gas Proportional Detector Parameters

	No. of Points	Mean 2 u_{MR}	Mean u_{MR}	φ_{MR} values
Ra-226	6	0.55	0.28	5.5%
Ra-228	17	0.91	0.46	9.1%
U-234	15	1.4	0.70	14%
U-238	12	0.885	0.44	8.85%
GA (900.0)	37	2.88	1.44	28.8%
GB (900.0)	33	2.79	1.40	27.9%
GA (7110C)	29	2.23	1.12	22.3%

The mean σ values are used as the u_{MR} values to determine the warning and control limits for the alpha spectrometry and gas proportional detector parameters. The warning and control limits for laboratory replicate waters measured by alpha spectrometry and gas proportional detection are provided in Table 9-4. As in Section 9.1, the quantity used to construct replicate control charts is $|X_1 - X_2|$ when $\overline{X}$ < UBGR and 100 x $|X_1 - X_2| / \overline{X}$ when $\overline{X}$ > UBGR.

Table 9-4. Warning and Control Limits for Laboratory Replicate Water Results for Maywood Analytes Measured by Alpha Spectrometry and Gas Proportional Detectors

Analyte	$\overline{X}$ < UBGR		$\overline{X}$ > UBGR	
	Warning Limit, 2.83 uMR	Control Limit, 4.24 uMR	Warning Limit, 100 X 2.83 φMR	Control Limit, 100 X 4.24 φMR
Ra-226	0.778	1.17	15.6%	23.3%
Ra-228	1.29	1.93	25.8%	38.9%
U-234	1.98	2.97	19.8%	29.7%
U-238	1.25	1.88	12.5%	18.8%
GA (900.0)	4.08	6.11	27.2%	40.7%
GB (900.0)	3.95	5.91	7.90%	11.8%
GA (7110C)	3.16	4.73	21.0%	31.5%

9.2 Verification

If replicate analyses are required but not performed, or if the required data are not present in the report, the validator should request the data from the laboratory. If they are still not available, their absence should be noted in the data validation report because overall analytical precision may be impacted. The validator must be provided with the warning and control limits as displayed in Tables 9-2 and 9-4 and defined in the beginning of Section 9.1 of this guidance.

9.3 Validation

If replicate values fall between the warning and control limits, all samples of the same matrix in the batch shall be qualified estimated J. If the LREP statistic is outside the control limits, the laboratory shall qualify all samples associated with that replicate using the letter P. The validator shall then use professional judgment to determine whether to J qualify, or to reject the data (i.e., R qualifier). Data shall not be rejected based upon lab replicate results alone.

Chapter 10
Field Duplicate Analysis (see Appendix C, Section C.4.2.2 of MARLAP, titled Duplicate Analyses)

10.1 Criteria

Field duplicate samples shall be taken and analyzed as an indication of overall precision. A field duplicate is a collocated sample that is sent "blind" to the lab by labeling it such that it cannot be determined from which sample it was split.

10.2 Verification

If duplicate analyses are required but not performed, or if the required data are not present in the report, the validator should request the data from the laboratory. If it is not available, this should be noted in the validation report, since overall data precision may be impacted.

10.3 Validation

The same criteria for lab replicates (see section 9 above) apply to field duplicates and are summarized below:

If $\overline{X}$ < UBGR:

Statistic:	$\left\|X_1 - X_2\right\|$
Warning limit:	2.83 u_{MR}
Control limit:	4.24 u_{MR}

If $\overline{X}$ >= UBGR:

Statistic:	RPD = 100 x $\left\|X_1 - X_2\right\|$ / $\overline{X}$
Warning limit:	2.83 φ_{MR} x 100%
Control limit:	4.24 φ_{MR} x 100%

Warning and control limits for the Maywood parameters of interest are provided within Tables 9-2 and 9-4. If duplicate values fall between the warning and control limits, all samples of the same matrix in the batch shall be qualified estimated J. If the field replicate statistic is outside the control limits, the validator shall qualify the results of all samples associated with the field replicate with the letter P. The validator shall then use professional judgment to determine whether to further qualify the results estimated J, or to reject the sample results. Data shall not be rejected based upon field duplicate data alone.

Chapter 11
Spectrometry Resolution

11.1 Gamma Spectroscopy

11.1.1 Criteria

The target radionuclide energy must be within 2 keV of the observed peak (MARLAP 15.6.3). This criteria does not apply for isotopes present at a values less than the MDA.

11.1.2 Verification

a. Check that the peak search algorithm of the instrument is set at 2 keV of the standard library energy for the identified radionuclide.

b. Compare isotope concentrations with equilibrium concentrations. Unless enrichment is suspected, these concentrations should be comparable.

11.1.3 Validation

Qualify the data as follows:

a. For radionuclide peaks that are detected but fail to meet the positive identification criteria; i.e., the peak energy is > 2 keV from the theoretical peak energy, qualify the data as rejected (R).

b. The validator may contact the lab to resolve differences and request additional information in an effort to resolve discrepancies.

11.2 Alpha Spectroscopy

Chemical separation specificity is the contract laboratory's ability to separate various radionuclides by chemical separation techniques. The chemical separation specificity can be verified for alpha spectroscopy measurements by observation of the alpha energy spectrum.

11.2.1 Criteria

The energy of the radionuclide of interest must be within 40 keV of the theoretical peak energy. This criteria does not apply for isotopes present at values less than the MDA.

11.2.2 Verification

Randomly check that the energy of the observed peak of interest is within 40 keV of the theoretical energy for the radionuclide of interest.

11.2.3 Validation

If the energy of the peak of interest is more than 40 keV from the energy for the radionuclide of interest, qualify the results as rejected (R). Corrective actions for this type of exceedance may include careful cleaning of the detector, or changing the amplifier settings. In either case, communication with the instrument manufacturer technical support group is recommended.

Chapter 12
Radionuclide Quantitation and Detection Limits

12.1 Criteria

The objective is to ensure that the reported quantitation results are accurate and that the required detection limits have been met. When detection limit requirements are not met, the data quality objectives may not have been met. All results shall be evaluated relative to the uncertainty associated with the analysis and the sample reports shall report the uncertainty.

Radionuclide quantitation must be calculated according to the appropriate procedures specified in the contractual SOW. Detection limits specified in the specific procedures must be met unless other detection limits are specified in the SOW.

Analytical uncertainties must be reported with all results in order to qualify the data. Results and uncertainties must be reported for all required analyses regardless of the size or sign of the result. The reported uncertainty must include all uncertainties associated with the analysis. An example calculation of the total propagated uncertainty or error must be provided to the data validator if requested.

12.2 Verification

The raw data shall be examined to verify the correct calculation of sample results reported by the laboratory.

a. Examine the raw data for any anomalies (i.e., omissions, legibility, etc.). Recalculate a few of the results if there is a suspicion the results have not been calculated properly. If calculation errors are found, (e.g., if sample results cannot be reproduced through manual calculations), contacting the laboratory may be necessary to resolve the problem. Qualifiers should be placed using professional judgment. Verify that all analytical uncertainties have been propagated and reported or otherwise documented.

b. Verify that uncertainties have been reported for all results. If a sample result is less than its uncertainty (or indistinguishable from background) or falls between its uncertainty and its MDA, the result shall be validated as directed in Section 12.3 below.

12.3 Validation

When significant errors are found in the calculations, qualify all affected results as rejected, R.

a. For net negative results that have uncertainties smaller than their absolute value, qualify the data “R” as rejected. This is an indication of improper blank subtraction or background shift.

b. For negative results that have uncertainties greater than the absolute value of the result, qualify the result U.

c. If a result is greater than its uncertainty, but less than its MDA, the result is non-detect, or less than background, since it is less than the MDA. While there is a finite possibility that the true result is >MDA, there is a greater probability that the result is less than the MDA. Qualify the result non-detect, U.

d. If a result is greater than its MDA, but less than its uncertainty, the probability that the result is >MDA is greater than the probability that it is less than the MDA. The result is accepted but qualified estimated J, since there will likely be significant probability (typ. 15-25%) for <MDA or negative values.

e. If a result is less than both its uncertainty and its MDA, qualify the result non-detect, U. There is a greater probability that the true result is less than its MDA.

f. When analytical uncertainties cannot be obtained from the lab, qualify the results "R" as rejected.

g. If a result is < critical level, qualify the result non-detect, U. The critical level is the upper 95% confidence interval of the background, essentially the background + 2σ

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted based on the reviewer's professional judgment.

Chapter 13
Matrix Density (gamma spectrometry only)

Matrix densities vary from sample to sample. Since analyte signal is dependant to some extent on sample density, this evaluation criterion takes into account the impact of variations in sample density.

13.1. Criteria

The sample density of the dried and ground sample must be within 70 – 130% of the density of the calibration standard.

13.2. Verification

Calculate each sample density by dividing the weight of the dried and ground sample by the volume of the sample within the sample container.

13.3. Validation

If the density of any sample is not within 70 – 130% of the density of the calibration standard, qualify the results for that sample as estimated J.

Chapter 14
Data Qualifier Definitions

Table 14-1. Data Qualifier Definitions

Data Qualifier	Definition
U	A normal, non-detected (< critical value) result
Q	A reported combined standard uncertainty, which exceeds the project's required method uncertainty
J	An unusually uncertain or estimated result
R	A rejected result: the problems (quantitative or qualitative) are severe; rejected data may still be usable depending upon the intended use of the data and the reason for data rejection
S	A result with a related spike result (laboratory control sample [LCS], matrix spike [MS] or matrix spike duplicate [MSD]) that is outside the control limit for recovery (%R); "S+" or "S-" used to indicate high or low recovery
P	A result with an associated replicate result that exceeds the control limit
B	A result with an associated blank result, which is outside the control limit, "B+" or "B-" used to indicate high or low results

Chapter 15
Glossary

Table 15-1. Glossary of Terms

Term	Definition
Calibration Curve	An analytical curve based on the pulse energy, detector efficiency, energy absorbance or other measured characteristic obtained from standard sources and a reagent blank.
Calibration Source	A radionuclide source counted daily to verify the calibration of a counting system.
Case	A finite (usually predetermined) number of samples collected over a given time period for a particular site. A case consists of one or more sample delivery group(s).
Chemical Tracer	A trace quantity of a different radioisotope of the same element or a carrier quantity of an inactive isotope of the same or a chemically similar element
Critical Level (CL)	The net count rate that must be exceeded before there is a specific degree of confidence that the sample contains any measurable radioactive material above background.
Laboratory Replicate	Two aliquots taken from a homogenized sample and analyzed as individual samples. These are used to determine the precision of the method.
Field Blank	A sample of radionuclide-free media which is taken to the field in sealed containers and transferred from one vessel to another at the sampling site and preserved with the appropriate reagents. This serves as a-check on reagent and environmental contamination. These blanks are treated as actual samples but may not be used for matrix spikes or sample replicates.
Field Replicate	A sample that is collected in the field, homogenized, and split into two separate samples, which are then sent to the laboratory as blind splits, or field replicates. These samples are useful for determination of the precision of the sample collection and preparation processes, as well as the analytical testing process.
Full Width at Half Maximum (FWHM)	The width of the distribution at a level that is half the maximum ordinate of the peak.
Holding Times	The time between the date of collection of sample and the date of sample analysis.
Laboratory Control Sample (LCS)	A control sample of known composition. Aqueous and solid laboratory control samples are analyzed using the same sample preparation, reagents and analytical methods employed for the unknown samples being analyzed. The results from the analysis of the controls are plotted and compared to control limits to determine the usability of the data.
Matrix Spike Sample (MSS)	An aliquot of sample spiked with a known concentration of target radionuclide(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix. (Some Federal Regulations require that data be corrected for spike recovery prior to reporting. Environmental Protection Agency recommends a minimum of 10 times the method detection Limit or 2 to 4 times the measured quantity.)

Table 15-1. Glossary of Terms

Term	Definition
Method Blank	A radionuclide-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process and should not be used for matrix spikes or sample duplicates.
Method Detection Limit (MDL)	The minimum concentration of a radionuclide that can be measured and reported with a specific degree of confidence that the radionuclide's activity is greater than zero and is determined for analysis of a sample in a given matrix type. MDL is equivalent to LLD, MDA, etc.
Percent Recovery (%R)	The fractional amount of the known activity of the radionuclide of interest that was obtained in the analysis.
Quality Control (QC)	An aggregate of activities designed to ensure adequate quality of analytical data.
QC Chart	A graphic representation on which the values obtained on the analysis of backgrounds, blanks, calibrations, and laboratory control samples are plotted sequentially. The chart usually consists of a central line and two control limit lines parallel to the central line. The distribution of the plotted values with respect to the control limits provides valuable visual and statistical information on the quality of the analyses.
Standard Operating Procedure (SOP)	Established or prescribed methods to be followed routinely for the performance of design area operations or in designated situations.
Scope of Work (SOW)	A detailed description of work to be performed by a contracted laboratory or facility.
Target Radionuclide List (TRL)	A listing of radionuclides for which a quantitative analysis is required. Net quantitation with uncertainties must be provided for all TRL radionuclides whether or not the radionuclide is identified in the computerized peak search and identification routine.

Chapter 16
References

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US EPA
Hazardous Waste Support Branch
Validating Semivolatile Organic Compounds
By Gas Chromatography/Mass Spectrometry
SW-846 Method 8270D

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Annual Review

Reviewed by: _____ Date: _____
Name

Reviewed by: _____ Date: _____
Name

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INTRODUCTION

Scope and Applicability

This SOP offers detailed guidance in evaluating laboratory data generated according to "SW846-Method 8270D" January 1998. Method 8270D is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. The validation methods and actions discussed in this document are based on the requirements set forth in SW846 Method 8270D, Method 8000C and the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," January 2005. This document covers technical problems specific to each fraction and sample matrix; however, situations may arise where data limitations must be assessed based on the reviewer's professional judgement.

Summary of Method

To ensure a thorough evaluation of each result in a data case, the reviewer must complete the checklist within this SOP, answering specific questions while performing the prescribed "ACTIONS" in each section. Qualifiers (or flags) are applied to questionable or unusable results as instructed. The data qualifiers discussed in this document are defined on page 5.

The reviewer must prepare a detailed data assessment to be submitted along with the completed SOP checklist. The Data Assessment must list all data qualifications, reasons for qualifications, instances of missing data and contract non-compliance.

Reviewer Qualifications

Data reviewers must possess a working knowledge of SW846 Analytical Methods and National Functional Guidelines mentioned above.

DEFINITIONS

Acronyms

BNA - base neutral acid(another name for Semi Volatiles)
CLP - Contract Laboratory Program
CRQL - Contract Required Quantitation Limit
%D - percent difference
DCB -decachlorobiphenyl
DDD - dichlorodiphenyldichloroethane
DDE - dichlorodiphenylethane
DDT - dichlorodiphenyltrichloroethane
DoC - Date of Collection
GC - gas chromatography
GC/ECD - gas chromatograph/electron capture detector
GC/MS - gas chromatograph/mass spectrometer
GPC - gel permeation chromatography
IS - internal standard
kg - kilogram
µg - microgram
MS - matrix spike
MSD - matrix spike duplicate
ℓ - liter
mℓ - milliliter
PCB - Polychlorinated biphenyl
PE - performance evaluation
PEM - Performance Evaluation Mixture
QC - quality control
RAS - Routine Analytical Services
RIC - reconstructed ion chromatogram
RPD - relative percent difference
RRF - relative response factor
RRF - average relative response factor (from initial calibration)
RRT - relative retention time
RSD - relative standard deviation
RT - retention time
RSCC - Regional Sample Control Center
SDG - sample delivery group
SMC - system monitoring compound
SOP - standard operating procedure
SOW - Statement of Work
SVOA - semivolatile organic acid
TCL - Target Compound List
TCLP - Toxicity Characteristics Leachate Procedure

TCX -tetrachloro-m-xylene
TIC - tentatively identified compound
TOPO - Task Order Project Officer
TPO - Technical Project Officer
VOA - Volatile organic
VTSR - Validated Time of Sample Receipt

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

JN - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

LAB QUALIFIERS:

D - The positive value is the result of an analysis at a secondary dilution factor.

B - The analyte is present in the associated method blank as well as in the sample. This qualifier has a different meaning when validating inorganic data.

YES NO N/A

E - The concentration of this analyte exceeds the calibration range of the instrument.

A - Indicates a Tentatively Identified Compound (TIC) is a suspected adol-condensation product.

X,Y,Z- Laboratory defined flags. The data reviewer must change these qualifiers during validation so that the data user may understand their impact on the data.

I. PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____ LAB:_____

SITE NAME:_____

1.0 Data Completeness and Deliverables

1.1 Has all data been submitted in CLP deliverable format? [ ] ___ ___

ACTION: If not, note the effect on review of the data in the data assessment narrative.

2.0 Cover Letter, SDG Narrative

2.1 Is a laboratory narrative or cover letter present? [ ] ___ ___

2.2 Are case number and SDG number(s) contained in the narrative or cover letter? [ ] ___ ___

YES NO N/A

II. SEMIVOLATILE ANALYSES

1.0 Traffic Reports and Laboratory Narrative

1.1 Are the Traffic Report Forms present for all samples? [ ] ___ ___

ACTION: If no, contact lab for replacement of missing or illegible copies.

1.2 Do the Traffic Reports or Lab Narrative indicate any problems with sample receipt, condition of samples, analytical problems or special notations affecting the quality of the data? ___ [ ] ___

ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated ("J"). If a soil sample, other than TCLP, contains more than 90% water, all non-detects data are qualified as unusable (R), and detects are flagged “J”.

ACTION: If samples were not iced, or if the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (10^{o}C), flag all positive results "J" and all non-detects "UJ".

2.0 Holding Times

2.1 Have any semivolatile technical holding times, determined from date of collection to date of extraction, been exceeded? ___ [ ] ___

Continuous extraction of water samples for semivolatile analysis must be started within **7** days of the date of collection. Soil/sediment samples must be extracted within **14** days of collection. Extracts must be analyzed within

40 days of the date of extraction.

Table of Holding Time Violations

(See Traffic Report)

Sample ID	Sample Matrix	Date Sampled	Date Lab Received	Date Extracted	Date Analyzed

ACTION: If technical holding times are exceeded, flag all positive results as estimated ("J") and sample quantitation limits as estimated ("UJ"), and document in the narrative that holding times were exceeded.

If analyses were done more than 14 days beyond holding time, either on the first analysis or upon re analysis, the reviewer must use professional judgement to determine the reliability of the data and the effects of additional storage on the sample results. At a minimum, all results should be qualified "J", but the reviewer may determine that non-detect data are unusable ("R"). If holding times are exceeded by more than 28 days, all non-detect data are unusable (R).

S))Q

		YES	NO	N/A
3.0	Surrogate Recovery (Form II/Equivalent)			
3.1	Have the semi volatile surrogate recoveries been listed on CLP Surrogate Recovery forms (Form II) for each of the following matrices:			
	a. Low Water	[ ]	___	___
	b. Low/Med Soil	[ ]	___	___
3.2	If so, are all the samples listed on the appropriate Surrogate Recovery Summary forms for each matrix:			
	a. Low Water	[ ]	___	___
	b. Low/Med Soil	[ ]	___	___
	ACTION: If CLP deliverables are unavailable, document the effect(s) in data assessments. In some cases the lab may have to be contacted to obtain the data necessary to complete the validation.			
3.3	Were outliers marked correctly with an asterisk?	[ ]	___	___
	ACTION: Circle all outliers in red.			
3.4	Were two or more base neutral OR acid surrogate recoveries out of specification for any sample or method blank (Reviewer should use lab in house recovery limits. Use surrogate recovery limits from USEPA National Functional Guidlines January 2005 page 130, if in house limits are not available. See Method 8000B-43 or 80000C-24).	[ ]	___	___
	Note: Examine lab in house limits for reasonableness.			
	If yes, were samples re-analyzed?	[ ]	___	___

YES NO N/A

Were method blanks re-analyzed? [ ] ___ ___

ACTION: If all surrogate recoveries are > 10% but two within the base-neutral or acid fraction do not meet method specifications, for the affected fraction only (i.e. either base-neutral or acid compounds):

1. Flag all positive results as estimated ("J").

2. Flag all non-detects as estimated detection limits ("UJ") when recoveries are less than the lower acceptance limit.

3. If recoveries are greater than the upper acceptance limit, do not qualify non-detects.

If any base-neutral or acid surrogate has a recovery of < 10%:

1. Positive results for the fraction with < 10% surrogate recovery are qualified with "J".

2. Non-detects for that fraction should be qualified as unusable (R) .

NOTE: Professional judgement should be used to qualify data that have method blank surrogate recoveries out of specification in both original and reanalyses. Check the internal standard areas.

3.5 Are there any transcription/calculation errors between raw data and Form II? ___ [ ] ___

ACTION: If large errors exist, call lab for explanation/resubmittal, make any necessary corrections and document

YES NO N/A

effect in data assessments.

4.0 Matrix Spikes (Form III/Equivalent)

4.1 Have the semivolatile Matrix Spike and Matrix Spike Duplicate/or duplicate unspiked Sample recoveries been listed on the Recovery Form (Form III)? [ ] ___ ___

NOTE: Method 3500B/page 4 states the spiking compounds:

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

Note: Some projects may require the spiking of specific compounds of interest.

Note: See Method 8270D-sec 8.4.2 for deciding on whether to prepare and analyze duplicate samples or a martix spike/matrix spike duplicate. If samples are expected to contain target analytes, then laboratory may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratory should use a matrix spike and matrix spike duplicate pair.

4.2 Were matrix spikes analyzed at the required frequency for each of the following matrices:

a. Low Water [ ] ___ ___

b. Low Solid [ ] ___ ___

c. Med Solid [ ] ___ ___

YES NO N/A

ACTION: If any matrix spike data are missing, take the action specified in 3.2 above. It may be necessary to contact the lab to obtain the required data.

NOTE: If the data has not been reported on CLP equivalent form, then the laboratory must provide the information necessary to evaluate the spike recoveries in the MS and MSD. The required data which should have been provided by the lab include the analytes and concentrations used for spiking, background concentrations of the spiked analytes (i.e., concentrations in unspiked sample), methods and equations used to calculate the QC acceptance criteria for the spiked analytes, percent recovery data for all spiked analytes.

The data reviewer must verify that all reported equations and percent recoveries are correct before proceeding to the next section.

4.3 Were matrix spikes performed at concentration equal to 100ug/L for acid compounds, and 200ug/l for base compounds (Method 3500B-4), or those specified in project plan. [ ] ___ ___

4.4 How many semivolatile spike recoveries are outside Laboratory in house MS/MSD recovery limits (use recovery limits values in Method 8270D-43&44 Table 6 if in house values not available).

Water	Solids
____ out of ____	____ out of ____

YES NO N/A

4.5 How many RPD's for matrix spike and matrix spike duplicate recoveries are outside QC limits?

Water	Solids
____ out of ____	____ out of ____

ACTION: Circle all outliers with red pencil.

ACTION: No action is taken on MS/MSD data alone. However, using informed professional judgement, the data reviewer may use the matrix spike and matrix spike duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data.

4.6 Was a Laboratory Control Sample (LCS) analyzed with each analytical batch? [ ] ___ ___

NOTE: When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

5.0 Blanks (Form IV/Equivalent)

5.1 Is the Method Blank Summary (Form IV) present? [ ] ___ ___

5.2 Frequency of Analysis:

Has a reagent/method blank analysis been reported per 20 samples of similar matrix, or concentration level, and for each extraction batch? [ ] ___ ___

5.3 Has a method blank been analyzed either after

	YES	NO	N/A
the calibration standard or at any other time during the analytical shift for each GC/MS system used ?	[ ]	___	___

ACTION: If any method blank data are missing, call lab for explanation/resubmittal. If not available, use professional judgement to determine if the associated sample data should be qualified.

5.4 Chromatography: review the blank raw data - chromatograms (RICs), quant reports or data system printouts and spectra.			
Is the chromatographic performance (baseline stability) for each instrument acceptable for the semivolatiles?	[ ]	___	___

ACTION: Use professional judgement to determine the effect on the data.

6.0 Contamination

NOTE: "Water blanks", "drill blanks" and "distilled water blanks" are validated like any other sample and are not used to qualify the data. Do not confuse them with the other QC blanks discussed below.

6.1 Do any method/instrument/reagent blanks have positive results for target analytes and/or TICs? When applied as described below, the contaminant concentration in these blanks are multiplied by the sample dilution factor and corrected for percent moisture where necessary.	___	[ ]	___
6.2 Do any field/rinse/ blanks have positive results for target analytes and/or TICs (if required, see section 10 below)?	___	[ ]	___

ACTION: Prepare a list of the samples associated with each of the contaminated blanks. (Attach a separate sheet.)

NOTE: All field blank results associated to a particular group of samples (may exceed one per case) must be used to qualify data. Blanks may not be qualified because of contamination in another blank. Field Blanks must be qualified for outlying surrogates, poor spectra, instrument performance or calibration QC problems.

ACTION: Follow the directions in the table below to qualify sample results due to contamination. Use the largest value from all the associated blanks. If gross contamination exists, all data in the associated samples should be qualified as unusable (R).

Blank Action for Semivolatile Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Field	Detects	Not detected	No qualification required
	< CRQL *	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification required
	= CRQL *	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification required
	> CRQL *	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank contamination	Report concentration of sample with a U
		≥ CRQL and ≥ blank contamination	No qualification required

NOTE: Analytes qualified "U" for blank contamination are still considered as "hits" when qualifying for calibration criteria.

NOTE: If the laboratory did not report TIC analyses, check the project plans to verify whether or not it was required.

6.3 Are there field/rinse/equipment blanks associated with every sample? [ ] ___ ___

ACTION: For low level samples, note in data assessment that there is no associated field/rinse/equipment blank. Exception: samples taken from a drinking water tap do not have associated field blanks.

6.4 Was a instrument blank analyzed after each sample/dilution which contained a target compound

	YES	NO	N/A
that exceeded the initial calibration range.	[ ]	___	___
6.5 Does the instrument blank have positive results for target analytes and/or TICs?	___	[ ]	___

Note: Use professional judgement to determine if carryover occurred and qualify analytes accordingly.

7.0 GC/MS Apparatus and Materials

	YES	NO	N/A
7.1 Did the lab use the proper gas chromatographic column for analysis of semivolatiles by Method 8270D? Check raw data, instrument logs or contact the lab to determine what type of column was used. The method requires the use of 30 m x 0.25 mm ID (or 0.32 mm ID), silicone-coated, fused silica, capillary column.	[ ]	___	___

ACTION: If the specified column, or equivalent, was not used, document the effects in the data assessment. Use professional judgement to determine the acceptability of the data.

8.0 GC/MS Instrument Performance Check (Form V/Equivalent)

	YES	NO	N/A
8.1 Are the GC/MS Instrument Performance Check Forms (Form V) present for decafluorotriphenylphosphine (DFTPP)?	[ ]	___	___

NOTE: The performance solution should also contain 4,4-DDT, pentachlorophenol, and benzidine to verify injection port inertness and column performance. The degradation of DDT to DDE and DDD must be less than 20% total and the response of pentachlorophenol and benzidine should be within normal ranges for these compounds (based upon lab experience) and show no peak degradation or tailing before samples are analyzed. (see section 5.5

YES NO N/A

page 8270D-12).

8.2 Are the enhanced bar graph spectrum and mass/charge (m/z) listing for the DFTPP provided for each twelve hour shift? [ ] ___ ___

8.3 Has an instrument performance check solution been analyzed for every twelve hours of sample analysis per instrument? [ ] ___ ___

ACTION: List date, time, instrument ID, and sample analyses for which no associated GC/MS tuning data are available.

DATE	TIME	INSTRUMENT	SAMPLE NUMBERS
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

ACTION: If lab cannot provide missing data, reject ("R") all data generated outside an acceptable twelve hour calibration interval.

ACTION: If mass assignment is in error, flag all associated sample data as unusable (R).

8.4 Have the ion abundances been normalized to m/z 198? [ ] ___ ___

8.5 Have the ion abundance criteria been met for each instrument used? [ ] ___ ___

ACTION: List all data which do not meet ion abundance criteria (attach a separate sheet).

	YES	NO	N/A
ACTION: If ion abundance criteria are not met, take action specified in section 3.2			
8.6 Are there any transcription/calculation errors between mass lists and Form Vs? (Check at least two values but if errors are found, check more.)	___	[ ]	___
8.7 Have the appropriate number of significant figures (two) been reported?	[ ]	___	___
ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and document effect in data assessments.			
8.8 Are the spectra of the mass calibration compound acceptable?	[ ]	___	___
ACTION: Use professional judgement to determine whether associated data should be accepted, qualified, or rejected.			

9.0 Target Analytes

9.1 Are the Organic Analysis Data Sheets (Form I) present with required header information on each page, for each of the following:			
a. Samples and/or fractions as appropriate	[ ]	___	___
b. Matrix spikes and matrix spike duplicates	[ ]	___	___
c. Blanks	[ ]	___	___
9.2 Has any special cleanup, such as GPC, been performed on all soil/sediment sample extracts (see section 7.2, page 8270D-14)?	[ ]	___	___

YES NO N/A

ACTION: If data suggests that extract cleanup was not performed, use professional judgement. Make note in the data assessment narrative.

9.3 Are the Reconstructed Ion Chromatograms, mass spectra for the identified compounds, and the data system printouts (Quant Reports) included in the sample package for each of the following?

a. Samples and/or fractions as appropriate [ ] ___ ___

b. Matrix spikes and matrix spike duplicates (Mass spectra not required) [ ] ____ ___

c. Blanks [ ] ___ ___

ACTION: If any data are missing, take action specified in 3.2 above.

9.4 Are the response factors shown in the Quant Report? [ ] ___ ___

9.5 Is chromatographic performance acceptable with respect to:

Baseline stability? [ ] ___ ___

Resolution? [ ] ___ ___

Peak shape? [ ] ___ ___

Full-scale graph (attenuation)? [ ] ___ ___

Other:_____ [ ] ___ ___

ACTION: Use professional judgement to determine the acceptability of the data.

9.6 Are the lab-generated standard mass spectra of identified semivolatile compounds present for

	YES	NO	N/A
each sample?	[ ]	___	___

ACTION: If any mass spectra are missing, take action specified in 3.2 above. If the lab does not generate their own standard spectra, make a note in the data assessment narrative. If spectra are missing, reject all positive data.

9.7 Is the RRT of each reported compound within 0.06 RRT units of the standard RRT in the continuing calibration?	[ ]	___	___
9.8 Are all ions present in the standard mass spectrum at a relative intensity greater than 10% (of the most abundant ion) also present in the sample mass spectrum?	[ ]	___	___
9.9 Do the relative intensities of the characteristic ions in the sample agree within ± 30% of the corresponding relative intensities in the reference spectrum?	[ ]	___	___

ACTION: Use professional judgement to determine acceptability of data. If it is determined that incorrect identifications were made, all such data should be rejected (R), flagged "N" (Presumptive evidence of the presence of the compound) or changed to not detected (U) at the calculated detection limit. In order to be positively identified, the data must comply with the criteria listed in 9.7, 9.8, and 9.9.

ACTION: When sample carry-over is a possibility, professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification.

YES NO N/A

10.0 Tentatively Identified Compounds (TIC)

10.1 If Tentatively Identified Compounds were required for this project, are all Form Is, Part B present; and do listed TICs include scan number or retention time, estimated concentration and "JN" qualifier?

NOTE: Review sampling reports to determine if the lab was required to identify non target analytes (refer to section 7.6.2,page 8270D-21).

10.2 Are the mass spectra for the tentatively identified compounds and associated "best match" spectra included in the sample package for each of the following: [ ] ___ ___

a. Samples and/or fractions as appropriate [ ] ___ ___

b. Blanks [ ] ___ ___

ACTION: If any TIC data are missing, take action specified in 3.2 above.

ACTION: Add "JN" qualifier only to analytes identified by CAS #.

10.3 Are any target compounds from one fraction listed as TIC compounds in another (e.g., an acid compound listed as a base neutral TIC)? ___ [ ] ___

ACTION: i. Flag with "R" any target compound listed as a TIC.

ii. Make sure all rejected compounds are properly reported in the other fraction.

10.4 Are all ions present in the reference mass spectrum with a relative intensity greater than 10% (of the most abundant ion) also present in the

	YES	NO	N/A
sample mass spectrum?	[ ]	___	___
10.5 Do TIC and "best match" standard relative ion intensities agree within ± 20%?	[ ]	___	___

ACTION: Use professional judgement to determine acceptability of TIC identifications. If it is determined that an incorrect identification was made, change the identification to "unknown" or to some less specific identification (example: "C3 substituted benzene") as appropriate and remove "JN". Also, when a compound is not found in any blank, but is a suspected artifact of a common laboratory contaminant, the result should be qualified as unusable, "R."

11.0 Compound Quantitation and Reported Detection Limits

	YES	NO	N/A
11.1 Are there any transcription/calculation errors in Form I results? Check at least two positive values. Verify that the correct internal standard, quantitation ion, and RRF were used to calculate Form I result. Were any errors found?	___	[ ]	___

NOTE: Structural isomers with similar mass spectra, but insufficient GC resolution (i.e. percent valley between the two peaks > 25%) should be reported as isomeric pairs. The reviewer should check the raw data to ensure that all such isomers were included in the quantitation (i.e., add the areas of the two coeluting peaks to calculate the total concentration).

	YES	NO	N/A
11.2 Are the method detection limits adjusted to reflect sample dilutions and, for soils, sample moisture?	[ ]	___	___

YES NO N/A

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and document effect in data assessments.

ACTION: When a sample is analyzed at more than one dilution, the lowest detection limits are used (unless a QC exceedance dictates the use of the higher detection limit from the diluted sample data). Replace concentrations that exceed the calibration range in the original analysis by crossing out the "E" and it's associated value on the original Form I (if present) and substituting the data from the analysis of the diluted sample. Specify which Form I is to be used, then draw a red " X" across the entire page of all Form I's that should not be used, including any in the summary package.

12.0 Standards Data (GC/MS)

12.1 Are the Reconstructed Ion Chromatograms, and data system printouts (Quant, Reports) present for initial and continuing calibration? [ ] ___ ___

ACTION: If any calibration standard data are missing, take action specified in 3.2 above.

13.0 GC/MS Initial Calibration (Form VI/Equivalent)

13.1 Is the Initial Calibration Form (Form VI/ Equivalent) present and complete for the semivolatile fraction? [ ] ___ ___

ACTION: If any calibration forms or standard row data are missing, take action specified in 3.2 above.

13.2 Are all base neutral or acid RRFs > 0.050? [ ] ___ ___

YES NO N/A

Check the **average RRFs** of the four System Performance Check Compounds (SPCCs): N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. These compounds must have **average RRFs** greater than or equal to 0.05 before running samples and should not show any peak tailing.

ACTION: Circle all outliers in red.

ACTION: For any target analyte with **average RRF <0.05**

1. "R" all non-detects;

2. "J" all positive results.

13.3 Are response factors for base neutral or acid target analytes stable over the concentration range of the calibration (% Relative standard deviation [%RSD] < 15.0%)? [ ] ___ ___

NOTE: The % RSD for each individual Calibration Check Compound (CCC, Method 8270D-40 see Table 4) must be less than 30% before analysis can begin. If grater 30%, the lab must clean and recalibrate the instrument.

CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol

YES NO N/A

Benzo(a)pyrene

ACTION: If the %RSD for any CCC >30% and no corrective action taken, then "J" qualify all positive hits and "UJ" qualify all non-detects.

ACTION: Circle all outliers in red.

ACTION: If the % RSD is $\geq$ 15.0%, qualify positive results for that analyte "J" and non-detects using professional judgement. When RSD > 90%, flag all non- detect results for that analyte "R," unusable. Alternatively, the lab should calculate first or second order regression fit of the calibration curve and select the fit which introduces the least amount of error.

NOTE: Analytes previously qualified "U" due to blank contamination are still considered as "hits" when qualifying for calibration criteria.

13.4 Did the laboratory calculate the calibration curve by the least squares regression fit? ___ [ ] ___

13.5 Are there any transcription/calculation errors in the reporting of average response factors (RRF) or % RSD? (Check at least two values but if errors are found, check more.) ___ [ ] ___

ACTION: Circle Errors in red.

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and note errors in data assessments.

13.5 Do the target compounds for this SDG include Pesticides? [ ] ___ ___

YES NO N/A

13.6 If the pesticide compounds include DDT, was the percent breakdown of DDT to DDD and DDE greater than 20%? ___ [ ] ___

ACTION: If DDT percent breakdown exceeds 20%:

i. Qualify all positive results for DDT with "J". If DDT was not detected, but DDD and DDE results are positive, qualify the quantitation limit for DDT as unusable, "R".

ii. Qualify all positive results for DDD and DDE as presumptively present at an approximate concentration "JN".

14.0 GC/MS Calibration Verification (Form VII/Equivalent)

14.1 Are the Calibration Verification Forms (Form VII) present and complete for all compounds of interest? [ ] ___ ___

14.2 Has a calibration verification standard been analyzed for every twelve hours of sample analysis per instrument? [ ] ___ ___

ACTION: List below all sample analyses that were not within twelve hours of a calibration verification analysis for each instrument used.

_____

_____

_____

ACTION: If any forms are missing or no calibration verification standard has been analyzed within twelve hours of every sample analysis,

YES NO N/A

call lab for explanation/resubmittal. If continuing calibration data are not available, flag all associated sample data as unusable ("R").

14.3 Do any of the SPCCs have an RRF <0.05? ___ [ ] ___

If YES, make a note in data assessment if the lab did not take corrective action specified in section 7.4.4, page 8270D-18. [ ] ___ ___

14.4 Do any of the CCCs have a %D between the initial and continuing RRF which exceeds 20.0%?

ACTION: If yes, make a note in data assessment.

14.5 Do any semivolatile compounds have a % Difference (% D) between the initial and continuing RRF which exceeds 20.0%? ___ [ ] ___

ACTION: Circle all outliers in red.

ACTION: Qualify both positive results and non-detects for the outlier compound(s) as estimated (J). When %D is above 90%, qualify all non-detects for that analyte as "R", unusable.

14.6 Do any semivolatile compounds have a RRF < 0.05? ___ [ ] ___

ACTION: Circle all outliers in red.

ACTION: If RRF < 0.05, qualify as unusable ("R") associated non-detects and "J" associated positive values.

14.7 Are there any transcription/calculation errors in the reporting of average response factors (RRF) or percent difference (%D) between initial and continuing RRFs? (Check at least two values but if errors are found, check more). ___ [ ] ___

YES NO N/A

ACTION: Circle errors in red.

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and document effect(s) in the data assessments.

15.0 Internal Standards (Form VIII)

15.1 Are the internal standard areas (Form VIII) of every sample and blank within the upper and lower limits (-50% to + 100%) for each continuing calibration? [ ] ___ ___

ACTION: List each outlying internal standard below.

Sample ID	IS #	Area	LowerLimit	Upper Limit

(Attach additional sheets if necessary.)

Note: Check Table 5, 8270D-41 for associated analytes.

ACTION: i. If the internal standard area count is outside the upper or lower limit, flag with "J" all positive results and non-detects (U values) quantitated with this internal standard.

ii. Non-detects associated with IS > 100% should not be qualified.

YES NO N/A

iii. If the IS area is below the lower limit (<50%), qualify all associated non-detects (U-values) "J". If extremely low area counts are reported (<25%) or if performance exhibits a major abrupt drop off, flag all associated non-detects as unusable (R).

15.2 Are the retention times of all internal standards within 30 seconds of the associated calibration standard? [ ] ___ ___

ACTION: Professional judgement should be used to qualify data if the retention times differ by more than 30 seconds.

16.0 Laboratory Control Samples (LCS)

16.1 Were any LCS samples run in order to verify analytes which failed criteria for spike recovery? [ ] ___ ___

16.2 Did the lab spike LCS sample spiked with the same analytes and the same concentrations as the matrix spike? [ ] ___ ___

16.3 Were the mean and standard deviation of all analytes within the QC acceptance ranges as shown in Table 6, 8270D-43? [ ] ___ ___

ACTION: If the recovery of any analyte falls out of the designated range, the analytical results for that compound is suspect and should be qualified "J" in the unspiked samples.

17.0 Field Duplicates

17.1 Were any field duplicates submitted for semivolatile analysis? [ ] ___ ___

S))Q
YES NO N/A

ACTION: Compare the reported results for field duplicates and calculate the relative percent difference.

ACTION: Any gross variation between field duplicate results must be addressed in the reviewer narrative. However, if large differences exist, identification of field duplicates should be confirmed by contacting the sampler.

USEPA
Hazardous Waste Support Branch
Validating Volatile Organic Compounds
By Gas Chromatography/Mass Spectrometry
SW-846 Method 8260B

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Annual Review

Reviewed by: _____ Date: _____
Name

Reviewed by: _____ Date: _____
Name

Scope and Applicability

This SOP offers detailed guidance in evaluating laboratory data generated according to the USEPA SW-846, Method 8260B December 1996. The validation methods and actions discussed in this document are based on the requirements set forth in USEPA SW-846, Method 8260B and Method 8000C, Rev 3, March 2003; and "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," January, 2005. This document covers technical as well as method specific problems; however situations may arise where data limitations must be assessed based on the reviewer's own professional judgement.

Summary

To ensure a thorough evaluation of each result in a data case, the reviewer must complete the checklist within this SOP, answering specific questions while performing the prescribed "ACTIONS" in each section. Qualifiers (or flags) are applied to questionable or unusable results as instructed. The data qualifiers discussed in this document are defined on page 4.

The reviewer must prepare a detailed data assessment to be submitted along with the complete SOP checklist. The Data Assessment must list all data qualifications, reasons for qualifications, instances of missing data, and contract non-compliance.

DEFINITIONS

Acronyms

BNA - base neutral acid(another name for Semi Volatiles)
CLP - Contract Laboratory Program
CRQL - Contract Required Quantitation Limit
CF - calibration factor
%D - percent difference
DCB -decachlorobiphenyl
DDD - dichlorodiphenyldichloroethane
DDE - dichlorodiphenylethane
DDT - dichlorodiphenyltrichloroethane
DoC - Date of Collection
GC - gas chromatography
GC/ECD - gas chromatograph/electron capture detector
GC/MS - gas chromatograph/mass spectrometer
GPC - gel permeation chromatography
IS - internal standard
kg - kilogram
µg - microgram
MS - matrix spike
MSD - matrix spike duplicate
ℓ - liter
mℓ - milliliter
PCB - Polychlorinated biphenyl
PE - performance evaluation
PEM - Performance Evaluation Mixture
QC - quality control
RAS - Routine Analytical Services
RIC - reconstructed ion chromatogram
RPD - relative percent difference
RRF - relative response factor
RRF - average relative response factor (from initial calibration)
RRT - relative retention time
RSD - relative standard deviation
RT - retention time
RSCC - Regional Sample Control Center
SDG - sample delivery group
SMC - system monitoring compound
SOP - standard operating procedure
SOW - Statement of Work
SVOA - semivolatile organic acid
TCL - Target Compound List
TCLP - Toxicity Characteristics Leachate Procedure
TCX -tetrachloro-m-xylene
TIC - tentatively identified compound

TOPO - Task Order Project Officer
TPO - Technical Project Officer
VOA - Volatile organic
VTSR - Validated Time of Sample Receipt

Data Qualifiers

U -The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J -The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N -The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

JN -The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ -The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R -The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

LAB QUALIFIERS:

D - The positive value is the result of an analysis at a secondary dilution factor.

B - The analyte is present in the associated method blank as well as in the sample. This qualifier has a different meaning when validating inorganic data.

E - The concentration of this analyte exceeds the calibration range of the instrument.

A - Indicates a Tentatively Identified Compound (TIC) is a suspected adol-condensation product.

X,Y,Z- Laboratory defined flags. The data reviewer must change these qualifiers during validation so that the data user may understand their impact on the data.

YES NO N/A

I. PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____ LAB:_____

SITE NAME:_____

1.0 Data Completeness and Deliverables

1.1 Has all data been submitted in CLP deliverable format or CLP Forms Equivalent? [ ] ___ ___

ACTION: If not, note the effect on review of the data in the Data Assessment narrative.

2.0 Cover Letter, SDG Narrative

2.1 Is a laboratory narrative, and/or cover letter signed release present? [ ] ___ ___

2.2 Are case number and SDG number(s) contained in the narrative or cover letter? [ ] ___ ___

ACTION: If not, note the effect on review of the data in the Data Assessment narrative.

II. VOLATILE ANALYSES

1.0 Traffic Reports and Laboratory Narrative

1.1 Are the Traffic Reports, and/or Chain of Custodies from the field samplers present for all samples sign release present? [ ] ___ ___

ACTION: If no, contact the laboratory/sampling team for replacement of missing or illegible copies.

1.2 Is a sampling trip report present (if required)? [ ] ___ ___

1.3 Sample Conditions/Problems

YES NO N/A

1.3.1 Do the Traffic Reports, Chain of Custodies, or Lab Narrative indicate any problems with sample receipt, condition of samples, analytical problems or special notations affecting the quality of the data? ___ [ ] ___

ACTION: If all the VOA vials for a sample have air bubbles or the VOA vial analyzed had air bubbles, flag all positive results "J" and all non-detects "R".

ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated ("J"). If a soil sample, other than TCLP, contains more than 90% water, flag all positive results “J” and all non-detects “R”.

ACTION: If samples were not iced or if the ice was melted upon receipt at the laboratory and the temperature of the cooler was elevated (>10°C), flag all positive results "J" and all non-detects non"UJ".

2.0 Holding Times

2.1 Have any volatile holding times, determined from date of collection to date of analysis, been exceeded?

___ [ ] ___

The maximum holding time for aqueous samples is 14 days.

The maximum holding time for soils non aqueous samples is 14 days.

NOTE: If unpreserved, aqueous samples maintained at 4°C for aromatic hydrocarbons analysis must be analyzed within 7 days. If preserved with HCL acid to a pH<2 and stored at 4°C,then aqueous samples must be analyzed within 14 days from time of collection. For non-aqueous samples for volatile components that are frozen (less than 7°C) or are properly cooled (4°C ± 2°C) and perserved with $NaHSO_4$, the maximum holding time is 14 days from sample collection. If

YES NO N/A

uncertain about preservation, contact the laboratory /sampling team to determine whether or not samples were preserved.

ACTION: Qualify sample results according to Table 1:

Table 1. Holding Time Actions for Trace Volatile Analysis

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤7 days	No qualifications	
	No	> 7 days	J	R
	Yes	≤14 days	No qualifications	
	Yes	> 14 days	J	R
Non Aqueous	No	≤ 14 days	J	R
	Yes	≤ 14 days	No qualifications	
	Yes/No	> 14 days	J	R

3.0 Surrogate Recovery (CLP Form II Equivalent)

3.1 Have the volatile surrogate recoveries been listed on Surrogate Recovery forms for each of the following matrices:

a. Water [ ] ___ ___

b. Soil [ ] ___ ___

3.2 If so, are all the samples listed on the appropriate Surrogate Recovery forms for each matrix:

a. Water [ ] ___ ___

b. Soil [ ] ___ ___

ACTION: If large errors exist, deliverables are unavailable or information is missing, document the effect(s) in Data

YES NO N/A

Assessments and contact the laboratory/project officer/appropriate official for an explanation /resubmittal,make any necessary corrections and document effect in the Data Assessment.

3.3 Were the surrogate recovery limits followed per Table 2. If Table 2 criteria were not followed, the laboratory may use in-house performance criteria (per SW-846, Method 8000C, sectiom 9.7). Other compounds may be used as surrogates, depending upon the analysis requirements. [ ] ___ ___

Table 2. Surrogate Spike Recovery Limits for Water and Soil/Sediments

DMC	Recovery Limits (%)Water	Recovery Limits Soil/Sediment
4-Bromofluorobenzene	80-120	70-130
Dibromofluoromethane	80-120	70-130
Toluene-d_8	80-120	70-130
Dichloroethane-d_4	80-120	70-130

Note: Use above table if laboratory did not provide in house recovery criteria.

Note: Other compounds may be used as surrogated depending upon the analysis requirements.

3.4 Were outliers marked correctly with an asterisk? [ ] ___ ___

ACTION: Circle all outliers with a red pencil.

3.5 Were one or more volatile surrogate recoveries out of specification for any sample or method blank. Table 2. [ ] ___ ___

If yes, were samples reanalyzed? [ ] ___ ___

Were method blanks reanalyzed? [ ] ___ ___

YES NO N/A

ACTION: If all surrogate recoveries are > 10% but 1 or more compounds do not meet method specifications:

1. Flag all positive results as estimated ("J").
2. Flag all non-detects as estimated detection limits ("UJ") when recoveries are less than the lower acceptance limit.
3. If recoveries are greater than the upper acceptance limit, do not qualify non-detects, but qualify positive results as estimated “J”.

If any surrogate has a recovery of < 10%:

1. Positive results are qualified with ("J").
2. Non-detects for that should be qualified as unusable ("R").

NOTE: Professional judgement should be used to qualify data that have method blank surrogate recoveries out of specification in both original and reanalyses. The basic concern is whether the blank problems represent an isolated problem with the blank alone or whether there is a fundamental problem with the analytical process. If one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose the blank problem to be an isolated occurrence.

3.6 Are there any transcription/calculation errors between raw data and reported data? [ ] ___ ___

ACTION: If large errors exist, take action as specified in section 3.2 above.

4.0 Laboratory Control Sample(Form III/Equivalent)

4.1 Is the LCS prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, per SDG. [ ] ___ ___

YES NO N/A

Note: LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume.

ACTION: If any Laboratory Control Sample data are missing, call the lab for explanation /resubmittals. Make note in the data assessment.

4.2 Were the Laboratory Control Samples analyzed at the required frequency for each of the following matrices:

A. Water [ ] ___ ___

B. Soil [ ] ___ ___

C. Med Soil [ ] ___ ___

Note: The LCS is spiked with the same analytes at the same concentrations as the matrix spike (SW-846 8000C, Section 9.5). If different make note in data assessment. Matrix/LCS spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigating. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene.

ACTION: If any MS/MD, MS/MSD or replicate data are missing, take the action specified in 3.2 above.

4.3 Have in house LCS recovery limits been developed (Method 8000C, Sect 9.7). [ ] ___ ___

4.4 If in house limits are not developed, are LCS acceptance recovery limits between 70 - 130% (Method 8000c Sect 9.5)? [ ] ___ ___

4.5 Were one or more of the volatile LCS recoveries outside the in house laboratory recovery criteria for spiked analytes? If in house limits are not present use 70 - 130% recovery limits.
[ ] ___ ___

YES NO N/A

Table 3. LCS Actions for Volatile Analysis

Criteria	Action	
	Detected Spiked Compounds	**Non-Detected Spiked Compounds**
%R > Upper Acceptance Limit	J	No Qualifiers
%R < Lower Acceptance Limit	J	UJ
Lower Acceptance Limit ≤ %R	No Qualifications	

5.0 Matrix Spikes(Form III or equivalent)

5.1 Are all data for matrix spike and matrix duplicate or matrix spike duplicate (MS/MD or MS/MSD) present and complete for each matrix? [ ] ___ ___

NOTE: The laboratory should use one matrix spike and a duplicate analysis of an unspiked field sample if target analytes are expected in the sample. If the sample is not expected to contain target analytes, a MS/MSD should be analyzed (SW-846, Method 8260B, Sect 8.4.2).

5.2 Have MS/MD or MS/MSD results been summarized on modified CLP Form III? [ ] ___ ___

ACTION: If any data are missing take action as specified in section 3.2 above.

5.3 Were matrix spikes analyzed at the required frequency for each of the following matrices? (One MS/MD, MS/MSD or laboratory replicate must be performed for every 20 samples

YES NO N/A

of similar matrix or concentration level. Laboratories analyzing one to ten samples per month are required to analyze at least one MS per month [page 8000C, section 9.5.])

a. Water [ ] ___ ___

b. Waste [ ] ___ ___

c. Soil/Solid [ ] ___ ___

Note: The LCS is spiked with the same analytes at the same concentrations as the matrix spike (SW-846 8000C, Section 9.5). If different make note in data assessment. Matrix/LCS spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigating. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The concentration of the LCS should be determined as described SW-Method 8000C Section 9.5.

ACTION: If any MS/MD, MS/MSD or replicate data are missing, take the action specified in 3.2 above.

5.4 Have in house MS recovery limits been developed (Method 8000C, Sect 9.7)for each matrix. [ ] ___ ___

5.5 Were one or more of the volatile MS/MSD recoveries outside of the in-house laboratory recovery criteria for spiked analytes? If none are present, then use 70-130% recovery as per SW-846, 8000C, Sect. 9.5.4. [ ] ___ ___

ACTION: Circle all outliers with a red pencil.

NOTE: If any individual % recovery in the MS (or MSD) falls outside the designated range for recovery the reviewer should determine if there is a matrix effect. A matrix effect is indicated if the LCS data are within limits but the MS data exceeds the limits.

YES NO N/A

NOTE: No qualification of data is necessary on MS and MSD data alone. However, using informed professional judgement, the data reviewer may use MS and MSD resuts in conjunction with other QC criteria to determine the need for some qualificatios.

Note: The data reviewer should first try to determine to what extent the results of the MS and MSD affect the associated data. This determination should be made with regard to he MS and MSD sample itself, as welll as specific analytes for all samples associated with the MS and MSD.

Note: In those instances where it can be determned that the results of the MS and MSD affect only the sample spiked, limit qualification to this sample only. However, it may be determined through the MS and MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes that affect all associated samples, and the reviewer must use professional judgement to qualify the data from all associated samples.

Note: The reviewer must use professional judgement to determine the need for qualification of non-spiked compounds.

ACTION: Follow criteria in Table 4 when professional judgement deems qualification of sample.

Table 4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Actions for Volatile Analysis

Criteria	Action	
	Detected Spiked Compounds	**Non-Detected Spiked Compounds**
%R > Upper Acceptance Limit	J	No Qualifiers
%R < Lower Acceptance Limit	J	UJ
Lower Acceptance Limit ≤ %R	No Qualifications	

YES NO N/A

6.0 Blank (CLP Form IV Equivalent)

6.1 Is the Method Blank Summary form present? [ ] ___ ___

6.2 Frequency of Analysis: Has a method blank been analyzed for every 20 (or less) samples of similar matrix or concentration or each extraction batch? [ ] ___ ___

6.3 Has a method blank been analyzed for each GC/MS system used ? [ ] ___ ___

ACTION: If any blank data are missing, take action as specified above (section 3.2). If blank data is not available, reject (R) all associated positive data. However, using professional judgement, the data reviewer may substitute field blank data for missing method blank data.

6.4 Chromatography: review the blank raw data - chromatograms, quant reports or data system printouts.

Is the chromatographic performance (baseline stability) for each instrument acceptable for volatile organic compounds? [ ] ___ ___

7.0 Contamination

NOTE: "Water blanks", "drill blanks" and "distilled water blanks" are validated like any other sample and are not used to qualify the data. Do not confuse them with the other QC blanks discussed below.

7.1 Do any method/instrument/reagent blanks have positive results for target analytes and/or TICs? When applied as described below, the contaminant concentration in these blanks are multiplied by the sample dilution factor and corrected for percent moisture where necessary.
[ ] ___ ___

YES NO N/A

7.2 Do any field/rinse blanks have positive volatile organic compound results? ___ [ ] ___

ACTION: Prepare a list of the samples associated with each of the contaminated blanks. (Attach a separate sheet.)

NOTE: All field blank results associated to a particular group of samples (may exceed one per case or one per day) may be used to qualify data. Blanks may not be qualified because of contamination in another blank. Field blanks must be qualified forsurrogate, or calibration QC problems.

ACTION: Follow the directions in Table 5 below to qualify sample results due to contamination. Use the largest value from all the associated blanks.

Table 5. Volatile Organic Analysis Blank Contamination Criteria

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Storage, Field, Trip, Instrument**	Detects	Not detected	No qualification
	< CRQL*	< CRQL	Report CRQL value with a U
		≥ CRQL	Use professional judgement
	> CRQL*	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank contamination	Report the concentration for the sample with a U, or quanity the data as unusable R
		≥ CRQL and ≥ blank contamination	Use professional judgement
	= CRQL*	< CRQL	Report CRQL value with a U
		≥ CRQL	Use professional judgement
	Gross contam-ination	Detects	Qualify results as unusable R

* 2x the CRQL for methylene chloride, 2-butanone, and acetone

** Qualifications based on instrument blank results affect only the sample analyzed immediately after the sample that has target compounds that exceed the calibration range or non-target compounds that exceed 100 ug/L.

NOTE: If gross blank contamination exists(e.g., saturated peaks, “hump-o-grams,” “junk” peaks), all affected positive compounds in the associated samples should be qualified as unusable “R”, due to interference. Non-detected volatile organic target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

YES NO N/A

7.3 Are there field/rinse/equipment blanks associated with every sample? [ ] ___ ___

ACTION: For low level samples, note in data assessment that there is no associated field/rinse/equipment blank. Exception: samples taken from a drinking water tap do not have associated field blanks.

8.0 GC/MS Apparatus and Materials

8.1 Did the lab use the proper gas chromatographic column(s) for analysis of volatiles by Method 8260B? Check raw data, instrument logs or contact the lab to determine what type of column(s) was (were) used. [ ] ___ ___

NOTE: For the analysis of volatiles, the method requires requires the use of 60 m. x 0.75 mm capillary column, coated with VOCOL(Supelco) or equivalent column. (see SW-846, page 8260B-7, section 4.9.2)

ACTION: If the specified column, or equivalent, was not used, document the effects in the Data Assessment. Use professional judgement to determine the acceptability of the data.

9.0 GC/MS Instrument Performance Check (CLP Form V Equivalent)

9.1 Are the GC/MS Instrument Performance Check forms present for Bromofluorobenzene (BFB), and do these forms list the associated samples with date/time analyzed? [ ] ___ ___

9.2 Are the enhanced bar graph spectrum and mass/charge (m/z) listing for the BFB provided for each twelve hour shift? [ ] ___ ___

9.3 Has an instrument performance check solution (BFB)

YES NO N/A

been analyzed for every twelve hours of sample analysis per instrument?(see Table 4, SW-846, page 8260B-36) [ ] ___ ___

ACTION: List date, time, instrument ID, and sample analyses for which no associated GC/MS GC/MS tuning data are available.

ACTION: If the laboratory/project officer cannot provide missing data, reject ("R") all data generated outside an acceptable twelve hour calibration interval.

ACTION: If mass assignment is in error, flag all associated sample data as unusable, "R".

9.4 Have the ion abundances been normalized to m/z 95? [ ] ___ ___

9.5 Have the ion abundance criteria been met for each instrument used? [ ] ___ ___

ACTION: List all data which do not meet ion abundance criteria (attach a separate sheet).

ACTION: If ion abundance criteria are not met, take action as specified in section 3.2.

9.6 Are there any transcription/calculation errors between mass lists and reported values? (Check at least two values but if errors are found, check more.) ___ [ ] ___

9.7 Have the appropriate number of significant figures (two) been reported? [ ] ___ ___

ACTION: If large errors exist, take action as specified in section 3.2.

9.8 Are the spectra of the mass calibration compounds acceptable. [ ] ___ ___

ACTION: Use professional judgement to determine wheather associated data should be accepted, qualified, or rejected.

YES NO N/A

10.0 Target Analytes (CLP Form I Equivalent)

10.1 Are the Organic Analysis reporting forms present with required header information on each page, for each of the following:

a. Samples and/or fractions as appropriate [ ] ___ ___

b. Matrix spikes and matrix spike duplicates [ ] ___ ___

c. Blanks [ ] ___ ___

d. Laboratory Control Samples [ ] ___ ___

10.2 Are the reconstructed Ion Chromatograms, mass spectra for the identified compounds, and the data system printouts (Quant Reports) included in the sample package for each of the following?

a. Samples and/or fractions as appropriate [ ] ___ ___

b. Matrix spikes and matrix spike duplicates (Mass spectra not required) [ ] ___ ___

c. Blanks [ ] ___ ___

d. Laboratory Control Samples [ ] ___ ___

ACTION: If any data are missing, take action specified in 3.2 above.

10.3 Is chromatographic performance acceptable with respect to:

Baseline stability? [ ] ___ ___

YES NO N/A

Resolution? [ ] ___ ___

Peak shape? [ ] ___ ___

Full-scale graph (attenuation)? [ ] ___ ___

Other:_____

ACTION: Use professional judgement to determine the acceptability of the data.

10.4 Are the lab-generated standard mass spectra of identified volatile compounds present for each sample? [ ] ___ ___

ACTION: If any mass spectra are missing, take action specified in 3.2 above. If the lab does not generate their own standard spectra, make a note in the Data Assessment. If spectra are missing, contact the lab.

10.5 Is the RRT of each reported compound within 0.06 RRT units of the standard RRT in the continuing calibration? [ ] ___ ___

10.6 Are all ions present in the standard mass spectrum at a relative intensity greater than 10% (of the most abundant ion) also present in the sample mass spectrum? [ ] ___ ___

10.7 Do the relative intensities of the characteristic ions in the sample agree within ± 30% of the corresponding relative intensities in the reference spectrum? [ ] ___ ___

ACTION: Use professional judgement to determine acceptability of data. If it is determined that incorrect identifications were made, all such data should be rejected (“R”), flagged (“N") - Presumptive evidence of the presence of the compound) or changed to non detected (“U”) at the calculated detection limit. In order to be

YES NO N/A

positively identified, the data must comply with the criteria listed in 9.6, 9.7, and 9.8.

ACTION: When sample carry-over is a possibility, professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification.

11.0 Tentatively Identified Compounds (TIC) (CLP Form I/TIC Equivalent)

11.1 If Tentatively Identified Compound were required for this project, are all Tentatively Identified Compound reporting forms present; and do listed TICs include scan number or retention time, estimated concentration and a qualifier? [ ] ___ ___

NOTE: Add "N" qualifier to all TICs which have CAS number, if missing.

NOTE: Have the project officer/appropriate official check the project plan to determine if lab was required to identify non-target analytes (SW-846, page 8260B-23, Sect. 7.6.2).

11.2 Are the mass spectra for the tentatively identified compounds and associated "best match" spectra included in the sample package for each of the following:

a. Samples and/or fractions as appropriate [ ] ___ ___

b. Blanks [ ] ___ ___

ACTION: If any TIC data are missing, take action specified in 3.2 above.

ACTION: Add "JN" qualifier only to analytes identified by a CAS#.

NOTE: If TICs are present in the associated blanks take action as specified in section 3.2 above.

YES NO N/A

11.3 Are any priority pollutants listed as TIC compounds (i.e., an BNA compound listed as a VOA TIC)? [ ] ___ ___

ACTION: 1. Flag with "R" any target compound listed as a TIC.

2. Make sure all rejected compounds are properly reported if they are target compounds.

11.4 Are all ions present in the reference mass spectrum with a relative intensity greater than 10% (of the most abundant ion) also present in the sample mass spectrum? [ ] ___ ___

11.5 Do TIC and "best match" standard relative ion intensities agree within ± 20%? [ ] ___ ___

ACTION: Use professional judgement to determine acceptability of TIC identifications. If it is determined that an incorrect identification was made, change the identification to "unknown" or to some less specific identification (example: "C3 substituted benzene") as appropriate. Also, when a compound is not found in any blank, but is a suspected artifact of a common laboratory contaminant, the result should be qualified as unusable, "R". (Common lab contaminants: CO_2(M/E 44), Siloxanes (M/E 73), Hexane, Aldol Condensation Products, Solvent Preservatives, and related byproducts).

12.0 Compound Quantitation and Reported Detection Limits

12.1 Are there any transcription/calculation errors in organic analysis reporting form results? Check at least two positive values. Verify that the correct internal standard, quantitation ion, and average initial RRF/CF were used to calculate organic analysis reporting form result. Were any errors found? [ ] ___ ___

NOTE: Structural isomers with similar mass spectra, but insufficient GC resolution (i.e. percent valley between the two peaks > 25%) should be

YES NO N/A

reported as isomeric pairs. The reviewer should check the raw data to ensure that all such isomers were included in the quantitation (i.e., add the areas of the two coeluting peaks to calculate the total concentration).

12.2 Are the method CRQL's adjusted to reflect sample dilutions and, for soils, sample moisture? [ ] ___ ___

ACTION: If errors are large, take action as specified in section 3.2 above.

ACTION: When a sample is analyzed at more than one dilution, the lowest detection limits are used (unless a QC exceedance dictates the use of the higher detection limit from the diluted sample data). Replace concentrations that exceed the calibration range in the original analysis by crossing out the "E" and it's associated value on the original reporting form (if present) and substituting the data from the analysis of the diluted sample. Specify which organic analysis reporting form is to be used, then draw a red "X" across the entire page of all reporting forms that should not be used, including any in the summary package.

13.0 Standards Data (GC/MS)

13.1 Are the Reconstructed Ion Chromatograms, and data system printouts (Quant Reports) present for initial and continuing calibration? [ ] ___ ___

ACTION: If any calibration standard data are missing, take action specified in section 3.2 above.

14.0 GC/MS Initial Calibration (CLP Form VI Equivalent)

YES NO N/A

14.1 Are the Initial Calibration reporting forms present and complete for the volatile fraction? [ ] ___ ___

ACTION: If any calibration forms or standard raw data are missing, take action specified in section 3.2 above.

ACTION: If the percent relative standard deviation (% RSD) is > 20%, (8000C-39)qualify positive results for that analyte “J”. When % RSD > 90%,. Qualify all positive results for that analyte “J” and all non-detects results for that analyte “R”.

14.2 Are all average RRFs > 0.050? [ ] ___ ___

NOTE: (Method Requirement) For SPCC compounds, the individual RRF values must be ≥ the values in the following list. If individual RRF values reported are below the listed values document in the Data Assessment.

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

ACTION: Circle all outliers with red pencil.

ACTION: For any target analyte with average RRF < 0.05, or for the requirements for the 5 compounds in 14.2 above, qualify all positive results for that analyte "J" and all non-detect results for that analyte "R".

14.3 Are response factors stable over the concentration range of the calibration. [ ] ___ ___

NOTE: (Method Requirement) For the following CCC compounds, the %RSD values must be ≤ 30.0%. If %RSD values reported are > 30.0% document in the Data Assessment.

YES NO N/A

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl chloride

ACTION: Circle all outliers with a red pencil.

ACTION: If the % RSD is > 20.0%, or > 30% for the 6 compounds in 14.3 above, qualify positive results for that analyte "J" and non-detects using professional judgement. When RSD > 90%, qualify all positive results for that analyte "J" and all non-detect results for that analyte "R".

NOTE: The above data qualification action applies regardless of method requirements.

NOTE: Analytes previously qualified "U" due to blank contamination are still considered as "hits" when qualifying for calibration criteria.

14.4 Was the % RSD determined using RRF or CF? [ ] ___ ___

If no, what method was used to determine the linearity of the initial calibration? Document any effects to the case in the Data Assessment.

14.5 Are there any transcription/calculation errors in the reporting of RRF or % RSD? (Check at least two values but if errors are found, check more.) [ ] ___ ___

ACTION: Circle errors with a red pencil.

ACTION: If errors are large, take action as specified in section 3.2 above.

15.0 GC/MS Calibration Verification (CLP Form VII Equivalent)

YES NO N/A

15.1 Are the Calibration Verification reporting forms present and complete for all compounds of interest? [ ] ___ ___

15.2 Has a calibration verification standard been analyzed for every twelve hours of sample analysis per instrument? [ ] ___ ___

ACTION: List below all sample analyses that were not within twelve hours of a calibration verification analysis for each instrument used.

_____

ACTION: If any forms are missing or no calibration verification standard has been analyzed twelve hours prior to sample analysis, take action as specified in section 3.2 above. If calibration verification data are not available, flag all associated sample data as unusable ("R").

15.3 Was the % D determined from the calibration verification determined using RRF or CF? [ ] ___ ___

If no, what method was used to determine the calibration verification? Document any effects to the case in the Data Assessment.

15.4 Do any volatile compounds have a % D (difference or drift) between the initial and continuing RRF or CF which exceeds 20% (SW-846, page 8260B-19, section 7.4.5.2). [ ] ___ ___

NOTE: (Method Requirement) For the following CCC compounds, the %D values must be ≤ 20.0%. If %D values reported are > 20.0% document in the Data Assessment.

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl chloride

YES NO N/A

ACTION: Circle all outliers with a red pencil.

ACTION: Qualify both positive results and non-detects for the outlier compound(s) as estimated, “J”. When %D is above 90%, qualify all positive results for that analyte "J" and all non-detect results for that analyte "R".

NOTE: The above data qualification action applies regardless of method requirements.

15.5 Do any volatile compounds have a RRF < 0.05? [ ] ___ ___

NOTE: (Method Requirement) For SPCC compounds, the individual RRF values must be ≥ the values in the following list for each calibration verification. If average RRF values reported are below the listed values document in the data assessment.

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

ACTION: Circle all outliers with a red pencil.

ACTION: If RRF < 0.05, or < the the requirements for the 5 compounds is section 15.5 above, qualify all positive results for that analyte "J" and all non-detect results for that analyte "R".

NOTE: The above data qualification action applies regardless of method requirements.

16.0 Internal Standards (CLP Form VIII Equivalent)

16.1 Are the internal standard (IS) areas on the internal standard reporting forms of every sample and blank within the upper and lower limits (-50% to + 100%) for each initial mid-point calibration (SW-846, 8260B-20, Sect. 7.4.7)? [ ] ___ ___

YES NO N/A

ACTION: If errors are large or information is missing, take action as specified in section 3.2 above.

ACTION: List each outlying internal standard below.

Sample ID	IS #	Area Lower Limit	Area Upper Limit

(Attach additional sheets if necessary.)

ACTION: 1. If the internal standard area count is outside the upper or lower limit, flag with "J" all positive results quantitated with this internal standard.

2. Do not qualify non-detects when the associated IS are counts area > + 100%.

3. If the IS area is below the lower limit (< -50%), qualify all associated non-detects (U-values) "J".

4. If extremely low area counts are reported (< -25%) or if performance exhibits a major abrupt drop off, flag all associated non-detects as unusable “R” and positive results as estimated “J”.

16.2 Are the retention times of all internal standards within 30 seconds of the associated initial mid-point calibration standard (SW-846, 8260B-20, Sect. 7.4.6)? [ ] ___ ___

ACTION: Professional judgement should be used to qualify data if the retention times differ by more than 30 seconds.

YES NO N/A

17.0 Field Duplicates

17.1 Were any field duplicates submitted for volatile analysis? [ ] ___ ___

ACTION: Compare the reported results for field duplicates and calculate the relative percent difference.

ACTION: Any gross variation between field duplicate results must be addressed in the Data Assessment. However, if large differences exist, take action specified in section 3.2 above.

USEPA
Hazardous Waste Support Branch
Validating Pesticide Compounds
Organochlorine Pesticides By Gas Chromatography
SW-846 Method 8081B

Prepared by: George Karras Date: 12/8/06
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Prepared by: Russell Arnone Date: 12-8-06
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Approved by: Robert Runyon Date: 12/11/06
Robert Runyon, Chief
Hazardous Waste Support Branch

Annual Review

Reviewed by: _____ Date: _____
Name

Reviewed by: _____ Date: _____
Name

INTRODUCTION

Scope and Applicability

This SOP offers detailed guidance in evaluating laboratory data generated according to "SW846-Method 8081B November 2000. Method 8081B is used to determine the concentration of pesticide compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. The validation methods and actions discussed in this document are based on the requirements set forth in SW846 Method 8081B, Method 8000C and the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," January 2005. This document covers technical problems specific to each fraction and sample matrix; however, situations may arise where data limitations must be assessed based on the reviewer's professional judgement.

Summary of Method

To ensure a thorough evaluation of each result in a data case, the reviewer must complete the checklist within this SOP, answering specific questions while performing the prescribed "ACTIONS" in each section. Qualifiers (or flags) are applied to questionable or unusable results as instructed. The data qualifiers discussed in this document are defined on page 4.

The reviewer must prepare a detailed data assessment to be submitted along with the completed SOP checklist. The Data Assessment must list all data qualifications, reasons for qualifications, instances of missing data and contract non-compliance.

Reviewer Qualifications

Data reviewers must possess a working knowledge of SW846 Analytical Methods and National Functional Guidelines mentioned above.

DEFINITIONS

Acronyms

CLP - Contract Laboratory Program
CRQL - Contract Required Quantitation Limit
%D - percent difference
DCB - decachlorobiphenyl
DoC - Date of Collection
GC - gas chromatography
GC/ECD - gas chromatograph/electron capture detector
GC/MS - gas chromatograph/mass spectrometer
GPC - gel permeation chromatography
IS - internal standard
kg - kilogram
µg - microgram
MS - matrix spike
MSD - matrix spike duplicate
ℓ - liter
mℓ - milliliter
PCB - Polychlorinated biphenyl
PE - performance evaluation
PEM - Performance Evaluation Mixture
QC - quality control
RAS - Routine Analytical Services
RIC - reconstructed ion chromatogram
RPD - relative percent difference
RRF - relative response factor
RRF - average relative response factor (from initial calibration)
RRT - relative retention time
RSD - relative standard deviation
RT - retention time
RSCC - Regional Sample Control Center
SDG - sample delivery group
SMC - system monitoring compound
SOP - standard operating procedure
SOW - Statement of Work
SVOA - semivolatile organic acid
TCL - Target Compound List
TCLP - Toxicity Characteristics Leachate Procedure
TCMX -tetrachloro-m-xylene
TIC - tentatively identified compound
TOPO - Task Order Project Officer
TPO - Technical Project Officer
VOA - Volatile organic
VTSR - Validated Time of Sample Receipt

Data Qualifiers

U- The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J- The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N- The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

JN- The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ- The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R- The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

LAB QUALIFIERS:

D - The positive value is the result of an analysis at a secondary dilution factor.

B - The analyte is present in the associated method blank as well as in the sample. This qualifier has a different meaning when validating inorganic data.

E - The concentration of this analyte exceeds the calibration range of the instrument.

A - Indicates a Tentatively Identified Compound (TIC) is a suspected adol-condensation product.

X,Y,Z- Laboratory defined flags. The data reviewer must change these qualifiers during validation so that the data user may understand their impact on the data.

PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____ SDG# _____
LAB:_____ SITE:_____

1.0 Data Completeness and Deliverables	YES	NO	N/A
1.1 Has all the data been submitted in CLP deliverable format?	[ ]	___	___
1.2 Have any missing deliverables been received and added to the data package?	[ ]	___	___

ACTION: Call lab for explanation/resubmittal of any missing deliverables. If lab cannot provide them, note the effect on review of the data in the reviewer narrative.

2.0 Cover Letter, SDG Narrative			
2.1 Is a laboratory narrative or cover letter present?	[ ]	___	___
2.2 Are the case number and/or SDG number contained in the narrative or cover letter?	[ ]	___	___

3.0 Data Validation Checklist			
3.1 Does this data package contain:			
Water data?	[ ]	___	___
Waste data?	[ ]	___	___
Soil/solid data?	[ ]	___	___

ORGANOCHLORINE PESTICIDE

YES NO N/A

1.0 Traffic Reports and Laboratory Narrative

1.1 Are traffic report and chain-of-custody forms present for all samples? [ ] ___ ___

ACTION: If no, contact lab for replacement of missing or illegible copies.

1.2 Do the traffic reports, chain-of-custody forms or SDG narrative indicate any problems with sample receipt, condition of the samples, analytical problems or special circumstances affecting the quality of the data? ___ [ ] ___

ACTION: If any sample analyzed as a soil, other than than TCLP, contains 50%-90% water, all data should be qualified as estimated, "J." If a soil sample, other than TCLP, contains more than 90% water, all non detects are qualified as unusable, "R", and positive results flagged “J”.

ACTION: If samples were not iced or if the ice was melted upon arrival at the laboratory and the temperature of the cooler was elevated (> 10° C), flag all positive results "J" and all non-detects "UJ".

2.0 Holding Times

2.1 Have any organochlorine pesticide technical holding times, determined from date of collection to date of extraction, been exceeded? ___ [ ] ___

Water and waste samples for organochlorine pesticide analysis must be extracted within 7 days of the date of collection. Extracts must be analyzed within 40 days of the date of extraction Soils and solid samples must be extracted within 14 days of collection and analyzed within 40 days of extraction.

ACTION: Qualify sample results according to Table 1.

Table 1. Holding Time Criteria

Matrix	Preserved	Criteria	Action	
			Detected compounds	Non-detected compounds
Aqueous	No	≤ 7 days(extraction) ≤ 40 days(analysis)	J*	UJ*
	No	> 7 days(extraction) > 40 days(analysis)	J*	UJ
	Yes	≤ 7 days(extraction) ≤ 40 days(analysis)	No qualification	
	Yes	> 7 days(extraction) > 40 days(analysis)	J	UJ
	Yes/No	> 28 days (gross exceedance)	J	R
Non-aqueous	No	≤ 14days(extraction) ≤ 40 days (analysis)	J*	UJ*
	No	> 14days(extraction) >40 days(analysis)	J	UJ
	Yes	≤ 14days(extraction) ≤ 40 days(analysis)	No qualification	
	Yes	> 14days(extraction) > 40 days(analysis)	J	UJ
	Yes/No	> 28 days (gross exceedance)	J	R

* only if cooler temperature exceeds 10°C; no action required if cooler temperature < 10°C.

YES NO N/A

3.0 Surrogate Recovery (Form II/Equivalent)

3.1 Were the recoveries of tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) presented on CLP Surrogate Recovery Summary forms (Form II), or equivalent, for each of the following matrices?

a. Water/Waste [ ] ___ ___

b. Soil/Solid [ ] ___ ___

3.2 Are all the pesticide samples listed on the appropriate surrogate recovery form for each of the following matrices?

a. Water [ ] ___ ___

b. Waste [ ] ___ ___

c. Soil/Solid [ ] ___ ___

ACTION: Call lab for explanation/resubmittals. If missing deliverables are unavailable, document the effect in the data assessment.

3.3 Are all recovery limits for the surrogates TCMX and DCB between 30-150% for all samples, including MS and MSDs, LCSs and all blanks? [ ] ___ ___

Note: Reviewer shall use lab in-house recover limits if available. In-house criteria should be examined for reasonableness.

ACTION: Circle all outliers in red. Follow surrogate action Table 2.

3.5 Were surrogate retention times (RT) within the windows established during the initial 5-point analysis? [ ] ___ ___

ACTION: Follow surrogate action, Table 2 below.

YES NO N/A

Table 2. Surrogate Recovery Criteria

Criteria	**Action**	
	Detected Target Compounds	**Non-detected Target Compounds**
%R > 200%	J	Use professional judgement
150% < %R ≤ 200%	J	No qualification
30% ≤ %R ≤ 150%	No qualification	
10% ≤ %R < 30%	J	UJ
%R < 10% (sample dilution not a factor)	J	R
%R < 10% (sample dilution is a factor)	Use professional judgement	
RT out of RT window	Use professional judgement	
RT within RT window	No qualification	

3.6 Are there any transcription/calculation errors between raw data and Form II? [ ] ___ ___

ACTION: If large errors exist, call lab for explanation/resubmittal. Make any necessary corrections and document the effect in data assessments.

4.0 Laboratory Control Sample(LCS)

4.1 Is the LCS prepared, extracted, analyzed, and reported once for every 20 field samples. [ ] ___ ___

ACTION: If any Laboratory Control Sample data are missing, call the lab for explanation /resubmittals. Make note in the data assessment.

YES NO N/A

4.2 Were Laboratory Control Samples analyzed at the required concentration for all analytes of interest as specified in Table 3 below. [ ] ___ ___

Note: Use lab in-house criteria, if available.

Table 3. LCS Spiking Criteria

LCS Spike Compound	Spiking solution ug/l	Amount spiked to 100ml aqueous sample or 30g soil sample ml	Recovery Limits (%)
gamma-BHC	0.05	1	50-120
Heptachor epoxide	0.05	1	50-120
Dieldrin	0.01	1	30-130
4,4'-DDE	0.01	1	50-150
Endrin	0.01	1	50-120
Endosulfan sulfate	0.01	1	50-120
gamma-Chloradane	0.05	1	30-130
Tetrachloro-m-xylene(surrogate)	0.20	3	30-150
Decachlorobiphenyl (surrogate)	0.40	3	30-150

Note: The LCS might be spiked with the same analytes at the same concentration as the matrix spike.

ACTION: If Laboratory Control Samples were not analyzed at the required concentration or the required frequency, make note in the data assessment and use professional judgement to determined the affect on the data.

4.3 Do average recovery for each analyte meet the corresponding QC acceptance criteria listed in table above? [ ] ___ ___

YES NO N/A

ACTION: For LCS % recovery not meeting the required recovery, follow the required action in Table 4 below.

Table 4. LCS Recovery Criteria

Criteria	**Action**	
	Detected Associated Compounds	**Non-Detected Compounds**
%R > Upper Acceptance Limit	J	No qualification
%R < Upper Acceptance Limit	J	R
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualifications	

5.0 Matrix Spikes (Form III/Equivalent)

5.1 Are all data for matrix spike and matrix duplicate or matrix spike duplicate (MS/MD or MS/MSD) present and complete for each matrix? [ ] ___ ___

NOTE: For soil and waste samples showing detectable amounts of organics, the lab may substitute replicate samples in place of the matrix spike (see page 8000B-40, section 8.5.3).

5.2 Have MS/MD or MS/MSD results been summarized on Form III/Equivalent? [ ] ___ ___

ACTION: If any data are missing take action as specified in section 3.2 above.

5.3 Were matrix spikes analyzed at the required frequency for each of the following matrices? (One MS/MD, MS/MSD or laboratory replicate must be performed for every 20 samples of similar matrix or concentration level. Laboratories analyzing one to ten samples per month are required to analyze at least one MS per month [page 8000B-39, section 8.5.])

YES NO N/A

a. Water [ ] ___ ___

b. Waste [ ] ___ ___

c. Soil/Solid [ ] ___ ___

ACTION: If any MS/MD, MS/MSD or replicate data are missing, take the action specified in 3.2 above.

5.4 We Were Matrix Spike Samples analyzed at the required concentration for all analytes of interest as specified in Table 5 below. [ ] ___ ___

Note: Spiking analytes may differ from those in Table 5. Check QA project plan or task order.

Table 5. Matrix Spiking Criteria

Matrix Spike Compound	Spiking solution ug/l	Amount spiked to 100ml aqueous sample or 30g soil sample ml
gamma-BHC	0.05	1
Heptachor	0.05	1
Aldrin	0.05	1
Dieldrin	1.0	1
Endrin	1.0	1
4,4'-DDT	1.0	1

Note: For aqueous organic extractable, the spike concentration should be:

1) For regulatory compliance monitoring - the regulatory concentration limit or 1 to 5 times the expected background concentration, whichever is higher;

2) For all other aqueous samples - the larger of either 1 to 5 x times the expected background

YES NO N/A

concentration, or the same as the QC check sample concentration (see section 4 above);

3) For soil/solid and waste samples - the recommended concentration is 20 times the estimated quantitation limit (EQL).

No action is taken based on MS or replicate data alone. However, using informed professional judgement, the data reviewer may use the matrix spike or laboratory replicate results in conjunction with other QC criteria and determine the need for some qualification of the data. In some instances it may be determined that only the replicate or spiked samples are affected. Alternatively, the data may suggest that the laboratory is having a systematic problem with one or more analytes, thereby affecting all associated samples.

5.5 Do average recovery for each analyte meet the corresponding QC acceptance criteria listed in Table 6 below. [ ] ___ ___

Note: Use lab in-house criteria, if available.

Table 6. Matrix Spike Recovery Criteria

Compound	% Recovery Water	RPD Water	% Recovery Soil	RPD Soil
gamma-BHC	56-123	0-15	46-127	0-50
Heptachor	40-13	0-20	35-130	0-31
Aldrin	40-120	0-22	34-132	0-43
Dieldrin	52-126	0-18	31-134	0-38
Endrin	56-121	0-21	42-139	0-45
4,4'-DDT	38-127	0-27	23-134	0-50

NOTE: The actual number of MS analytes depends on the number analytes being measured (e.g., total number of MS plus MSD compounds). If only chlordane or toxaphene are the analytes of

YES NO N/A

interest, the spiked sample should contain the most representative multi-component analyte.

ACTION: Follow the matrix spike actions (Table 7) for pesticide analyses.

Table 7. Matrix Spike Qualifying Criteria

Criteria	**Action**	
	Detected Associated Compounds	**Non-Detected Compounds**
%R or RPD > Upper Acceptance Limit	J	No qualification
20% R ≤ %R < Lower Acceptance Limit	J	UJ
%R < 20%	J	Use professional judgement
Lower Acceptance Limit ≤ %R; RPD ≤ Upper Acceptance Limit	No qualifications	

Note: When the results of the matrix spike analyses indicates a potential problem due to the sample matrix itself, the LCS results are used to verify the laboratory can perform analyses in a clean matrix.

6.0 Blanks (Form IV/Equivalent)

6.1 Was reagent blank data reported on Method Blank Summary form(s) (Form IV)?

6.2 Frequency of Analysis: Has a reagent blank been analyzed for every 20 (or less) samples of similar matrix or concentration or each extraction batch? [ ] ___ ___

Note: Method blank should be analyzed, either after the calibration standard or at any other time during the analytical shift.

YES NO N/A

ACTION: If any blank data are missing, take action as specified above (section 3.2). If blank data is not available, reject (R) all associated positive data. However, using professional judgement, the data reviewer may substitute field blank data for missing method blank data.

6.3 Chromatography: review the blank raw data - chromatograms, quant reports or data system printouts.

Is the chromatographic performance (baseline stability) for each instrument acceptable for pesticides? [ ] ___ ___

ACTION: Use professional judgement to determine the effect on the data.

7.0 Contamination

NOTE: "Water blanks", "distilled water blanks" and "drilling water blanks" are validated like any other sample and are not used to qualify the data. Do not confuse them with the other QC blanks discussed below.

7.1 Do any method/instrument/reagent/cleanup blanks have positive results for organochlorine pesticides? When applied as described below, the contaminant concentration in these blanks are multiplied by the sample Dilution Factor and corrected for % moisture when necessary. ___ [ ] ___

7.2 Do any field/rinse blanks have positive organochlorine pesticide results? ___ [ ] ___

ACTION: Prepare a list of the samples associated with each of the contaminated blanks. (Attach a separate sheet.)

NOTE: All field blank results associated to a particular group of samples (may exceed one per case or one per day) may be used to qualify data. Blanks may not be qualified because of contamination in

YES NO N/A

another blank. Field blanks must be qualified for surrogate, or calibration QC problems.

ACTION: Follow the directions in Table 8 below to qualify sample results due to contamination. Use the largest value from all the associated blanks.

Table 8. Blank Contamination Criteria

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Clean up, Instrument, Field	Detects	Not detected	No qualification
	< CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification
	> CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank contamination	Report the concentration for the sample with a U
		≥ CRQL and ≥ blank contamination	No qualification
	= CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification
	Gross contamination	Detects	Qualify results as unusable R

Note: Analytes qualified “U” for blank contamination are treated as “hits” when qualifying the calibration criteria.

Note: When applied as described in Table 8 above, the contaminant concentration in the blank is multiplied by the sample dilution factor.

NOTE: If gross blank contamination exists(e.g., saturated peaks, “hump-o-grams”, “junk peaks”), all affected positive compounds in the associated samples should be qualified as unusable “R”, due to interference.

YES NO N/A

Non-detected pesticide target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

7.3 Are there field/rinse/equipment blanks associated with every sample? [ ] ___ ___

ACTION: For low level samples, note in data assessment that there is no associated field/rinse/equipment blank. Exception: samples taken from a drinking water tap do not have associated field blanks.

8.0 Gas Chromatography with Electron Capture Detector (GC/ECD)Instrument Performance Check (CLP Form VI and Form VII Equivalent)

8.1 Was the proper gas chromatographic column used for the analysis of organochlorine pesticides? Check raw data, instrument logs, or contact the lab to determine what type of columns were used. (See Method 8081B-8, section 4.2) [ ] ___ ___

8.2 If capillary columns were used, were they both wide bore (.53 mm ID) fused silica GC columns, such as DB-608 and DB-1701 or equivalent. Indicate the specific type of column used for:

column 1: _____

column 2: _____

ACTION: Note any changes to the suggested materials in section 8.1 above in the data assessment. Also note the impact (positive or negative) such changes have on the analytical results.

9.0 Calibration and GC Performance

9.1 Are the following Gas Chromatograms and Data Systems Printouts for both columns present for all samples, blanks, MS, replicates?

a. DDT/endrin breakdown check [ ] ___ ___

		YES	NO	N/A
b.	toxaphene	[ ]	___	___
c.	technical chlordane	[ ]	___	___
d.	5 pt. initial calibration standards	[ ]	___	___
e.	calibration verification standards	[ ]	___	___
f.	LCS	[ ]	___	___
g.	Method blanks	[ ]	___	___

ACTION: If no, take action specified in 3.2 above.

9.2 Has a DDT/endrin breakdown check standard (at the mid-concentration level) been analyzed at the beginning of each analytical sequence on both columns (page 8081B-24, section 8.2.3)? [ ] ___ ___

ACTION: If no, take action as specified in 3.2 above.

9.3 Has the individual % breakdown exceeded 20.0% on either column for:

- 4,4' - DDT? ___ [ ] ___
- endrin? ___ [ ] ___

ACTION: If any % breakdown has failed the QC criteria in the breakdown check standard, qualify all sample analyses in the entire analytical sequence as described below.

a. If 4,4'-DDT breakdown is greater than 20.%:

i. Qualify all positive results for DDT with 'J". If DDT was not detected, but DDD and DDE are positive, then qualify the quantitation limit for DDT as unusable ("R").

ii. Qualify positive results for DDD and DDE as presumptively present at an approximated quantity ("NJ").

YES NO N/A

b. If endrin breakdown is greater than 20.0%:

i. Qualify all positive results for endrin with "J". If endrin was not detected, but endrin aldehyde and endrin ketone are positive, then qualify the quantitation limit for endrin as unusable ("R").

ii. Qualify positive results for endrin ketone and endrin aldehyde as presumptively present at an approximated quantity ("NJ").

9.4 Are data summary forms (containing calibration factors or response factors) for the initial 5 pt. calibration and daily calibration verification standards present and complete for each column and each analytical sequence? [ ] ___ ___

NOTE: If internal standard calibration procedure is used (page 8000B-16, section 7.4.2.2), then response factors must be used for %RSD calculations and compound quantitation. If, external standard calibration procedures are used (page 8000B-16, section 7.4.2.1), then calibration factors must be used.

ACTION: If any data are missing or it cannot be determined how the laboratory calculated calibration factors or response factors, contact the lab for explanation/resubmittals. Make necessary corrections and note any problems in the data assessment.

9.5 Are there any transcription/calculation errors between raw data and data summary forms. ___ [ ] ___

ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and document the effect in data assessments.

9.6 Are standard retention time (RT) windows for each analyte of interest presented on modified CLP summary forms? [ ] ___ ___

YES NO N/A

ACTION: If any data are missing, or it cannot be determined how RT windows were calculated, call the lab for explanation/resubmittals. Note any problems in the data assessment.

NOTE: Retention time windows for all pesticides are established using retention times from three calibration standards analyzed during the entire analytical sequence (page 8081B-15, section 7.4.6).

A 72 hr. sequence is not required with this method, however, the method states that best results are obtained using retention times which span the entire sequence; i.e., using the mid level from the 5 pt. calibration, one of the mid-concentration standards analyzed during mid-sequence and one analyzed at the end.

9.7 Were RT windows on the confirmation column established using three standards as described above? [ ] ___ ___

NOTE: RT windows for the confirmation column should be established using a 3 pt. calibration, preferably spanning the entire analytical sequence as described in 9.6 above. If RT windows on one column are tighter than the other, this may result in false negatives when attempting to identify compounds in the samples.

ACTION: Note potential problems, if any, in the data assessment.

9.8 Do all standard retention times in each level of the initial 5 pt. calibrations for pesticides fall within the windows established during the initial calibration sequence?

[ ] ___ ___

ACTION: i. If no, all samples in the entire analytical sequence are potentially affected. Check to see if three standards, spanning the entire sequence were used to obtained RT windows. If the lab used three standards from the 5 pt., RT windows

YES NO N/A

may be too tight. If so, RT windows should be recalculated as per page 8081B-15, section 7.4.6.2

ii. Alternatively, check to see if the chromatograms contain peaks within an expanded window surrounding the expected retention times.

If no peaks are found and the surrogates are visible, non-detects are valid. If peaks are present but cannot be discerned through pattern recognition or by using revised RT windows, qualify all positive results and non-detects as unusable, "R".

ACTION: For toxaphene and chlordane, the RT may be outside the RT window, but these analytes may still be identified from their individual patterns.

9.9 Has the linearity criteria for the initial calibration standards been satisfied for both columns? (% RSD must be < allowable limits* for all analytes). [ ] ___ ___

ACTION: If no, follow the actions in Table 9 below.

Table 9. Initial Calibration Linearity Criteria

Criteria	**Criteria**	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
% RSD exceeds allowable limits*	J	No qualification
% RSD within allowable limits*	NO qualifications	

* %RSD ≤ 20% for single component compounds except alpha-BHC and delta-BHC.
%RSD ≤ 25% for alpha-BHC and delta-BHC
%RSD ≤ 30% for Toxaphene peaks
%RSD ≤ 30% for surrogates(tetrachloro-m-xylene and decachlorobiphenyl).

9.10 Has a calibration verification standard containing all analytes of interest been analyzed on each

YES NO N/A

working day, prior to sample analyses (pages 8081B-15,sections 7.5.2)? [ ] ___ ___

9.11 Has a calibration verification standard also been analyzed after every 10 samples and at the end of each analytical sequence (page 8081B-15, section 7.5.2)? [ ] ___ ___

ACTION: If no, take action as specified in section 3.2 above.

9.12 Has no more than 12 hours elapsed from the injection of the opening CCV and the end of the analytical sequence (closing CCV). Has no more than 72 hours elapsed from the injection of the sample with a Toxaphene detection and the Toxaphene CCV? [ ] ___ ___

ACTION: See Table 10 below.

9.13 Has the percent difference (%D) exceeded ± 20% for any organochlorine pesticide analyte in any calibration verification standard? ___ [ ] ___

9.14 Has a new 5 pt. calibration curve been generated for those analytes which failed in the calibration verification standard (page 8081B-16, section 7.5.2.2), and all samples which followed the out-of-control standard (page 8081B-16, section 7.5.2.3)reinjected? [ ] ___ ___

ACTION: If the %D for any analyte exceeded the ± 20% criterion and the instrument was not recalibrated for those analytes, see table below.

9.15 Have <u>daily</u> retention time windows been properly calculated for each analyte of interest (page 8081B-16, section 7.5.3)), using RTs from the associated mid concentration standard and standard deviation from the initial calibration)? [ ] ___ ___

YES NO N/A

ACTION: If no, take action specified in section 3.2 above or recalculate RT windows using the procedure outlined in method 8081B-16, section 7.5.3.

9.16 Do all standard retention times for each mid concentration standard fall within the windows established during the initial calibration sequence? [ ] ___ ___

9.17 Do all standard retention times for each mid-concentration standard (analyzed after every 10 samples) fall within the daily RT windows (page 8081B-16, section 7.5.3)? [ ] ___ ___

ACTION: If the answer to either 9.15 or 9.16 above is no, check the chromatograms of all samples which followed the last in-control standard. All samples analyzed after the last in-control standard must be re-injected, if initial analysis indicated the presence of the specific analyte that exceeded the retention time criteria (page 8081B-18, section 7.5.7.). If samples were not re-analyzed, document under Contract Non-compliance in the Data Assessment.

Reviewer has two options to determine how to qualify questionable sample data. First option is to determine if possible peaks are present within daily retention time window. If no possible peaks are found, non-detects are valid. If possible peaks are found (or interference), qualify positive hits as presumptively present "NJ" and non-detects are rejected "R". Second option is to use the ratio of the retention time of the analyte over the retention time of either surrogate. The passing criteria is ± 0.06 RRT units of the RRT of the standard component. Reject "R" all questionable analytes exceeding criteria, and "NJ" all other positive hits.

For any multi-response analytes, retention time windows should be used but analyst and reviewer should rely primarily on pattern recognition or use option 2 specified in paragraph above.

YES NO N/A

See Table 10 below.

Table 10. CCV Criteria

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
RT out of RT window	Use professional judgement	
%D not within +/- 20%	J	UJ
Time elapsed greater than section 9.12 criteria.	R	
%D, time elapsed, RT are all within acceptable limits.	No qualifications	

9.18 Are there any transcription/calculation errors between raw data and data summary forms? ___ [ ] ___

ACTION: If large errors exists, call lab for explanation/resubmittal, make any necessary corrections and document the effect in data assessments under "Conclusions".

10.0 Analytical Sequence Check (Form VIII-PEST/Equivalent)

10.1 Have all samples been listed on CLP Form VIII or equivalent, and are separate forms present for each column? [ ] ___ ___

ACTION: If no, take action specified in 3.2 above.

10.2 Was the proper analytical sequence followed for each initial calibration and subsequent analyses? [ ] ___ ___

ACTION: If no, use professional judgement to determine the severity of the effect on the data and qualify it

YES NO N/A

accordingly. Generally, the effect is negligible unless the sequence was grossly altered or the calibration was also out of limits.

11.0 Extraction Method Cleanup Efficiency Verification (Form IX/Equivalent)

11.1 Method 8081B permits a variety of extraction techniques to be used for sample preparation. Which extraction procedure was used?

1. Aqueous samples:

1. Separatory funnel (Method 3510)_____

2. Continuous liquid-liquid extraction (Method 3520)_____

3. Solid phase extraction (Method 3535)_____

4. Other _____

2. Solid samples:

1. Soxhlet (Method 3540) _____

2. Automated Soxhlet (Method 3541)_____

3. Pressurized fluid (Method 3545) _____

4. Microwave extraction (Method 3546)_____

5. Ultrasonic extraction (Method 3550)_____

6. Supercritical fluid (Method 3562) _____

7. Other _____

11.2 Is Form IX - Pest-1/Equivalent present and complete for each lot of Florisil/Cartridges used? (Florisil Cleanup, Method 3620A, is required for all organochlorine pesticide extracts.) [ ] ___ ___

YES NO N/A

ACTION: If no, take action specified in 3.2 above. If data suggests that florisil cleanup was not performed, make note in the reviewer narrative.

NOTE: Method 3620A uses Florisil, while the SOW/CLP allows for Florisil cartridges. Method 3620A does not list which pesticides and surrogate(s) to use to verify column efficiency. The reviewer must check project plan to verify method used as well as the correct pesticide list. If not stated or available, use the CLP listing or accept what the laboratory used.

11.3 Are all samples listed on modified CLP Pesticide Florisil/Cartridge Check Form? [ ] ___ ___

ACTION: If no, take action specified in 3.2 above.

11.4 If GPC Cleanup was performed, is Form IX - Pest-2/ Equivalent present? [ ] ___ ___

ACTION: If GPC was not performed and sample results indicate significant sulfur interference, make note in the data assessment.

NOTE: GPC cleanup is not required and is optional. The reviewer should check Project Plan to verify requirement.

11.5 Were the same compounds on Form IX used to check the efficiency of the cleanup procedures? [ ] ___ ___

11.6 Are percent recoveries (% R) of the pesticide and surrogate compounds used to check the efficiency of the cleanup procedures within QC limits listed on Form IX:

80-120% for florisil cartridge check? [ ] ___ ___

80-110% for GPC calibration? [ ] ___ ___

YES NO N/A

Qualify only the analyte(s) which fail the recovery criteria as follows:

ACTION: If % R are < 80%, qualify positive results "J" and quantitation limits "UJ". Non-detects should be qualified "R" if zero %R was obtained for pesticide compounds. Qualify positive results “J” (estimated).

NOTE: If 2,4,5-trichlorophenol was used to measure the efficiency of the Florisil cleanup and the recovery was > 5%, sample data should be evaluated for potential interferences.

12.0 Pesticide Identification

12.1 Has CLP Form X, showing retention time data for positive results on the two GC columns, been completed for every sample in which a pesticide was detected? [ ] ___ ___

ACTION: If no, take action specified in 3.2 above, or compile a list comparing the retention times for all sample hits on the two columns.

12.2 Are there any transcription/calculation errors between raw data and data summary forms (initial calibration summaries, calibration verification summaries, analytical sequence summaries, GPC and Florisil cleanup verification forms)? ___ [ ] ___

ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and note error in the data assessment.

12.3 Are retention times (RT) of sample compounds within the established RT windows for both analyses? [ ] ___ ___

Note: Confirmation can be supported by other qualitative techniques such as GC/MS (Method 8270), or GC/AED (Method 8085) if sensitivity permits.

YES NO N/A

ACTION: Qualify as unusable (R) all positive results which were not confirmed by second GC column analysis. Also qualify "R", unusable, all positive results not within RT windows unless associated standard compounds are similarly biased. The reviewer should use professional judgement to assign an appropriate quantitation limit.

12.4 Check chromatograms for false negatives, especially if RT windows on each column were established differently (see section 9.7 above). Also check for false negatives among the multiple peak compounds toxaphene and chlordane. Were there any false negatives? ___ [ ] ___

ACTION: Use professional judgement to decide if the compound should be reported. If there is reason to believe that peaks outside retention RT windows should be reported, make corrections to data summary forms (Form I) and note in data assessment.

12.5 Was GC/MS confirmation used as the second column Confirmation? (This is not required). [ ] ___ ___

12.6 Is the percent difference (%D) calculated for the positive sample results on the two GC columns <25.0%? [ ] ___ ___

NOTE: The method 8081B requires quantitation from one column. The second column is to confirm the presence of an analyte. Calibration for the Confirmation column is a one point calibration. It is the reviewer's responsibility to verify from the project plan what the lab was required to report. If the lab was required to report concentrations from both columns, continue with validation for % Difference. If required, but not reported, either contact the lab for results or calculate the concentrations from the calibration. If not required, skip this section. Document actions in Data Assessment.

YES NO N/A

ACTION: If the reviewer finds neither column shows interference for the positive hits, the data should be qualified as follows:

% Difference	Qualifier
0-25%	none
26-70%	"J"
71-100%	"NJ"
101-200% (No Interference)	"R"
101-200% (Interference detected) "NJ"	
>50% (Pesticide vale is <CRQL)	"U"
>201%	"R"

Note: The lower of the two values is reported on Form I. If using professional judgement,the reviewer determines that the higher result was more acceptable, the reviewer should replace the value and indicate the reason for the change in the data assessment.

13.0 Compound Quantitation and Reported Detection Limits

13.1 Are there any transcription/calculation errors in Form I results? Check at least two positive values. Were any errors found? ___ [ ] ___

NOTE: Single-peak pesticide results can be checked for rough agreement between quantitative results obtained on the two GC columns. The reviewer should use professional judgement to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interference is suspected, the lower of the two values should be reported and qualified according to section 12.6 above. This necessitates a determination of an estimated concentration on the confirmation column. The narrative should indicate that the presence of interferences has led to the quantitation of the second column confirmation results.

YES NO N/A

13.2 Are the EDLs (Estimated Detection Limits) adjusted to reflect sample dilutions and, for soils, % moisture? [ ] ___ ___

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and document effect in data assessments.

ACTION: When a sample is analyzed at more than one dilution, the lowest EDLs are used (unless a QC exceedance dictates the use of the higher EDL data from the diluted sample analysis). Replace concentrations that exceed the calibration range in the original analysis by crossing out the value on the original Form I and substituting it with data from the analysis of diluted sample. Specify which Form I is to be used, then draw a red "X" across the entire page of all Form I's that should not be used, including any in the summary package.

ACTION: EDLs affected by large, off-scale peaks should be qualified as unusable, "R". If the interference is on-scale, the reviewer can provide a modified EDL flagged "UJ" for each affected compound.

14.0 Chromatogram Quality

14.1 Were baselines stable? [ ] ___ ___

14.2 Were any electropositive displacement (negative peaks) or unusual peaks seen? ___ [ ] ___

ACTION: Note all system performance problems in the data assessment.

15.0 Field Duplicates

15.1 Were any field duplicates submitted for organochlorine pesticide analysis? [ ] ___ ___

ACTION: Compare the reported results for field duplicates and calculate the relative percent difference.

ACTION: Any gross variation between field duplicate results must be addressed in the reviewer narrative. However, if large differences exist, the identity of the field duplicates is questionable. An attempt should be made to determine the proper identification of field duplicates.

USEPA
Hazardous Waste Support Branch
Validating PCB Compounds
PCBs By Gas Chromatography SW-846 Method 8082A

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Hazardous Waste Support Branch

Annual Review

Reviewed by:_____ Date:_____
Name

Reviewed by:_____ Date:_____
Name

Yes NO N/A

INTRODUCTION

Scope and Applicability

This SOP offers detailed guidance in evaluating laboratory data generated according to "SW846-Method 8082A" November 2000. Method 8082A is used to determine the concentration of PCB compounds in extracts prepared from many types of solid waste matrices, soils, and water samples. The validation methods and actions discussed in this document are based on the requirements set forth in SW846 Method 8082A, Method 8000C and the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," January 2005. This document covers technical problems specific to each fraction and sample matrix; however, situations may arise where data limitations must be assessed based on the reviewer's professional judgement.

Summary of Method

To ensure a thorough evaluation of each result in a data case, the reviewer must complete the checklist within this SOP, answering specific questions while performing the prescribed "ACTIONS" in each section. Qualifiers (or flags) are applied to questionable or unusable results as instructed. The data qualifiers discussed in this document are defined on page 4.

The reviewer must prepare a detailed data assessment to be submitted along with the completed SOP checklist. The Data Assessment must list all data qualifications, reasons for qualifications, instances of missing data and contract non-compliance.

Reviewer Qualifications

Data reviewers must possess a working knowledge of SW846 Analytical Methods and National Functional Guidelines mentioned above.

Yes NO N/A

DEFINITIONS

Acronyms

BNA - base neutral acid(another name for Semi Volatiles)
CLP - Contract Laboratory Program
CRQL - Contract Required Quantitation Limit
%D - percent difference
DCB -decachlorobiphenyl
DoC - Date of Collection
GC - gas chromatography
GC/ECD - gas chromatograph/electron capture detector
GC/MS - gas chromatograph/mass spectrometer
GPC - gel permeation chromatography
IS - internal standard
kg - kilogram
µg - microgram
MS - matrix spike
MSD - matrix spike duplicate
ℓ - liter
mℓ - milliliter
PCB - Polychlorinated biphenyl
PE - performance evaluation
PEM - Performance Evaluation Mixture
QC - quality control
RAS - Routine Analytical Services
RIC - reconstructed ion chromatogram
RPD - relative percent difference
RRF - relative response factor
RRF - average relative response factor (from initial calibration)
RRT - relative retention time
RSD - relative standard deviation
RT - retention time
RSCC - Regional Sample Control Center
SDG - sample delivery group
SMC - system monitoring compound
SOP - standard operating procedure
SOW - Statement of Work
SVOA - semivolatile organic acid
TCL - Target Compound List
TCLP - Toxicity Characteristics Leachate Procedure ___
TCMX -tetrachloro-m-xylene
TIC - tentatively identified compound
TOPO - Task Order Project Officer
TPO - Technical Project Officer
VOA - Volatile organic

Yes NO N/A

VTSR - Validated Time of Sample Receipt

Data Qualifiers

U- The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J- The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

– The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

JN- The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ- The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R- The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

LAB QUALIFIERS:

D- The positive value is the result of an analysis at a secondary dilution factor.

B- The analyte is present in the associated method blank as well as in the sample. This qualifier has a different meaning when validating inorganic data.

E- The concentration of this analyte exceeds the calibration range of the instrument.

A- Indicates a Tentatively Identified Compound (TIC) is a suspected adol-condensation product.

X,Y,Z- Laboratory defined flags. The data reviewer must change these qualifiers during validation so that the data user may understand their impact on the data.

Yes NO N/A

PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____ SDG# _____

LAB:_____ SITE:_____

1.0 Data Completeness and Deliverables

1.1 Has all the data been submitted in CLP deliverable format? [ ] ___ ___

1.2 Have any missing deliverables been received and added to the data package? [ ] ___ ___

ACTION: Call lab for explanation/resubmittal of any missing deliverables. If lab cannot provide them, note the effect on review of the data in the reviewer narrative.

2.0 Cover Letter, SDG Narrative

2.1 Is a laboratory narrative or cover letter present? [ ] ___ ___

2.2 Are the case number and/or SDG number contained in the narrative or cover letter? [ ] ___ ___

3.0 Data Validation Checklist

3.1 Does this data package contain:

Water data? ____ ____

Waste data? ____ ____

Soil/solid data? ____ ____

POLYCHLORINATED BIPHENYLS

1.0 Traffic Reports and Laboratory Narrative

1.1 Are traffic report and chain-of-custody forms present for all samples? [ ] ___ ___

Yes NO N/A

ACTION: If no, contact lab for replacement of missing or illegible copies.

1.2 Do the traffic reports, chain-of-custody forms or SDG narrative indicate any problems with sample receipt, condition of the samples, analytical problems or special circumstances affecting the quality of the data? ___ [ ] ___

ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be qualified as estimated, "J." If a soil sample, other than TCLP, contains more than 90% water, non detects shall be qualified as unusable, "R."

ACTION: If samples were not iced or if the ice was melted upon arrival at the laboratory and the temperature of the cooler was elevated (> 10° C), flag all positive results "J" and all non-detects "UJ".

2.0 Holding Times

2.1 Have any PCB technical holding times, determined from date of collection to date of extraction, been exceeded? ___ [ ] ___

Water and waste samples for PCB analysis must be extracted within 7 days of the date of collection. Extracts must be analyzed within 40 days of the date of extraction. Soils and solid samples must be extracted within 14 days of collection and analyzed within 40 days of extraction.

ACTION: If technical holding times are exceeded, flag all positive results as estimated, "J," and sample quantitation limits "UJ" and document in the narrative that holding times were exceeded. If analyses were done more than 14 days beyond holding time, either on the first analysis or upon re-analysis, the reviewer must use professional judgement to determine the reliability of the data and the effects of additional storage on the sample results. At a minimum, all the data should at least be

Yes NO N/A

qualified "J", but the reviewer may determine that non-detects are unusable,"R." (Table 1)

Table 1. Holding Time Criteria

Matrix	Preserved	Criteria	Action	
			Detected compounds	**Non-detected compounds**
Aqueous	No	≤ 7 days(extraction) ≤ 40 days(analysis)	J*	UJ*
	No	> 7 days(extraction) > 40 days(analysis)	J	UJ
	Yes	≤ 7 days(extraction) ≤ 40 days(analysis)	No qualification	
	Yes	> 7 days(extraction) > 40 days(analysis)	J	UJ
	Yes/No	> 28 days (gross exceedance)	J	R
Non-aqueous	No	≤ 14days(extraction) ≤ 40 days (analysis)	J*	UJ*
	No	> 14days(extraction) >40 days(analysis)	J	UJ
	Yes	≤ 14days(extraction) ≤ 40 days(analysis)	No qualification	
	Yes	> 14days(extraction) > 40 days(analysis)	J	UJ
	Yes/No	> 28 days(gross exceedance)	J	R

* only if cooler temperature exceeds 10°C; no action required if cooler temperature < 10°C.

3.0 Surrogate Recovery (Form II/Equivalent)

3.1 Were the recoveries of tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) presented on CLP Surrogate Recovery Summary forms (Form II), or equivalent, for each of the following matrices?

a. Water/Waste [ ] ___ ___

Yes NO N/A

b. Soil/Solid [ ] ___ ___

3.2 Are all the PCB samples listed on the appropriate surrogate recovery form for each of the following matrices?

a. Water [ ] ___ ___

b. Waste [ ] ___ ___

c. Soil/Solid [ ] ___ ___

ACTION: Call lab for explanation/resubmittals. If missing deliverables are unavailable, document the effect in the data assessment.

3.3 Are all recovery limits for the surrogates TCMX and DCB between 30-150% for all samples, including MS and MSDs, LCSs and all blanks? [ ] ___ ___

Note: Reviewer shall use lab in-house recovery limits, if available. In-house criteria should be examined for reasonableness.

ACTION: Circle all outliers in red. Follow surrogate criteria, Table 2.

Note: DCB is used when PCBs are determined as Aroclors. DCB is the internal standard when determining PCB congeners and TCMX the surrogate.

3.4 Were surrogate retention times (RT) within the windows established during the initial 5-point analysis? [ ] ___ ___

ACTION: Follow surrogate criteria, Table 2.

Table 2. Surrogate Recovery Criteria

Criteria	Action	
	Detected Target Compounds	**Non-detected Target Compounds**
%R > 200%	J	Use professional judgement

		Yes NO N/A
150% < %R ≤ 200%	J	No qualification
30% ≤ %R ≤ 150%	No qualification	
10% ≤ %R < 30%	J	UJ
%R < 10% (sample dilution not a factor)	J	R
%R < 10% (sample dilution is a factor)	Use professional judgement	
RT out of RT window	Use professional judgement	
RT within RT window	No qualification	

3.6 Are there any transcription/calculation errors between raw data and Form II? [ ] ___ ___

ACTION: If large errors exist, call lab for explanation/resubmittal. Make any necessary corrections and document the effect in data assessments.

4.0 Laboratory Control Sample (LCS)

4.1 Are raw data and percent recoveries present for all Laboratory Control samples as required by Method 8000B (section 8.5) and Method 8082A (section 8.4.2)? [ ] ___ ___

Verify that QC check samples were extracted and analyzed by the same procedures used for the actual samples.

ACTION: If any Laboratory Control Sample data are missing, call the lab for explanation/ resubmittals. Make note in the data assessment.

NOTE: For aqueous samples, an additional QC check sample must be prepared and analyzed when any analyte in a matrix spike fails the required acceptance criteria (see section 5.3 below).

Yes NO N/A

The additional QC check sample must contain each analyte that failed in the MS analysis.

Note: When the results for matrix spike analysis indicates a problem due to sample matrix effects, the LCS results are used to verify the laboratory can perform the analysis in a clean sample.

4.2 Were Laboratory Control Samples analyzed at the required concentration as specified in Method 8000B(sec 8.5) for all analytes as specified in Table 3. [ ] ___ ___

Note: Use lab in-house criteria, if available.

ACTION: If Laboratory Control Samples were not analyzed at the required concentration or the required frequency, make note in the data assessment and use professional judgement to determined the affect on the data.

4.3 Were the LCS recoveries within the percent recoveries as specified in Table 3. [ ] ___ ___

Table 3. LCS Criteria

Compound	% Recovery
Aroclor 1016	50-150
Aroclor 1260	50-150
Tetrachloro-m-xylene (surrogate)	30-150
decachlorobiphenyl (surrogate)	30-150

4.4 If no, were Laboratory Control Samples re-analyzed? [ ] ___ ___

ACTION: If QC check samples were not re-analyzed, or a general system problem is indicated by repeated failure to meet the QC acceptance criteria specified in the method, make note in the data assessment and use Table 4 recovery actions criteria.

Yes NO N/A

Table 4. LCS Recovery Actions

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Compounds**
%R > Upper Acceptance Limit	J	No qualification
%R < Lower Acceptance Limit	J	R
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualifications	

5.0 Matrix Spikes (Form III/Equivalent)

5.1 Are all data for one matrix spike and matrix duplicate (unspiked) pair (MS/Dup) or matrix spike/matric spike duplicate (MS/MSD)present and complete for each matrix (Method 8082A Section 8.4.1)? [ ] ___ ___

NOTE: For soil and waste samples showing detectable amounts of target analytes, the lab may substitute replicate samples in place of the matrix spike (see Method 8000B-40, section 8.5.3).

5.2 Have MS/Dup or MS/MSD results been summarized on modified CLP Form III? [ ] ___ ___

ACTION: If any data are missing take action as specified in section 3.2 above.

5.3 Were matrix spikes analyzed at the required frequency for each of the following matrices? (One MS/Dup, MS/MSD must be performed for every 20 samples of similar matrix or concentration level. Laboratories analyzing one to ten samples per month are required to analyze at least one MS per month (Method 8000B-39 (section 8.5)).

a. Water [ ] ___ ___

Yes NO N/A

b. Waste [ ] ___ ___

c. Soil/Solid [ ] ___ ___

ACTION: If any MS/Dup or MS/MSD data are missing, take the action specified in 3.2 above.

5.4 Were Laboratory Control Samples analyzed for all analytes as specified in Table 5, or did the lab use the optional QC acceptance criteria i.e., in-house criteria? [ ] ___ ___

List the criteria used and make note in data assessment.

Criteria used _____

Table 5. MS/MSD Criteria

Compound	Percent Recovery QC Limits	RPD
Aroclor 1016	29-135	0-15
Aroclor 1260	29-135	0-20

5.5 Was the matrix spike prepared at the proper spike concentration? (Method 8000B, section 8.5.1-8.5.2) [ ] ___ ___

For aqueous organic extractable, the spike concentration should be prepared according options in: Method 8000B-40, (section 8.5.1 and 8.5.2).

5.6 Were the matrix spike and matrix spike duplicate recovery and RPD limits met as specified in Table 5. Note: No qualification of the data is necessary on MS and MSD data alone. Use professional judgement to use the MS and MSD results in conjunction with other QC criteria to determine the need for some qualification of the data. If any MS and MSD, percent recovery, or RPD results in the Arcolor fraction is out of specification (Table 5), qualify data to include the consideration of the existence interference in the raw data. In some instances it may be determined that only the replicate or spiked samples are affected. Alternatively, the data may suggest that the laboratory is having a systematic problem with one or more analytes, thereby affecting all associated samples. Use professional judgement to determine the need for qualifications of detects of non-spiked compounds.

Yes NO N/A

[ ] ___ ___

Table 6. MS/MSD Actions for Analysis

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Compounds**
%R or RPD > Upper Acceptance Limit	J	No qualification
20% ≤ %R < Lower Acceptance Limit	J	UJ
%R < 20%	J	Use professional judgement
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualifications	

6.0 Blanks (Form IV/Equivalent)

6.1 Was reagent blank data reported on CLP equivalent Method Blank Summary form(s) (Form IV)? [ ] ___ ___

6.2 Frequency of Analysis: Has a reagent blank been analyzed for every 20 (or less) samples of similar matrix or concentration or each extraction batch? [ ] ___ ___

Note: Method blank should be analyzed, either after the calibration standard or at any time during the analytical shift.

ACTION: If any blank data are missing, take action as specified above (section 3.2) . If blank data is not available, reject (R) all associated positive data. However, using professional judgement, the data reviewer may substitute field blank data for missing method blank data.

6.3 Chromatography: review the blank raw data - chromatograms, quant reports or data system

Yes NO N/A

printouts.

Is the chromatographic performance (baseline stability) for each instrument acceptable for PCBs? [ ] ___ ___

7.0 Contamination

NOTE: "Water blanks", "distilled water blanks" and "drilling water blanks" are validated like any other sample and are not used to qualify the data. Do not confuse them with the other QC blanks discussed below.

7.1 Do any method/instrument/reagent/cleanup blanks have positive results for PCBs? When applied as described below, the contaminant concentration in these blanks are multiplied by the sample Dilution Factor and corrected for % moisture when necessary. ___ [ ] ___

7.2 Do any field/rinse blanks have positive PCB results? ___ [ ] ___

ACTION: Prepare a list of the samples associated with each of the contaminated blanks. (Attach a separate sheet.)

NOTE: All field blank results associated to a particular group of samples (may exceed one per case or one per day) may be used to qualify data. Blanks may not be qualified because of contamination in another blank. Field blanks must be qualified for surrogate, or calibration QC problems.

ACTION: Follow the directions in Table 7 below to qualify sample results due to contamination. Use the largest value from all the associated blanks.

Table 7. Blank Contamination Criteria

Blank Type	Blank Result	Sample Result	Action for Samples

Yes NO N/A

Method, Clean up, Instrument, Field	Detects	Not detected	No qualification
	< CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification
	> CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank contamination	Report the concentration for the sample with a U
		≥ CRQL and ≥ blank contamination	No qualification
	= CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification
	Gross contamination	Detects	Qualify results as unusable R

Note: Analytes qualified “U” for blank contamination are treated as “hits” when qualifying for calibration criteria.

Note: When applied as described in Table 7 above, the contaminant concentration in the blank is multiplied by the sample dilution factor.

NOTE: If gross blank contamination exists(e.g., saturated peaks, “hump-o-grams,” “junk” peaks), all affected positive compounds in the associated samples should be qualified as unusable “R”, due to interference. Non-detected pesticide target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

7.3 Are there field/rinse/equipment blanks associated with every sample? [ ] ___ ___

ACTION: For low level samples, note in data assessment that there is no associated field/rinse/equipment blank. Exception: samples taken from a drinking water tap do not have associated field blanks.

Yes NO N/A

8.0 Gas Chromatography with Electron Capture Detector (GC/ECD)Instrument Performance Check (CLP Form VI and Form VII Equivalent)

8.1 Was the proper gas chromatographic capillary column used for the analysis of PCBs? [ ] ___ ___

Action: Check raw data, instrument logs, or contact the lab to determine what type of columns were used. (Method 8082, section 4.2)

8.2 Indicate the specific type of narrow bore or wide bore (.53 mm ID, fused silica GC columns, such as DB-608 and DB-1701 or equivalent).

column 1: _____

column 2: _____

ACTION: Note any changes to the suggested materials in section 8.1 above in the data assessment. Also note the impact (positive or negative) such changes have on the analytical results.

9.0 Calibration and GC Performance

9.1 Are the following Gas Chromatograms and Data Systems Printouts for both columns present for all samples, blanks, MS, replicates?

a. Samples [ ] ___ ___

b. All blanks [ ] ___ ___

c. Matrix spike samples [ ] ___ ___

d. 5 pt. initial calibration standards [ ] ___ ___

e. calibration verification standards [ ] ___ ___

f. Laboratory Control samples (LCS) [ ] ___ ___

ACTION: If no, take action specified in 3.2 above.

9.2 Are data summary forms (containing calibration factors or response factors) for the initial 5

Yes NO N/A

pt. calibration and daily calibration verification standards present and complete for each column and each analytical sequence? [ ] ___ ___

Note: Calibration Aroclor mixtures other than 1016/1260 may be used (as per approved project QA plan)

NOTE: If internal standard calibration procedure is used (Method 8000B-15(section 7.4.2.2)), then response factors must be used for %RSD calculations and compound quantitation. If, external standard calibration procedures are used (Method 8000B-16 (section 7.4.2.1)), then calibration factors must be used. The internal standard approach is highly recommended for PCB congener analysis.

ACTION: If any data are missing or it cannot be determined how the laboratory calculated calibration factors or response factors, contact the lab for explanation/resubmittals. Make necessary corrections and note any problems in the data assessment.

9.3 Are there any transcription/calculation errors between raw data and data summary forms? ___ [ ] ___

ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and document the effect in data assessments.

9.4 Are standard retention time (RT) windows for each PCB peak of interest presented on modified CLP summary forms? [ ] ___ ___

ACTION: If any data are missing, or it cannot be determined how RT windows were calculated, call the lab for explanation/resubmittals. Note any problems in the data assessment.

NOTE: Retention time windows for all PCBs are established using retention times from three calibration standards analyzed during the entire analytical sequence (Method 8000B, section 7.6). Best results are obtained

Yes NO N/A

using retention times which span the entire sequence; i.e., using the calibration verification/continuing calibration standards analyzed every 12 hours.

9.5 Were RT windows on the confirmation column established using three standards as described above? [ ] ___ ___

NOTE: RT windows for the confirmation column should be established using a 3 pt. calibration, preferably spanning the entire analytical sequence as described in 9.4 above. If RT windows on one column are tighter than the other, this may result in false negatives when attempting to identify compounds in the samples.

ACTION: Note potential problems, if any, in the data assessment.

9.6 Do all standard retention times in each level of the initial 5 pt. calibrations for PCBs fall within the windows established during the initial calibration sequence? [ ] ___ ___

ACTION i: If no, all samples in the entire analytical sequence are potentially affected. Check to see if three standard spanning the entire sequence were used to obtained RT windows. If the lab used three standards from the 5 pt., RT windows may be too tight. If so, RT windows should be recalculated as per Method 8081B-15 (section 7.4.6).

ii. Alternatively, check to see if the chromatograms contain peaks within an expanded window surrounding the expected retention times.

If no peaks are found and the surrogates are visible, non-detects are valid. If peaks are present but cannot be discerned through pattern recognition or by using revised RT windows, qualify all positive results and non-detects as unusable, "R".

9.7 Has the linearity criteria for the initial calibration standards been satisfied for both

Yes NO N/A

columns? (% RSD for the calibration factors (CFs) for the three to five major peaks of each of the Aroclor compounds must be < 20.0%). [ ] ___ ___

ACTION: If no, follow Table 8 criteria.

Table 8. Initial Calibration CF Action for Aroclor Analysis

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
% RSD > 20%	J	UJ
% RSD within allowable limits	No qualifications	

9.8 Does the calibration verification/continuing calibration standard contain the PCB peaks of interest, analyzed on each working day, prior to sample analyses (Method 8082, sections 7.6.2)? [ ] ___ ___

9.9 Has a calibration verification/continuing calibration standard been analyzed after every 10 samples and at the end of each analytical sequence (Method 8082A, section 7.6.2). [ ] ___ ___

ACTION: If no, take action as specified in section 3.2 above.

9.10 Has the percent difference (%D) between the Calibration Factor (CF) of each of the three to five peaks used to identify the Aroclor in the CCV and the CF from these peaks in the initial calibration exceeded ± 15%. ___ [ ] ___

9.11 Has a new 5 pt. initial calibration curve been generated for those PCB analytes which failed in the calibration verification/continuing calibration standard (8000B, section 7.7.3), and all samples which followed the out-of-control

Yes NO N/A

calibration verification/standard continuing calibration Standard? [ ] ___ ___

ACTION: If the %D for any analyte exceeded the ± 15% criterion and the instrument was not recalibrated for those analytes, qualify positive results for all associated samples (those which followed the out-of-control standard) "J" and sample quantitation limits "UJ". (see Table 9)

9.12 Have retention time (RT) windows been properly calculated for each analyte of interest (Method 8000B, section 7.6), using RTs from the associated calibration verification/continuing standard? [ ] ___ ___

ACTION: If no, take action specified in section 3.2 above

9.13 Do all standard retention times for each calibration verification/continuing calibration standard fall within the windows established during the initial calibration sequence? [ ] ___ ___

9.14 Do all standard retention times for each mid-concentration standard (analyzed after every 10 samples) fall within the daily RT windows. [ ] ___ ___

ACTION: For any multi-response analytes, retention time windows should be used but analyst and reviewer should rely primarily on pattern recognition or use paragraph B below. If the answer to either 9.13 or 9.14 above is no, check the chromatograms of all samples which followed the last in-control standard. If samples were not re-analyzed, all samples analyzed after the last in-control standard must be evaluated using professional judgement.

(A) For non-detected target compounds, check to see if the sample chromatograms contain any peaks that are close to the expected RT window of the Arcolor of interest. If no peaks are present, no qualification of data is necessary. If peaks are present close th RT window of the Aroclor of interest, qualify the non-detected values as presumptively present “N”.

Yes NO N/A

(B) For detected compounds in the affected samples, if peaks within the RT window, no qualification necessary. If peaks are close to the expected RT window of the Aroclor of interest, the reviewer can examine the data package for the presence of three or more standards the Aroclor of interest that were run within the analytical sequence during which the sample was analyzed. If three or more such standards are present, the RT window can be reevaluated using the Mean Retention Times of the standards. If the peaks in the affectd sample fall within the revised window, qualify the detected target compounds “NJ”. If the reviewer cannot do anything with the data to resolve the problem of concern, qualify all non-detects as unusable “R”. (Table 9)

9.15 Has no more than 12 hours elapsed from the injection of the opening CCV and the end of the analytical sequence sequence (closing CCV). (Table 9) [ ] ___ ___

Table 9. CCV Criteria

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
RT out of RT window	Use professional judgement (Sec 9.14)	
%D not within +/- 15%	J	UJ
Time elapsed greater than section 9.15 criteria.	R	
%D, time elapsed, RT are all within acceptable limits.	No qualifications	

9.16 Are there any transcription/calculation errors between raw data and data summary forms? ___ [ ] ___

ACTION: If large errors exists, call lab for explanation/resubmittal, make any necessary corrections and document the effect in data assessments under "Conclusions".

10.0 Analytical Sequence Check (Form VIII-PEST/Equivalent)

10.1 Have all samples been listed on CLP Form VIII or equivalent, and are separate forms present for each column? [ ] ___ ___

Yes NO N/A

ACTION: If no, take action specified in 3.2 above.

10.2 Was the proper analytical sequence followed for each initial calibration and subsequent analyses? [ ] ___ ___

ACTION: If no, use professional judgement to determine the severity of the effect on the data and qualify it accordingly. Generally, the effect is negligible unless the sequence was grossly altered or the calibration was also out of limits.

10.3 Were the TCMX/DCB surrogate RTs for the samples within the mean surrogate RT from the initial calibration? [ ] ___ ___

Action: If no, see "Action" in section 9.14 above

11.0 Extraction Techniques for Sample Preparation

Method 8082A permits a variety of extraction techniques to be used for sample preparation. Check which extraction procedure was used?

1. Aqueous samples:

    1. Separatory funnel (Method 3510) [ ] ___ ___
    2. Continuous liquid-liquid extraction (Method 3520) [ ] ___ ___
    3. Solid phase extraction (Method 3535) [ ] ___ ___
    4. Other [ ] ___ ___

2. Solid samples:

    1. Soxhlet (Method 3540) [ ] ___ ___
    2. Automated Soxhlet (Method 3541) [ ] ___ ___
    3. Pressurized fluid (Method 3545) [ ] ___ ___
    4. Microwave extraction (Method 3546) [ ] ___ ___
    5. Ultrasonic extraction (Method 3550) [ ] ___ ___

Yes NO N/A

6. Supercritical fluid (Method 3562) [ ] ___ ___

7. Other [ ] ___ ___

11.1 Extract Cleanup - Efficiency Verification (Form IX/Equivalent)

11.1.1 Method 8082 (section 7.2) references method 3660 (sulfur) and 3665A (sulfuric acid) to use for cleaning extracts. Were one or both method used? [ ] ___ ___

ACTION: If no, take action specified in 3.2 above. If data suggests cleanup was not performed, make note in the data assessment.

NOTE: Method 3620A, Florisil, may be used per approved project QA plan. The method does not list which analytes and surrogate(s) to use to verify column efficiency. The reviewer must check project plan to verify method used as well as the correct PCB list. If not stated or available, use the CLP listing or accept what the laboratory used.

11.2 Are all samples listed on modified CLP PCBs Florisil/Cartridge Check Form? [ ] ___ ___

ACTION: If no, take action specified in 3.2 above.

11.3 Was GPC Cleanup (method 3640A) performed? [ ] ___ ___

NOTE: GPC cleanup is not required and is optional. The reviewer should check Project Plan to verify requirement.

11.4 Were the same PCB analytes used in calibration used to check the efficiency of the cleanup procedures? [ ] ____ ___

11.5 Are percent recoveries (% R) of the PCBs and surrogate compounds used to check the efficiency of the cleanup procedures within lab's in-house QC limits (use 70-130% if not available). [ ] ___ ___

Yes NO N/A

70-130% for GPC calibration? [ ] ___ ___

Qualify only the analyte(s) which fail the recovery criteria as follows:

ACTION: If % R are < 70%, qualify positive results "J" and quantitation limits "UJ". Non-detects should be qualified "R" if zero %R was obtained for PCBs. Use professional judgement to qualify positive results if recoveries are greater than the upper limit.

12.0 PCB Identification

12.1 Has CLP Form X or equivalent, showing retention time data for positive results on the two GC columns, been completed for every sample in which a PCB was detected? [ ] ___ ___

ACTION: If no, take action specified in 3.2 above, or compile a list comparing the retention times for all sample hits on the two columns.

12.2 Are there any transcription/calculation errors between raw data and data summary forms (initial calibration summaries, calibration verification summaries, analytical sequence summaries, GPC and cleanup verification forms)? ___ [ ] ___

ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and note error in the data assessment.

12.3 Are retention times (RT) of sample compounds within the established RT windows for both columns/analyses? [ ] ___ ___

ACTION: Qualify as unusable (R) all positive results which were not confirmed by second GC column analysis. Also qualify "R", unusable, all positive results not within RT windows unless associated standard compounds are similarly biased. The reviewer should use professional judgement to assign an appropriate quantitation limit.

Yes NO N/A

12.4 Check chromatograms for false negatives, especially if RT windows on each column were established differently.
Were there any false negatives? ___ [ ] ___

ACTION: Use professional judgement to decide if the compound should be reported. If there is reason to believe that peaks outside retention RT windows should be reported, make corrections to data summary forms (Form I) and note in data assessment.

12.5 Was GC/MS confirmation provided when sample concentration was sufficient (> 10 ug/ml) in the final extract? [ ] ___ ___

ACTION: Indicate with red pencil which Form I results were confirmed by GC/MS and also note in data assessment. GC/MS confirmation is an option, see section 7.10 of Method 8082A-20. If GC/MS confirmation is not available, follow action in section 3.2.

12.6 Is the percent difference (%D) calculated for the positive sample results on the two GC columns <25.0%? [ ] ___ ___

NOTE: The method requires quantitation from one column. The second column is to confirm the presence of an analyte. It is the reviewer's responsibility to verify from the project plan what the lab was required to report. If the lab was required to report concentrations from both columns, continue with validation for % Difference. If required, but not reported, either contact the lab for results or calculate the concentrations from the calibration. If not required, skip this section. Document actions in Data Assessment.

ACTION: If the reviewer finds neither column shows interference for the positive hits, the data should be qualified as follows:

% Difference	Qualifier

Yes NO N/A

0-25%	none
26-70%	"J"
71-100%	"NJ"
101-200% (No Interference)	"R"
101-200% (Interference detected)	"NJ"
>50% (PCBs value is <CRQL)	"U"
>200%	"R"

Note: The lower of the two values is reported on Form I. If using professional judgement,the reviewer determines that he higher result was more acceptable, the reviewer should replace the value and indicate the reason for the change in the data assessment.

13.0 Compound Quantitation and Reported Detection Limits

13.1 Are there any transcription/calculation errors in Form I results? Check at least two positive values. Were any errors found? ___ [ ] ___

NOTE: Single-peak PCBs results can be checked for rough agreement between quantitative results obtained on the two GC columns. The reviewer should use professional judgement to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interference is suspected, the lower of the two values should be reported and qualified according to section 12.6 above. This necessitates a determination of an estimated concentration on the confirmation column. The narrative should indicate that the presence of interferences has led to the quantitation of the second column confirmation results.

13.2 Are the EDLs (Estimated Detection Limits) adjusted to reflect sample dilutions and, for soils, % moisture? [ ] ___ ___

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and document effect in data assessments.

Yes NO N/A

ACTION: When a sample is analyzed at more than one dilution, the lowest EDLs are used (unless a QC exceedance dictates the use of the higher EDL data from the diluted sample analysis). Replace concentrations that exceed the calibration range in the original analysis by crossing out the value on the original Form I and substituting it with data from the analysis of diluted sample. Specify which Form I is to be used, then draw a red "X" across the entire page of all Form I's that should not be used, including any in the summary package.

ACTION: EDLs affected by large, off-scale peaks should be qualified as unusable, "R". If the interference is on-scale, the reviewer can provide a modified EDL flagged "UJ" for each affected compound.

14.0 Chromatogram Quality

14.1 Were baselines stable? [ ] ___ ___

14.2 Were any electropositive displacement (negative peaks) or unusual peaks seen? ___ [ ] ___

ACTION: Note all system performance problems in the data assessment.

15.0 Field Duplicates

15.1 Were any field duplicates submitted for PCB analysis? [ ] ___ ___

ACTION: Compare the reported results for field duplicates and calculate the relative percent difference.

ACTION: Any gross variation between field duplicate results must be addressed in the reviewer narrative. However, if large differences exist, the identity of the field duplicates is questionable. An attempt should be made

Yes NO N/A

to determine the proper identification of field duplicates.

Validation of Metals for the Contract Laboratory Program (CLP) based on SOW ILMO5.3 (SOP Revision 13)

PREPARED BY: Hanif Sheikh Date: 12-08-06
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Hazardous Waste Support Section

Peer Reviewed by: Russell Arnone Date: 12-08-06
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Concurred by: Linda M. Mauel Date: 12/8/06
Linda Mauel, Chief
Hazardous Waste Support Section

Approved by: Robert M. Runyon Date: 12/11/06
Robert Runyon, Chief
Hazardous Waste Support Branch

Annual Review

Reviewed by: _____ Date: _____
Name

Reviewed by: _____ Date: _____
Name

Table of Contents

I.0 Scope

I.I This Standard Operating Procedure (SOP) applies to the evaluation of Routine Analytical Services (RAS) inorganic data generated in accordance with the EPA Contract Laboratory Program (CLP) protocols.

1.2 This Region 2 inorganic data validation SOP is used to determine the usability of analytical data generated from water and soil/sediment samples collected from Superfund sites in EPA Region 2.

1.3 Data should be generated and validated in accordance with the site specific Project Quality Objectives (PQOs) developed prior to the sample collection event. This SOP can be customized to validate the data according to the site specific PQOs. If the site specific DQOs are not available, this SOP must be used in its entirety.

1.4 This SOP is based, for the most part, upon analytical and quality assurance requirements specified in the Statement of Work SOW-ILM05.3, as well as in the final (October 2004) of the USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review. The SOP Checklist, Appendix A.1, provides guidance in conducting the data validation. The result of the use of this SOP is a **Total Review** of the data: **Technical plus Contract - Compliance Review.**

2.0 Contract Compliance Review

This type of review is the first step in data validation which is carried out to ensure that the CLP laboratory has analyzed the environmental samples in accordance with the Statement of Work (SOW), and provided a data package which is both complete and compliant. This means that laboratory's procedures were performed exactly as specified in the CLP Statement of Works (SOW) and the data package contains all the deliverables including the information required under the contract.

2.1 Completeness

The data validator must check the entire data package to ensure that all deliverables required under the CLP contract are present and legible. In addition, copies of the Contract Compliance Screening (CCS) report, re-submittal from the laboratory, and Regional documentation should also be present in the data package. In Region 2, the data package completeness check is currently performed by the Regional Sample Control Coordinator (RSCC)for each Sample Delivery Group (SDG). The data package is not released to the data validator until all the required deliverables are received
from the laboratory.

2.2 Compliance

The data validator must check to ensure that all steps from sample receipt through sample preparation, analysis, data calculation and reporting are documented, and the information/data required under the contract is present in the appropriate reporting Forms and laboratory logs.

2.3 Contract Compliance Screening (CCS)

This screening step essentially checks the data package for the Completeness and Compliance requirements, and is performed by the Sample Management Office (SMO) currently operated by Computer Sciences Corporation (CSC), an EPA contractor. The CCS Report outlines the incomplete and non-compliant items as "Defects" in the data package, and is sent to the laboratory which is required to

provide additional or missing information/data required under the contract. The CCS Report for each SDG is transmitted electronically by the SMO to the Regional office. The CCS Report is intended to aid the data validator in locating any problems, both corrected and uncorrected. The incorrect original deliverable(s)of the data package must be replaced by the re-submittal(s)received from the laboratory in response to the CCS Report. The data validation should, however, be carried out even if the CCS Report is not available.

Web-based CCS is available for CLP laboratories to check their data prior to its delivery to EPA.

3.0 **Technical Review**

Technical review of the RAS data is carried out on the complete and compliant data to ensure its **validity** (i.e., data is of known quality and scientifically valid) and **usability** (i.e., data set is sufficiently complete and of sufficient quality to support a decision or an action described in the specific objectives of a data collection activity). The technical review process provides information on analytical limitations of data, if any, based on specific Quality Assurance/Quality Control (QA/QC) criteria. This is accomplished by performing an in-depth review of both the field deliverables which document the field sampling activities, and the laboratory analytical data deliverables which document the laboratory activities carried out to generate the reported data. Essentially, the validator shall first ensure that the data package is complete and compliant. The validator shall then evaluate data/information on all these deliverables (Final data sheets, Forms for QC analyses Chain-of-Custody/Traffic Report Forms, raw data, etc.) against the QA/QC acceptance criteria specified in the SOP “Checklist” (Appendix A.1). The validator must answer each question in the “ Checklist” and take an appropriate action as required under “Action” to qualify the data. As a result of the technical review, the data validator may qualify some of the data as **rejected** or as **estimated.** The data validator shall write a **Data Review Narrative** documenting the qualified data and the reason(s) for the qualification.

3.1 If the **raw data** necessary to support the reported results are not provided, the data validation must not be performed. The laboratory must be contacted to obtain missing raw data.

3.2 If batch quality control analyses are performed on samples other than **site specific samples**, data must not be validated
or at best be considered as estimated. The data user must be notified of this action.

3.3 **QA/QC Acceptance Criteria**

In order that reviews be consistent among reviewers, QA/QC protocol (stated in Appendix A.l) should be strictly adhered to. If a lab provides more than one set of QC analyses or more than one particular QC analysis for an SDG, the validator shall use the worst QC analysis to evaluate the SDG data. Professional judgement should only be used in the rare instances not addressed in the “Checklist”.

3.4 **Data Validation Flags**

Three types of data validation flags (J, R & U) are used in Region 2 to qualify the data.

3.4.1 **Flag "R" indicates Rejected Data**

Sample results determined to be unacceptable must preferably be lined over and flagged " R" with a red pencil only on the Inorganic Analysis Data Sheets (CLP Form I's). Data rejected on the basis of an unacceptable QC analysis should be excluded from further review or consideration. Data are rejected when associated QC analysis results exceed the expanded control limits of the QC criteria. The rejected data are known to contain significant errors based on documented information. The data user **must not** use the rejected data to make environmental decisions.

3.4.2 **Flag "J" indicates Estimated Data**

Sample results determined to be estimated must be flagged "J" with a red pencil only on the CLP Form I's. Data are flagged (J) when a QC analysis falls outside the primary acceptance limits. The qualified "J" data are not excluded from further review or consideration. However, only one flag (J) is applied to a sample result even though several associated QC analyses may fail. The "J" data may be biased high or low.

3.4.3 **Flg "U" indicates Non-Detects**

Sample results ≥ MDL associated with a contaminated blank are flagged "U" with a red pencil only on Form I's.

4.0 **Contractual Qualifiers**

The CLP laboratory applies contractual qualifiers on all Form I'S and the QC Forms when QC analyses are outside the control limits. These qualifiers are not applied on the Lotus or XLS spreadsheets with the exception of U and J. The contractual qualifiers and their meanings are as follows:

N : This qualifier indicates the lack of accuracy in the reported result, and is applied when matrix spiked sample recovery is outside the control limits.

E : This qualifier indicates the presence of interference, and is applied when the ICP serial dilution analysis is outside the control limits.

***** : This qualifier indicates the lack of precision, and is applied to sample results on Form I's and Form VI when the Lab Duplicate analysis is outside the control limits.

U : This is a concentration qualifier that laboratory applies to a non-detected result which is essentially less than the Method Detection Limit(MDL). A non-detected result of an analysis is indicated by the Contract Required Quantitation Limit (CRQL) of that analyze suffixed with "U".

J : This is a concentration qualifier that the laboratory applies to a positive result below the CRQL(i.e.,≥MDL but <CRQL).

NOTE: The laboratory qualifiers are crossed out and replaced with the appropriate data validation qualifiers (J, R or U) by the data validator.

4.0 Rounding Rule

The data reviewer must follow the standard practice to round off percent recoveries on the QC reporting forms.

5.0 Data Review Narrative (Appendix A.2)

The data review narrative should be written using the format of Appendix A.2. The narrative should indicate the QC analyses outside the acceptance limits and the actions taken to qualify the associated data. The narrative should be prepared on a Personal Computer or a typewriter. If hand-written, under no circumstances should a pencil be used to write the narrative. The Data Review Narrative should be written in four (4) Sections: (i)Data Case Description, (ii)Complete SDG File (CSF) Audit Section, (iii) Technical Review Section, and (iv) Contract-Problems/Non-Compliance Section.

5.1 Data Case Description Section

The data validator must briefly describe the data case in this Section, outlining important information such as the number of samples, their matrix, sampling date(s), analysis (TAL metals, mercury or cyanide), samples used for QC analyses, Field Blank(s), Field Duplicates, etc.

5.2 Complete SDG File (CSF) Audit Section

The data validator must perform an audit on each SDG in the data package to ensure that all SDG-specific documents (sampling, samples shipping and receiving, telephone contact logs, etc.) are present in the data case. The audit shall also discover any discrepancy in the deliverables. In Region 2, this audit is currently performed by the ESAT data validator and its findings reported under “Comments” on a CSF inventory checklist. The validator informs the CLP Project Officer (PO) of the missing or additional information/deliverable required for data validation. The PO then contacts the lab for the desired deliverable/information. The findings of the CSF audit are reported in the CSF Section of the Data Review Narrative (Appendix A.2).

5.3 Technical Review Section

The data validator shall report in this Section only the rejected (R) and estimated data (J) and the data rendered non-detects (U) as a result of technical review. It is imperative that the data reviewer highlights (i) QC analysis criteria applied to reject (R) or flag (J, U) the data, (ii) Samples rejected (R) or flagged (J, U), and (iii) the QC analysis out of control limits. The rest of the data that are not qualified (rejected or estimated) are not reported in this Section, and should be considered **fully useable.**

5.4 Contract-Problems/Non-Compliance Section

All the CLP non-compliant items detected during data review must be reported in this Section.

6.0 Computer-Aided Data Review and Evaluation (CADRE)

CADRE is a computer program that performs semi-automated Quality Assurance (QA) and Quality Control (QC) checks of results from the chemical analysis of soil and water samples according to the CLP protocols. After the CADRE data qualification is complete, a Lotus 1,2,3 spreadsheet or an XLS spreadsheet with data validation qualifiers (R,J,U) is generated for each SDG. Currently, Sample Management Office (SMO) performs this task using Data Assessment Tool (DAT), a software-driven process, and forwards to the Regions the customized electronic spreadsheets (Lotus 1,2,3 or XLS spreadsheet) and QC reports via the DART (Data Assessment Rapid Transmittal) system. Manual data validation is performed in conjunction with electronic data validation which can only be done by a trained and experienced data validator. The manual data review complements CADRE's findings to complete an assessment of data quality in a shorter time than by a solely manual process. The data validator must review the XLS or Lotus 1,2,3 spreadsheet against Form I's to ensure that the same results on Form I's and the Spreadsheet are qualified with the same data validation qualifiers. The spreadsheet for each SDG is provided with the Data Review Narrative.

7.0 Performance Evaluation Sample(PES)Based Data Validation Strategy

7.1 Scope and Summary

This strategy offers the use of Performance Evaluation Samples (PES) in the data validation process as a means of ensuring the quality of the CLP data while significantly reducing the validation time. The single blind PES provided by EPA (or any other reputable firm) is analyzed with samples of each matrix in a Sample Delivery Group (SDG). A software program (e.g.,PEAC TOOLS, SPS Web or equivalent)is used to determine whether or not the PES results fall within the previously statistically determined acceptance limits ("Action Low" and "Action High")for the Contaminants of Concern (**COC**). The PES results falling within the Action Limits are considered as acceptable results and may be designated as "Passed" analytes, and results of the analytes falling outside the Action Limits are considered as unacceptable and may be designated as "Failed" analytes. In either case ("Passed" Analytes or "Failed" analytes), the associated data is validated according to the Region 2 data validation SOP HW-2 in conjunction with the latest version of the WinCadre QC reports. The following strategy (procedure) is used:

7.2 "Passed" COC

If the COC in an SDG are within statistically generated Action Limits, the data validation is conducted according
to QC analyses indicated by check marks (√)in the "Review COC For" column of the Table I. The SDG samples are validated using the Region 2 data validation SOP in

conjunction with the latest version of the WinCADRE QC reports. The validation flags (J, R, U) are applied on Form I's as well on the CADRE Lotus 1,2,3 or XLS spreadsheet. Corrections, if needed, are
then made on the Lotus or XLS spreadsheet to ensure that all results on Form I's carry the same data validation and concentration flags as are on the Lotus or XLS Spreadsheet.

7.3 **"Failed" COC**

If the COC in an SDG are not within the statistically generated Action Limits, the data validation is conducted according to the data validation SOP QC Criteria indicated by check marks (√)in the "Review COC For" column of Table II. The SDG samples are validated using the Region 2 data validation SOP in conjunction with the latest version of the WinCADRE QC reports. The data validation flags (J,R,U) are applied on Form I's as well on the CADRE Lotus 1,2,3 or XLS Spreadsheet. Corrections, if needed, are then made on the Lotus or XLS spreadsheet to ensure that all results on Form I's carry the same data validation and concentration flags as are on the Lotus or XLS Spreadsheet.

7.4 **COC "Not Evaluated"**

Acceptance limits for the analytes not present/spiked in the PE sample are not provided on the PES Scoring Evaluation Report. Such analytes will be marked as "Not Evaluated" in the PES Evaluation Column. These analytes will be validated much the same way as the "Failed Analytes".

The failed analytes and the analytes not present/spiked in the PE sample require data validation according to the QC criteria specified in Table II, and are identified by the TOPO in the TDF for the Case/SDG.

Table I

Passed PES - All Contaminants of Concern are within the limits
(Action Low ≤ PES Result ≤ Action High)

QC Criteria	Review COC for
Holding Time & Preservation	√
Initial Calibration	
Initial Calibration Verification	
CRQL Standard	√
Blanks-Initial & Continuing	
Preparation Blank	
ICP Interference Check Sample	
Pre- Digestion/Distillation Matrix Spike	
Post Digestion Spike	
Laboratory Duplicate	
Field Duplicates Comparison	√
Lab Control Sample	
ICP Serial Dilution	
Field Blank Contamination	√
Percent Solids	√
Transcription/Computation Check	
Raw Data	
Total vs. Dissolved Concentrations Comparison	√

- The CSF (Complete SDG File) audit will be completed before the PES validation strategy is applied.
- Comparison of the Lotus or XLS Spreadsheet must be after the PES validation strategy is applied. The Contract
- Compliance can be checked after the PES validation strategy is applied.

Table II
Failed PES - Contaminants of Concern are not within the limits
(PES Result ≤ Action Low, PES Result ≥ Action High **OR** The Limits Not Established)

QC Criteria	Review COC for
Holding Time & Preservation	√
Initial Calibration	
Initial Calibration Verification	
CRQL Standard	√
Blanks-Initial & Continuing	
Preparation Blank	√
ICP Interference Check Sample	
Pre- Digestion/Distillation Matrix Spike	√
Post Digestion Spike	
Laboratory Duplicate	√
Field Duplicates Comparison	√
Lab Control Sample	√
ICP Serial Dilution	√
Field Blank Contamination	√
Percent Solids	√
Transcription/Computation Check	√
Raw Data	
Total vs. Dissolved Concentrations Comparison	√

- The CSF (Complete SDG File) audit will be completed before the PES validation strategy is applied.
- Comparison of the Lotus or XLS Spreadsheet must be after the PES validation strategy is applied.

- The Contract Compliance can be checked after the PES validation strategy is applied.

8.0 **Sampling Trip Report**

The sampler prepares a Sampling Trip Report for each sampling event and sends it to the RSCC. The report provides details of all activities performed for each sampling event on the Superfund site. It also lists the field QC samples such as Field Duplicates, Field/Rinse Blanks, sampling time and date for each sample, and samples associated with each field/rinse blank. The validator must use this information to evaluate the Field Duplicate pairs as well as the samples associated with contaminated Field/Rinse Blanks.

9.0 **Telephone Record Log (Appendix A.3)**

A Telephone Record Log (Appendix A.3) must be written by the data validator when a deliverable is missing or a clarification is needed about a lab procedure. The data validator should outline a basic profile of the Case on the Telephone Record Log Form, clearly indicating the reason(s) for inquiry and forward this Form to CLP PO/TOPO who will contact the lab to receive the missing document or information. The original Telephone Record Log is kept in the data package and a copy attached to the Data Review Narrative.

10.0 **Request for Re-Analysis (Appendix A.6)**

Data validator must note all items of contract non-compliance in the Data Review Narrative. If holding times and sample storage times have not been exceeded, the Project Officer (PO) may request re-analysis if items of non-compliance are critical to data assessment. Requests are to be made on "CLP Re-Analysis Request/Approval Record" form (Appendix A.4).

11.0 **CLP Data Assessment Summary Form (Appendix A.7)**

Fill in the total number of analytes performed by different methods and the number of analytes rejected (R) or flagged (J) as estimated due to corresponding quality control criteria. Place an "X" in boxes wherever analyses were not performed, or criteria do not apply.

12.0 **Data Review Log:**

It is recommended that the data validator maintain a log of the reviews completed to document:

a. Case number
b. SDG # (s)
c. number of samples
d. matrix of samples
e. contract laboratory
f. site name
g. start-date of the data case review
h. completion-date of the data case review
i. actual hours spent
j. reviewer's signature

13.0 **Record of Communication -**

This is a Regional document prepared and provided by the RSCC for each data package. The ROC indicates the Case #, site name, samples and sample matrix and the laboratory name. The presence of a ROC in a data package is an indication that the package has been reviewed by the RSCC for completeness and is ready for data validation.

14.0 **Forwarded Paperwork**

Upon completion of review, the following are to be forwarded to EPA for final review:

a. Data package
b. Completed data assessment checklist (Appendix A.1,original)
c. Original and a copy of completed data review narrative Appendix A.2)
d. CLASS Contract Compliance Screening (CCS) report
e. Telephone Record Log (Appendix A.3)
f. Field Duplicates Form (Appendix A.4)
g. Total/Dissolved Concentrations Form (Appendix A.5)
h. CLP Re-analysis Request/Approval Record Form (Appendix A.6)
i. Data Assessment Summary Form (Appendix A.7)
j. CADRE Spreadsheet on a computer diskette.

ACRONYMS

AA Atomic Absorption
AOC Analytical Operations/Data Quality Center
CADRE Computer-Aided Data Review and Evaluation
CCB Continuing Calibration Blank
CCS Contract Compliance Screening
CCV Continuing Calibration Verification
CLP Contract Laboratory Program
CO Contracting Officer
COC Contaminants of Concern
CRI CRQL Check Standard
CRQL Contract Required Quantitation Limit
CSF Complete SDG File
CVAA Cold Vapor AA
DART Data Assessment Rapid Transmittal
DAT Data Assessment Tool
DF Dilution Factor
DQO Data Quality Objective
ICB Initial Calibration Blank
ICP Inductively Coupled Plasma
ICP-AES Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS Inductively Coupled Plasma - Mass Spectrometry
ICS Interference Check Sample
ICV Initial Calibration Verification
LCS Laboratory Control Sample
LRS Linear Range Sample
MDL Method Detection Limit
NIST National Institute of Standards and Technology
OERR Office of Emergency and Remedial Response
OSWER Office of Solid Waste and Emergency Response
PB Preparation Blank
PE Performance Evaluation
%D Percent Difference
%R Percent Recovery
%RI Percent Relative Intensity
%RSD Percent Relative Standard Deviation
%S Percent Solids
PO Project Officer
QA Quality Assurance
QAPP Quality Assurance Project Plan
QC Quality Control
RPD Relative Percent Difference
RSCC Regional Sample Control Center

SDG Sample Delivery Group
SMO Sample Management Office
SOP Standard Operating Procedure
SOW Statement of Work
TAL Target Analyze List
TR/COC Traffic Report/Chain of Custody Documentation

Inorganic Target Analyze List And Contract Required Quantitation Limits (CRQLs)

Analyze	CAS Number	ICP-AES CRQL Water Ug/L	ICP-AES CRQL Soil mg/kg	ICP-MS CRQL Water Ug/L
Aluminum	7429-90-5	200	20	---
Antimony	7440-36-0	60	6	2
Arsenic	7440-38-2	10	1	1
Barium	7440-39-3	200	20	10
Beryllium	7440-41-7	5	0.5	1
Cadmium	7440-43-9	5	0.5	1
Calcium	7440-70-2	5000	500	-----
Chromium	7440-47-3	10	1	2
Cobalt	7440-48-4	50	5	1
Copper	7440-50-8	25	2.5	2
Iron	7439-89-6	100	10	----
Lead	7439-92-1	10	1	1
Magnesium	7439-95-4	5000	500	-----
Manganese	7439-96-5	15	1.5	1
Mercury	7439-97-6	0.2	0.1	---
Nickel	7440-02-0	40	4	1
Potassium	7440-09-7	5000	500	-----
Selenium	7782-49-2	35	3.5	5
Silver	7440-22-4	10	1	1
Sodium	7440-23-5	5000	500	-----
Thallium	7440-28-0	25	2.5	1
Vanadium	7440-62-2	50	5	1
Zinc	7440-66-6	60	6	2
Cyanide	57-12-5	10	2.5	----

Site:

Case #:

SDG #:

Samples: Soil Water

	YES	NO	N/A
A.l.l **Contract Compliance Screening Report**			
Present?	[___]	___	___
ACTION: If no, contact RSCC/PO.			
A.l.2 **Record of Communication (from RSCC)**			
Present?	[___]	___	___
ACTION: If no, request from the RSCC.			
A.1.3 **Sampling Trip Report**			
Present and complete?	[___]	___	___
ACTION: If no, contact RSCC/PO.			
A.l.4 **Chain of Custody/Sample Traffic Report**			
Present?	[___]	___	___
Legible?	[___]	___	___
Signature of sample custodian present?	[___]	___	___
ACTION: If no, contact RSCC/WAM/PO.			
A.l.5 **Cover Page**			
Present?	[___]	___	___
Is the Cover Page properly filled in and the verbatim signed by the lab manager or the manager's designee?	[___]	___	___
Do the sample identification numbers on the Cover Page agree with sample Identification numbers on:			
(a) Traffic Report Sheet?	[___]	___	___

	YES	NO	N/A
(b) Form I's?	[___]	___	___
Is the number of samples on the Cover Page the same as the number of samples on the Traffic Report sheet and the Regional Record of Communication (ROC) for the data Case?	[___]	___	___

ACTION:
If no for any of the above, prepare Telephone Record Log and contact RSCC/PO for re-submittal of the corrected Cover Page from the laboratory.

A.1.6 **SDG Narrative, DC-1 & DC-2 Form**

Is the SDG Narrative present?	[___]	___	___
Is Sample Log-In Sheet(Form DC-1) present and complete?	[___]	___	___
Is Complete SDG Inventory Sheet(Form DC-2) present and complete?	[___]	___	___

ACTION:
If no, write in the Contract-Problems/ Non-Compliance Section of the Data Review Narrative.

A.1.7 **Form I to XV**

A.1.7.1 Are all the Form I through Form XV labeled with:

Laboratory Name?	[___]	___	___
Laboratory Code?	[___]	___	___
RAS/Non-RAS Case No.?	[___]	___	___
SDG No.?	[___]	___	___

		YES	NO	N/A
	Contract No.?	[___]	___	___

ACTION:
If no for any of the above, note under Contract Problem/Non-Compliance Section of the "Data Review Narrative" and contact PO for corrected Form(s) from the laboratory.

A.1.7.2	After comparing values on Forms I-IX against the raw data, do any computation/ transcription errors exceed 10% of the reported values on the Forms for:			
	(a) all analytes analyzed by ICP-AES?	___	[_]	___
	(b) all analytes analyzed by ICP-MS?	_	[___]	_
	(c) Mercury?	__	[_]	_____
	(d) Cyanide?	_	[_]	_

ACTION:
If yes, prepare Telephone Record Log and contact CLP PO/TOPO for the corrected data from the laboratory.

A.1.8 Raw Data

Data shall not be validated without the hard/electronic copies of the associated raw data for samples and QC samples.

A.1.8.1 Digestion/Distillation Log

Digestion Log for ICP-AES (Form XII)present?	[___]	___	___
Digestion Log for ICP-MS (Form XII) present?	[___]	___	___
Digestion Log for mercury (Form XII) present?	[___]	___	___
Distillation Log for cyanide (Form XII) present?	[___]	___	___
Are pH values for metals and			

	YES	NO	N/A
cyanide reported for each aqueous sample?	[___]	__	__
Are percent solids calculations present for soils/sediments?	[__]	___	___
Are preparation dates present on the sample preparation logs/bench sheets?	[___]	__	__

NOTE:
Digestion/Distillation log must include weights, volumes, and dilutions used to obtain the reported results.

A.1.8.2 Is the analytical instrument real-time printouts present for:

ICP-AES?	[___]	__	__
ICP-MS?	[___]	___	___
Mercury?	[__]	__	__
Cyanide?	[___]	___	___

Are all laboratory bench sheets and instrument raw data printouts necessary to support all sample analyses and QC operations:

Legible?	[__]	__	__
Properly labeled?	[__]	__	__

Are all field samples, QC samples and field QC samples present on:

Digestion/Distillation log?	[___]	___	___
Instrument Printouts?	[__]	__	__

ACTION:
If no for any of the above questions in Section A.1.8.1 and Section A.1.8.2, write Telephone Record Log and contact TOPO/PO for re-submittal from the laboratory.

		YES	NO	N/A

A.1.9 **Technical Holding Times**: (Aqueous and soil samples)

(Examine sample Traffic Reports and digestion/distillation logs to determine the holding time from the sample collection date to the sample preparation date.)

A.1.9.1	Cyanide distillation(14 days)exceeded?	__	[__]	__
	Mercury analysis(28 days) exceeded?	__	[___]	__
	Other Metals analysis(180 days)exceeded? ___	___	[__]	__

ACTION:
If yes, reject (R) and red-line non-detects and flag as estimated (J)results ≥ MDL even if sample(s) was preserved properly.

NOTE:
In addition to qualifying the data, a list of all samples and analytes which exceeded the holding times must be prepared. Report for each sample the number of days that were exceeded. (Subtract the sample collection date from the sample preparation date). Attach this list to the data review narrative.

A.1.9.2	Is pH of aqueous samples for:			
	Metals Analysis ≤ 2?	[___]	___	___
	Cyanide Analysis ≥ 12?	[__]	__	__

ACTION:
If no for any of the above, flag non-detects as “R” and detects as “J”.

A.1.9.3	Is the cooler temperature ≤ 10 C°?	[__]	__	__

ACTION:
If cooler temperature is >10 ^{0}C , flag non-detects as “UJ” and detects as “J”.

A.1.10 **Final Data Correctness - Form I**

A.1.10.1 Are Form I's for all samples

	YES	NO	N/A
present and complete?	[___]	___	___

ACTION:
If no, prepare Telephone Record Log and contact CLP PO/TOPO for submittal from the laboratory.

A.1.10.2 Verify there are no calculation and transcription errors in the results reported on Form I's. Circle on each Form I all results that are incorrect.

Is the calculation error less than 10% of the correct result?	[___]	__	__
Are results on Form I's reported in correct units (ug/L for aqueous and MG/KG for soils)?	[___]	___	___
Are results on Form I'S reported by correct significant figures?	[___]	___	__
Are soil sample results on Form I's corrected for percent solids?	[___]	___	___
Are all "less than MDL" values reported by the CRQLs and coded with "U"?	[___]	___	___
Are values less than the CRQLs but greater than or equal to the MDLs flagged with "J"?	[___]	___	___
Are appropriate contractual quality control and Method qualifiers used?	[___]	____	___

ACTION:
If no for any of the above questions, prepare Telephone Record Log, and contact CLP PO/TOPO for corrected data.

A.1.10.3 Do EPA sample identification numbers and the corresponding laboratory sample identification numbers match on the Cover Page, Form I's and in the raw data? [___] ___ ___

Was a brief physical description

		YES	NO	N/A
	of the samples before and after digestion given on the Form I's?	[___]	___	__
	Was any sample result outside the mercury/cyanide calibration range or the ICP-AES/ICP-MS linear range diluted and noted on the Form I?	[___]	___	___
	ACTION: If no for any of the above, note under the Contract-Problem/Non-Compliance Section of the Data Review Narrative.			

A.1.11 **Initial Calibration**

A.1.11.1	Is a record of at least 2 point (A blank and a standard)calibration present for ICP-AES analysis?	[___]	___	___
	Is a record of at least 2 point (a blank and a standard)calibration present for ICP-MS analysis?	[___]	___	___
	Is a record of at least 5 point calibration (a blank & 4 standards)present for Hg analysis?	[___]	___	___
	Is a record of at least 4 point calibration (a blank & 4 standards)present for cyanide?	[___]	___	___
	ACTION: If incomplete or no initial calibration was performed, reject (R) and red-line the associated data (detects & non-detects).			
	Is one initial calibration standard at the CRQL level for cyanide and mercury?	[___]	___	___
	ACTION: If no, write in the Contract Problem/ Non-Compliance Section of the Data Review Narrative.			
A.1.11.2	Is the curve correlation coefficient $\geq$ 0.995 for:			

		YES	NO	N/A
	Mercury Analysis?	[___]	___	___
	Cyanide Analysis?	[___]	___	___
	ICP-AES(more than 2 point Calib.)?	[___]	___	___
	ICP-MS (more than 2 point calib.)?	[___]	___	___

ACTION:
If no, qualify the associated sample results ≥ MDL as estimated "J" and non-detects as "UJ".

NOTE:
The correlation coefficient shall be calculated by the data validator using standard concentrations and the corresponding instrument response (e.g. absorbance, peak area, peak height, etc.).

A.1.12 **Initial and Continuing Calibration Verification- Form IIA**

A.1.12.1	Present and complete for every metal and cyanide?	[___]	___	___
	Present and complete for ICP-AES and ICP-MS when both these methods were used for the same analyte?	[___]	___	___

ACTION:
If no for any of the above, prepare a Telephone Record Log and contact PO/TOPO for re-submittal from the laboratory.

A.1.12.2	Was a Continuing Calibration Verification performed every 10 samples or every 2 hours whichever is more frequent?	[___]	___	___

ACTION:
If no for any of the above, write in the Contract-Problem/Non-Compliance Section of the Data Review Narrative.

A.1.12.3	Was an ICV or a mid-range standard distilled and analyzed with each batch of cyanide samples?	[___]	___	___

	YES	NO	N/A

ACTION:
If no for any of the above, write in the Contract-Problem/Non-Compliance Section of the Data Review Narrative and qualify results ≥ MDL as estimated (J).

A.1.12.2 Circle on each Form IIA all percent recoveries that are outside the contract windows.

Are ICV/CCVs within control limits for:

Metals - 90-110%R?	[___]	___	___
Hg - 80-120%R?	[___]	___	___
Cyanide - 85-115%R?	[___]	___	___

ACTION:
If no, qualify all samples between a previous technically acceptable CCV standard and a subsequent technically acceptable CCV standard as follows as follows:

Qualify as estimated (J) all detects and non-detects, if the ICV/CCV %R is between 75-89%(65-79% for Hg; 70-84% for CN). Qualify only positive results(≥ MDL) as "J" if the ICV/CCV %R is between 111-125%(121-135% for Hg;116-130% for CN). Reject (R) and red-line only
detects if the recovery is greater than 125% (135% for Hg; 130% for CN). Reject (R) and red-line all associated results (hits and non-detects)if the recovery is less than 75%(65% for Hg;70% for CN).

NOTE:
For ICV that does not fall within the acceptance limits, qualify all samples reported from the analytical run.

A.1.12.3 Was the distilled ICV or mid-range standard for cyanide within acceptance limits (85-115%)? [___] ___ ___

ACTION:
If no, Qualify all cyanide results ≥ MDL as "J".

A.1.13 **CRQL Standard Analysis - Form IIB**

A.1.13.1 For each ICP-AES run, was a CRI

	YES	NO	N/A
(CRQL or MDL when MDL > CRQL) standard analyzed? **(Note:CRI is not required for Al, Ba, Ca, Fe, Mg, Na and K.)**	[___]	___	___
For each ICP-MS run, was a CRI (CRQL or MDL when MDL > CRQL) standard analyzed for each mass/isotope used for the analysis?	[___]	___	___ ___
For each mercury run, was a CRQL standard analyzed?	[___]	___	___
For each cyanide run, was a CRQL standard analyzed?	[___]	___	___

ACTION:
If no for any of the above, write this deficiency in the Contract Problems/ Non-Compliance Section of the Data Review Narrative, inform CLP PO and flag results in the affected ranges (detects <2xCRQL)as J and non-detects UJ.

The affected ranges are:
ICP-AES Analysis - *True Value ± CRQL
ICP-MS Analysis - *True Value ± CRQL
Mercury Analysis - *True Value ± CRQL
Cyanide Analysis - *True Value ± CRQL
*** True value of the CRQL Standard**

A.1.13.2 Was a CRQL standard analyzed after the ICV/ICB, before the final CCV/CCB and once every 20 analytical samples in the analytical run for each analysis? [___] ___ ___

ACTION:
If no, write in the Contract Problem/ Non-Compliance Section of the "Data Review Narrative".

A.1.13.3 Circle on each Form IIB all percent recoveries that are outside the acceptance windows.

	YES	NO	N/A
Is the CRQL standard within control limits for:			
Metals(ICP-AES/ICP-MS)- 70 - 130%?	[___]	___	___
Mercury- 70 - 130%?	[___]	___	___
Cyanide - 70 - 130%?	[___]	___	___

ACTION:
If no, flag detects <2xCRQL as "J" and non-detects as "UJ" if the CRQL standard recovery is between 50-69%. Flag(J) only detects <2xCRQL if the recovery is between 131% and ≤180%. If the recovery is less than 150%, reject(R) and red-line non-detects and detects < 2xCRQL, and flag (J) detects between 2xCRQL and ICV/CCV. Reject and red-line only detects <2xCRQL and flag (J)detects ≥ 2xCRQL but < ICV/CCV if the recovery is > 180%.

NOTE:
1. Qualify all field samples analyzed between a previous technically acceptable analysis of the CRQL standard and a subsequent acceptable analysis of the CRQL standard
2. Flag (J) or reject (R) only the final sample results on Form I's when **Sample raw data** are within the affected ranges and the CRQL standard is outside the acceptance windows.
3. The samples and the CRQL standard must be analyzed in the same analytical run.

A.1.14 Initial and Continuing Calibration Blanks - Form III

		YES	NO	N/A
A.1.14.1	Present and complete for all the instruments used for the metals and cyanide analyses?	[___]	___	___
	Was an initial Calibration Blank analyzed after ICV?	[___]	___	___
	Was a continuing Calibration Blank analyzed after every CCV and every 10 samples or every 2 hours, whichever is more frequent?	[___]	___	___
	Were the ICB & CCB values ≥ MDL but < CRQL reported on Form III and flagged "J" by			

		YES	NO	N/A
	using MDLs from direct analysis(Preparation Method "NP1")? (Check Form III against the raw data)	[___]	___	___

ACTION:
If no, inform CLP PO/TOPO and make a note in the Contract-Problems/Non-Compliance Section of the "Data Review Narrative".

A.1.14.2 Circle with red pencil on each Form III all Calib. Blank values that are:

≥ MDL but ≤ CRQL

> CRQL

A.1.14.2.1	When MDL < CRQL, is any Calib. Blank value ≥ MDL but ≤ CRQL?	___	[___]	___

ACTION:
If yes, change sample results ≥ MDL but ≤ CRQL to the CRQL with a "U". Do not qualify non-detects.

A.1.14.2.2	When MDL < CRQL, is any Calib. Blank value > CRQL?	___	[___]	___

ACTION:
If yes, reject (R) and red line the associated sample results > CRQL but <ICB/CCB Blank Result. Flag as "J" detects > ICB/CCB blank value but < 10xICB/CCB value. Change the sample results ≥ MDL but ≤ the CRQL to CRQL with a "U".

A.1.14.2.3	Is any Calibration Blank value below the negative CRQL?	___	[___]	___

ACTION:
If yes, flag (J) as estimated all associated sample results ≥ CRQL but <10xCRQL.

NOTE:

1. For ICB that does not meet the technical QC Criteria, apply the action to all samples

	YES	NO	N/A

reported from the analytical run.

2. For CCBs that do not meet the technical QC criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of CCB and a subsequent technically acceptable analysis of the CCB in the analytical run.,

A.1.15 **Preparation Blank - FORM III**

NOTE:The Preparation Blank for mercury is the same as the calibration blank.

A.1.15.1 Was one Preparation Blank prepared with and analyzed for:

Each Sample Delivery Group (SDG)?	[___]	___	___
Each batch of the SDG samples digested/distilled?	[___]	___	___
Each matrix type?	[___]	___	___
All instruments used for metals and cyanide analyses?	[___]	___	___

ACTION:
If no for any of the above, flag as estimated (J) all the associated positive data <10xMDL for which the Preparation Blank was not analyzed.

NOTE:
If only one blank was analyzed for more than 20 samples, then the first 20 samples analyzed are not estimated(J),but all additional samples must be qualified (J).

A.1.15.2 Circle with red pencil on each Form III all Prep. Blank values that are:

$\geq$ MDL but $\leq$ CRQL, and

> CRQL

A.1.15.2.1 When MDL < CRQL, is any preparation blank value $\geq$ MDL but $\leq$ CRQL? ___ [___] ___

ACTION:
If yes, change sample result $\geq$ MDL

		YES	NO	N/A
	but ≤ CRQL to CRQL with a "U".			
A.1.15.2.2	When the MDL ≤ CRQL, is any Preparation Blank value greater than its CRQL?	___	[___]	___
	If yes, is the Prep. Blank value greater than the value of the associated Field Blank collected and analyzed with the SDG samples?	___	[___]	___
	If yes, is the lowest concentration of that analyte in the associated samples less than 10 times the Preparation Blank value?	___	[___]	___

ACTION:
If yes, reject (R) and red-line all associated sample results greater than the CRQL but less than the Prep.Blank value. Flag as "J" detects > Prep. Blank value but <10xPrep.Blank. If the sample result ≥ MDL but ≤ CRQL, replace it with CRQL-U.

If the Prep. Blank value is less than the same analyte value in the Field Blank, do not qualify the sample results due to the Prep. Blank criteria.

NOTE:
Convert soil sample result to mg/Kg on wet weight basis to compare with the soil Prep. Blank result on Form III.

A.1.15.2.3	Is the Prep. Blank concentration below the negative CRQL?	___	[___]	___

ACTION:
If yes, flag (J) all associated sample results less than 10xCRQL. Qualify non-detects as estimated (UJ).

A.1.15.2.4	When the MDL is greater than the CRQL, is the preparation blank concentration on Form III greater than two times the MDL?	___	[___]	___

ACTION:

		YES	NO	N/A
	If yes, reject (R) and red-line all positive sample results with sample raw data less than 10 times the Preparation Blank value.			

A.1.16 **ICP-AES/ICP-MS Interference Check Sample (ICS)- Form IV**

NOTE: Not required for CN, Hg, Al, Ca, Fe and Mg.

A.1.16.1	Present and complete?	[___]	___	___
	Was ICS analyzed at the beginning and end of each analytical run, and once for every 20 analytical samples?	[___]	___	___
	Was ICS analyzed at the beginning of the ICP-MS analytical run?	[___]	___	___

ACTION:
If no, flag as estimated (J) all sample results.

A.1.16.2 **ICP-AES Method**

A.1.16.2.1	**ICSA Solution:** For ICP-AES, are the ICSA "Found" analyte values within the control limits ± of CRQL of the true/established mean value?	[___]	___	___
	If no for any of the above, is the sample concentration of Al, Ca, Fe, or Mg in the same units (ug/L or MG/KG) greater than or equal to its respective concentration in the ICSA Solution on Form IV?	[___]	___	___

ACTION:
If yes, apply the following action to all samples analyzed between a previous technically acceptable analysis of the ICS and a subsequent technically acceptable analysis of the ICS in the analytical run:

Flag (J) as estimated only sample results ≥MDL

		YES	NO	N/A
	for which the ICSA "Found" value is greater than (True value+CRQL). Do not qualify non-detects. If the ICSA "Found" value is less than (True value-CRQL), flag non-detects as "UJ" and detects as "J".			
A.1.16.2.3	**ICSAB Solution** For ICP-AES, are all analyte results in ICSAB within the control limits of 80-120 of the true/established mean value?	[___]	___	___
	If no for any of the above, is the sample concentration of Al, Ca, Fe, or Mg in the same units (ug/L or MG/KG) greater than or equal to its respective concentration in the ICSAB Solution on Form IV?	[___]	___	___
	ACTION: If yes, apply the following action to all samples analyzed between a previous technically acceptable analysis of the ICS and a subsequent technically acceptable analysis of the ICS in the analytical run: Flag (J) as estimated those associated sample results ≥ MDL for which the ICSAB analyte recovery is greater than 120% but ≤ 150%. If the ICSAB recovery falls within 50-79%, qualify sample results ≥ MDL as "J" and non-detects as "UJ". Reject (R) and red-line all sample results (detects & non-detects) for which the ICSAB analyte recovery is less than 50%. If the recovery is above 150%, reject (R) and red-line only positive results.			
A.1.16.3	**ICP-MS Method**			
A.1.16.3.1	**ICSA Solution:** For ICP-MS, are the ICSA "Found" analyte values within the control limits of ±CRQL of the true/established mean value?	[___]	___	___
	ACTION: If no, apply the following action to all samples reported from the analytical run: Flag (J) as estimated only sample results ≥ MDL if the ICSA "Found" value is greater than (True value+CRQL). Do not qualify non-detects. If the ICSA "Found" value is less than (True value-CRQL), flag the associated sample detects as "J" and non-detects as "UJ".			

		YES	NO	N/A
A.1.16.3.3	**ICSAB Solution** For ICP-MS, are all analyte results in ICSAB within the control limits of 80-120% of the true/established mean value, whichever is greater?	[___]	___	___

ACTION:
If no, apply the following action to all samples reported from the analytical run:

Flag (J) as estimated those associated sample results ≥ MDL for which the ICSAB analyte recovery is greater than 120% but ≤ 150%. If the ICSAB recovery falls within 50-79% flag (J) as estimated the associated sample results ≥ MDL. Reject (R) and red-line those all sample detects and non-detects for which the ICSAB analyte recovery is less than 50%. If the recovery is above 150%,reject (R) and red-line only detects (≥ MDL).

A.1.17 **Spiked Sample Recovery: Pre-Digestion/Pre-Distillation)-Form V A**
Note:Not required for Ca,Mg,K,and Na(both matrices);Al and Fe (soil only)

A.1.17.1	Was Matrix Spike analysis performed:			
	For each matrix type?	[___]	___	___
	For each SDG?	[___]	___	___
	On one of the SDG samples?	[___]	___	___
	For each concentration range (i.e.,low, med., high)?	[___]	___	___
	For each analytical Method (ICP-AES,ICP-MS, Hg, CN)used?	[___]	___	___
	Was a spiked sample prepared and analyzed with the SDG samples?	[___]	___	___

ACTION:
If no for any of the above, flag as estimated(J)all the positive data for which a spiked sample was not analyzed.

NOTE:
If more than one spiked sample were analyzed for one SDG, then qualify the associated data based on the worst spiked sample analysis.

		YES	NO	N/A
A.1.17.2	Was a field blank or PE sample used for the spiked sample analysis?	___	[___]	___
	ACTION: If yes, flag (J) as estimated positive data of the associated SDG samples for which field blank or PE sample was used for the spiked sample analysis.			
A.1.17.3	Circle on each Form VA all spike recoveries that are outside the control limits (75-125%) that have sample concentrations less than four times the added spike concentrations.			
	Are all recoveries within the control limits when sample concentrations are less than or equal to four times the spike concentrations?	[___]	___	___
	NOTE: Disregard the out of control spike recoveries for analytes whose concentrations are greater than or equal to four times the spike added.			
	Are results outside the control limits (75-125%)flagged with Lab Qualifier "N" on Form I's and Form VA?	[___]	___	___
	ACTION: If no for any of the above, write in the Contract - Problems/Non-Compliance Section of the Data Review Narrative.			
A.1.17.4	**Aqueous**			
	Are any spike recoveries:			
	(a) less than 30%?	___	[___]	___
	(b) between 30-74%?	___	[___]	___
	(c) between 126-150%?	___	[___]	___
	(d) greater than 150%?	___	[___]	___
	ACTION: If the matrix spike recovery is less than 30%,reject (R) and red-line all associated aqueous data (detects & non-detects). If between 30-74%, qualify all associated aqueous data ≥ MDL as “J” and non-detects			

		YES	NO	N/A
	as "UJ". If between 126-150%, flag (J) all data ≥ MDL as "J". If greater than 150%, reject (R) and red-line all associated data ≥ MDL.			
	(**NOTE:**Replace "N" with "J", "R" as appropriate.)			
A.1.17.5	**Soil/Sediment**			
	Are any spike recoveries:			
	(a) less than 10%?	___	[___]	___
	(b) between 10-74%?	___	[___]	___
	(c) between 126-200%?	___	[___]	___
	(d) greater than 200%?	___	[___]	___
	ACTION: If yes for any of the above, proceed as follows:			
	If the matrix spike recovery is less than 10%,reject (R) and red-line all associated data (detects & non-detects); if between 10-74%,qualify all associated data ≥ MDL as "J" and non-detects as "UJ"; if between 126-200%, flag (J) all associated data ≥ MDL as "J" If greater than 200%, reject (R) and red-line all associated data ≥ MDL. (**NOTE:**Replace "N" with "J" or "R" as appropriate.)			
A.1.18	**Lab Duplicates) - Form VI**			
A.1.18.1	Was the lab duplicate analysis performed:			
	For each SDG?	[___]	___	___
	On one of the SDG samples?	[___]	___	___
	For each matrix type?	[___]	___	___
	For each concentration range (low or med.)?	[___]	___	___
	For each analytical Method (ICP-AES/ICP-MS,Hg,CN)Used?	[___]	___	___
	Was a lab duplicate prepared and analyzed with the SDG samples?	[___]	___	___

		YES	NO	N/A
	ACTION: If no for any of the above, flag (J) as estimated all the SDG sample results (detects & non-detects) for which the lab duplicate analysis was not performed.			
	NOTE: If more than one lab duplicate sample were analyzed for an SDG, then qualify the associated samples based on the worst lab duplicate analysis.			
A.1.18.2	Was a Field Blank or PE sample used for the Lab Duplicate analysis?	___	[___]	___
	ACTION: If yes, flag as estimated (J) all SDG sample results (hits & non-detects) for which Field Blank or PE sample was used for duplicate analysis.			
A.1.18.3	Circle on each Form VI all values that are:			
	RPD > 20%, or			
	Absolute Difference > CRQL			
	Are all values within control limits (RPD ≤ 20% or absolute difference ≤ ±CRQL)?	[___]	___	___
	If no, are all results outside the control limits flagged with an "*" (Lab Qualifier)on Form VI and on all Form I's?	[___]	___	___
	ACTION: If no, write in the Contract-Problems/ Non-Compliance Section of the Data Review Narrative.			
	NOTE: The laboratory is not required to report on Form VI the RPD when both values are non-detects.			
A.1.18.4	**Aqueous**			
A.1.18.4.1	When sample and duplicate values are both ≥ 5xCRQL (substitute MDL for CRQL when MDL > CRQL),			

	YES	NO	N/A
is any RPD > 20% but < 100%?	___	[___]	___
is any RPD ≥ 100%?	___	[___]	___

ACTION:
If the RPD is > 20% but < 100%, flag (J) as estimated the associated sample data ≥ CRQL. If the RPD is ≥ 100%, reject (R) and red-line the associated sample data ≥ CRQL.

(**NOTE:**Replace **"*"** with "J" or "R" as appropriate.)

A.1.18.4.2 When the sample and/or duplicate value <5xCRQL (substitute MDL for CRQL when MDL >CRQL), is the absolute difference between sample and duplicate values:

> ± CRQL?	___	[___]	___
> ± 2xCRQL?	___	[___]	___

ACTION:
If the absolute difference is > CRQL, flag as estimated all the associated sample results ≥ MDL but < 5xCRQL as "J" and non-detects as "UJ". If the absolute difference is > 2xCRQL, reject (R) and red-line all the associated non-detects and detects ≥ MDL but < 5xCRQL.
NOTE:
1. Replace "*" with "J", "UJ" or "R" as appropriate.)
2. If one value is >CRQL and the other value is non-detect, calculate the absolute difference between the value > CRQL and the MDL, and use this difference to qualify sample results.

A.1.18.5 **Soil/Sediment**

A.1.18.5.1 When sample and duplicate values are both ≥ 5xCRQL (substitute MDL for CRQL when MDL > CRQL),

is any RPD ≥ 35% but < 120%?	___	[___]	___
is any RPD ≥ 120%?	___	[___]	___

ACTION:
If the RPD is ≥ 35% and < 120%, flag (J) as estimated the associated sample

		YES	NO	N/A
	data ≥ CRQL. If the RPD is ≥ 120%, reject (R)and red-line the associated sample data ≥ CRQL.			
A.1.18.5.2	When the sample and/or duplicate value <5xCRQL(substitute MDL for CRQL when MDL > CRQL), is the absolute difference between sample and duplicate:			
	> ± 2 x CRQL?	___	[___]	___
	> ± 4 x CRQL	___	[___]	___

ACTION:
If the absolute difference is > 2 x CRQL, flag all the associated sample results ≥ MDL but < 5xCRQL as "J" and non-detects as "UJ". If the absolute difference is > 4xCRQL, reject (R) and red-line all the associated non-detects and detects ≥ MDL but <5xCRQL.

NOTE:
1. Replace "*" with "J", "UJ" or "R" as appropriate.)
2. If one value is >CRQL and the other value is non-detect, calculate the absolute difference between the value > CRQL and the MDL, and use this difference to qualify sample results.

A.1.19 Field Duplicates

Aqueous Field Duplicates

A.1.19.1	Was an aqueous Field Duplicate pair collected and analyzed? (Check Sampling Trip Report)	[___]	___	____

ACTION:
If yes, prepare a Form (Appendix A.4) for each aqueous Field Duplicate pair. Report the sample and Field Duplicate results on Appendix A.4 from their respective Form I's. Calculate and report RPD on Appendix A.4 when sample and its Field Duplicate values are both > 5xCRQL. Calculate and report the absolute difference on Appendix A.4 when at least one value (sample or duplicate) is <5xCRQL. Evaluate the aqueous Field Duplicate analysis in accordance with the

		YES	NO	N/A

QC criteria stated in Sections A.1.19.2 and A.1.19.3.

NOTE:
1. Do not transfer "*" from Form I's to Appendix A.4.
2. Do not calculate RPD when both values are non-detects.
3. Substitute MDL for CRQL when MDL > CRQL.
4. If one value is >CRQL and the other value is non-detect, calculate the absolute difference between the value > CRQL and the MDL, and use this the criteria to qualify the results.

A.1.19.2 Circle all values on the Form (Appendix A.4) for Field Duplicates that have:

RPD $\geq$ 20% or

Difference > $\pm$ CRQL

When sample and duplicate values are both $\geq$5xCRQL (substitute MDL for CRQL when MDL > CRQL),

is any RPD $\geq$ 20%?	___	[___]	___
is any RPD $\geq$ 100%?	___	[___]	___

ACTION:
If the RPD is >20% but < 100%, flag (J) only the associated sample and its Field Duplicate results $\geq$ CRQL. If the RPD is $\geq$ 100%, reject(R) and red-line only the associated sample and its Field Duplicate result $\geq$ CRQL.

A.1.19.3 When the sample and/or duplicate value(s) <5xCRQL (substitute MDL for CRQL when MDL >CRQL), is the absolute difference between sample and duplicate:

> $\pm$ CRQL?	___	[___]	___
> $\pm$ 2 x CRQL?	___	[___]	___

ACTION:
If the absolute difference is > CRQL, flag detects $\geq$ MDL but < 5xCRQL as "J" and non-detects as "UJ". If the difference is > 2xCRQL,reject (R) and red-line non-detects

		YES	NO	N/A
	and results ≥ MDL but <5xCRQL of the sample and its Field Duplicate.			

Soil/Sediment Field Duplicates

A.1.19.4	Was a soil field duplicate pair collected and analyzed? (Check Sampling Trip Report)	[___]	___	___

ACTION:
If yes, for each soil Field Duplicate pair proceed as follows:

Prepare Appendix A.4 for each Field Duplicate pair. Report on Appendix A.4 all sample and its Field Duplicate results in MG/KG from their respective Form I's. Calculate and report RPD when sample and its duplicate values are both greater than 5xCRQL. Calculate and report the absolute difference when at least one value (sample or duplicate)is < 5xCRQL. Evaluate the Field Duplicate analysis in accordance with the QC Criteria stated in Sections A.1.19.5 and A.1.19.6.

NOTE:
1. Do not transfer "*" from Form I's to Appendix A.4.
2. Do not calculate RPD when both values are non-detects.
3. Substitute MDL for CRQL when MDL > CRQL.
4. If one value is >CRQL and the other value is non-detect, calculate the absolute difference between the value > CRQL and the MDL, and apply the criteria to qualify the results.

A.1.19.5	Circle on each Appendix A.4 all values that have: RPD ≥ 35%, or Difference > ± 2xCRQL When sample and duplicate values are both ≥ 5xCRQL (substitute MDL for CRQL when MDL > CRQL),			
	is any RPD ≥ 35% but < 120%?	___	[___]	___
	is any RPD ≥ 120%?	___	[___]	___

ACTION:
If the RPD is ≥ 35% but < 120%,

		YES	NO	N/A
	flag only the associated sample and its Field Duplicate results ≥ CRQL as "J". If the RPD is ≥ 120%, reject (R) and red-line only the sample and its Field Duplicate results ≥ CRQL.			
A.1.19.6	When the sample and/or duplicate value(s) <5xCRQL (substitute MDL for CRQL when MDL > CRQL), is the absolute difference between sample and Field Duplicate:			
	> ± 2 x CRQL?	___	[___]	___
	> ± 4 x CRQL?	___	[___]	___
	ACTION: If the absolute difference is > 2xCRQL, flag Sample and its Field Duplicate resuts ≥ MDL but <5xCRQL as "J" and non-detects as "UJ". If the difference is >4xCRQL, reject(R) and red-line non-detects and detects ≥ MDL but <5xCRQL of the sample and its Field Duplicate.			
A.1.20	**Laboratory Control Sample (LCS)- Form VII**			
A.1.20.1	Was one LCS prepared and analyzed for:			
	Each SDG?	[___]	___	___
	Each matrix type?	[___]	___	___
	Each batch samples digested/distilled?	[___]	___	___
	For each Method(ICP-AES,ICP-MS,Hg,CN) used?	[___]	___	___
	Was an LCS prepared and analyzed with the samples?	[___]	___	___
	ACTION: If no for any of the above, prepare Telephone Record Log and contact CLP PO or TOPO for submittal of the LCS results. Flag (J) as estimated all the data for which an LCS was not analyzed.			
	NOTE: If only one LCS was analyzed for			

	YES	NO	N/A

more than 20 samples, then the first 20 samples analyzed are not flagged(J), but all additional samples must be qualified (J).

A.1.20.2 **Aqueous LCS**

Circle on each Form VII the LCS percent recoveries outside control limits 80-120%.

NOTE: 1.Use digested ICV as LCS for aqueous mercury
2.Use distilled ICV as LCS for aqueous cyanide

Is any LCS recovery:

Less than 50%?	___	[___]	___
Between 50% and 79%?	___	[___]	___
Between 121% and 150%?	___	[___]	___
Greater than 150%?	___	[___]	___

ACTION:
If the LCS recovery is less than 50%, reject (R) and red-line all associated sample data (detects & non-detects); for a recovery between 50-79%, flag detects as “J” all non-detects as “UJ”. if the LCS recovery is between 121-150%, flag only detects as “J”. if the recovery is greater than 150%, reject (R) and red-line all detects.

A.1.20.3 **Solid LCS**

If an analyte's MDL is equal to or greater than the true value of LCS, disregard the "Action" below for that analyte even though the LCS is out of control limits.

Is the LCS "Found" value greater than the Upper Control Limit reported on Form VII?	___	[___]	___

ACTION:

		YES	NO	N/A
	If yes, flag (J) all the associated detects ≥ MDL as estimated (J).			
	Is the LCS "Found" value lower than the Lower Control Limit reported on Form VII?	___	[___]	___
	ACTION: If yes, flag detects as "J" and non-dectes as "UJ".			
A.1.21	**ICP-AES/ICP-MS Serial Dilution - Form VIII** **NOTE**:Serial dilution analysis is required only when the initial concentration is equal to or greater than 50 x MDL.			
A.1.21.1	Was a Serial Dilution analysis performed:			
	For each SDG?	[___]	___	___
	On one of the SDG samples?	[___]	___	___
	For each matrix type?	[___]	___	___
	For each concentration range (low or med.)?	[___]	___	___
	Was a Serial Dilution sample analyzed with the SDG samples?	[___]	___	___
	ACTION: If no for any of the above, flag as estimated (J) detects ≥ MDL of all the SDG samples for which the ICP Serial Dilution Analysis was not performed.			
A.1.21.2	Was a Field Blank or PE sample used for the Serial Dilution Analysis?	___	[___]	___
	ACTION: If yes, flag as estimated (J) detects ≥ MDL of all the SDG samples			
A.1.21.3	Circle on Form VIII the Percent Differences (%D) between sample results and its dilution results that are outside the control limits ± 10%			

		YES	NO	N/A
	when initial concentrations ≥ 50 x MDLs.			
	Are results outside the control limits flagged with an "E"(Lab Qualifier) on Form VIII and all Form I's?	[___]	___	___
	ACTION: If no, write in the Contract-Problem/ Non-Compliance Section of the Data Review Narrative.			
A.1.21.4	Are any %D values:			
	> 10%?	___	[___]	___
	≥ 100%?	___	[___]	___
	ACTION: If the Percent Difference (%D) is greater than 10%, flag (J) as estimated all associated samples whose **raw data** ≥ MDL; if the %D is ≥ 100%, reject (R) and red-line all associated samples with **raw data** ≥ MDL.			
	(**NOTE:**Replace "E" with "J" or "R" as appropriate.)			
A.1.22	**Total/Dissolved or Inorganic/Total Analytes**			
A.1.22.1	Were any analyses performed for dissolved as well as total analytes on the same sample(s)?	___	[___]	___
	Were any analyses performed for inorganic as well as total analytes on the same sample(s)?	___	[___]	___
	ACTION: If yes, prepare a Form (Appendix A.5) to compare the differences between dissolved (or inorganic)and total analyte concentrations. Compute each difference on Appendix A.5 as a percent of the total analyte only when both of the following conditions are fulfilled:			
	(1) The dissolved(or inorganic)concentration is greater than total concentration, and (2) greater than or equal to 5xMDL.			
A.1.22.2	Is any dissolved (or inorganic) concentration greater than its total concentration by more than 20%?	___	[___]	___

		YES	NO	N/A
A.1.22.3	Is any dissolved(or inorganic) concentration greater than its total concentration by more than 50%?	___	[___]	___

ACTION:
If the percent difference is greater than 20%, flag (J) both dissolved/inorganic and total concentrations as estimated. If the difference is more than 50%, reject (R) and red-line both the values.

A.1.23 **Field Blank - Form I**
NOTE: **Designate "Field Blank" as such on Form I**

A.1.23.1	Was a Field/Rinsate Bank collected and analyzed with the SDG samples?	[___]	___	___
	If yes, is any Field/Rinsate Blank absolute value of an analyte on Form I greater than its CRQL(or 2xMDL when MDL>CRQL)?	___	[___]	___
	If yes, circle the Field Blank value on Form I that is greater than the CRQL,(or 2 x MDL when MDL > CRQL).			
	Is any Field Blank value greater than CRQL also greater than the Preparation Blank value?	___	[___]	___
	If yes, is the Field Blank value (> CRQL and > the prep. blank value) already rejected due to other QC criteria?	[___]	___	___

ACTION:
If the Field Blank value was not rejected, reject all associated sample data (except the Field Blank results)greater than the CRQL but less than the Field Blank value. Reject on Form I's the soil sample results whose raw values in ug/L in the instrument printout are greater than the CRQL but less than the Field Blank value in ug/L. Flag as "J" detects between the Field Blank value and 10xField Blank value. If the sample result $\geq$ MDL but $\leq$ CRQL, replace it with CRQL-U.

If the Field Blank value is less than the

		YES	NO	N/A
	Prep.Blank value, do not qualify the sample results due to the Field Blank criteria.			

NOTE:
1. Field Blank result previously rejected due to other criteria cannot be used to qualify field samples.
2. Do not use Rinsate Blank associated with soils to qualify water samples and vice versa.

A.1.24 **Verification of Instrumental Parameters - Form IX, XA, XB, XI**

A.1.24.1 Is verification report present for:

Method Detection Limits (Form IX-Annually)?	[___]	___	___
ICP-AES Interelement Correction Factors (Form XA & XB -Quarterly)?	[___]	___	___
ICP-AES & ICP-MS Linear Ranges (Form XI-Quarterly)?	[___]	___	___

ACTION:
If no, contact CLP PO/TOPO for submittal from the laboratory.

A.1.24.2 **Method Detection Limits - Form IX**

A.1.24.2.1 Are MDLs present on Form IX for:

All the analytes?	[___]	___	___
All the instruments used?	[___]	___	___
Digested and undigested samples and Calib.Blanks?	[___]	___	___
ICP-AES and ICP-MS when both instruments are used for the same analyte?	[___]	___	___

ACTION:
If no for any of the above, prepare Telephone Record Log and contact CLP PO/TOPO for submittal of the MDLs from the laboratory. Report to CLP PO and write in the Contract Problems/ Non-Compliance Section of the Data Review Narrative if the MDL concentration is not less than ½ CRQL.

		YES	NO	N/A
A.1.24.2.2	Is MDL greater than the CRQL for any analyte?	___	[___]	___
	If yes,is the analyte concentration on Form I greater than 5 x MDL for the sample analyzed on the instrument whose MDL exceeds CRQL?	[___]	___	___

ACTION:
If no, flag as estimated (J) all values less than five times MDL for the analyte whose MDL exceeds the CRQL.

A.1.24.3 **Linear Ranges - Form XI**

A.1.24.3.1	Was any sample result higher than the high linear range for ICP-AES or ICP-MS?	___	[___]	___
	Was any sample result higher than the highest calibration standard for mercury or cyanide?	___	[___]	___
	If yes for any of the above, was the sample diluted to obtain the result reported on Form I?	[___]	___	___

ACTION:
If no, flag (J) as estimated the affected detects ($\geq$ MDL) reported on Form I.

A.1.25 **ICP-MS Tune Analysis - Form XIV**

A.1.25.1	Was the ICP-MS instrument tuned prior to calibration?	[___]	___	___

ACTION:
If no, reject (R) and red-line all sample data for which tuning was not performed.

A.1.25.2	Was the tuning solution analyzed or scanned at least five times consecutively?	[___]	___	___
	Were all the required isotopes spanning the analytical range present in the tuning solution?	[___]	___	___
	Was the mass resolution within			

		YES	NO	N/A
0.1 amu for each isotope in the tuning solution?		[___]	___	___
	Was %RSD less than 5% for each isotope of each analyte in the tuning solution?	[___]	___	___
	ACTION: If no for any of the above, qualify all results ≥ MDL associated with that Tune as estimated "J", and all non-detects associated with that Tune as "UJ".			
A.1.26	**ICP-MS Internal Standards - Form XV**			
A.1.26.1	Were the Internal Standards added to all the samples and all QC samples and calibration standards (except the Tuning Solution)?	[___]	___	___
	Were all the target analyte masses bracketed by the masses of the five internal standards?	[___]	___	___
	ACTION: If none of the Internal Standards was added to the samples, reject (R) and red-line all the associated sample data (detects & non-detects). If internal standards were used but did not cover all the analyte masses, reject (R) and red-line only the analyte results not bracketed by the internal standard masses.			
A.1.26.2	Was the intensity of an Internal Standard in each sample within 60-125% of the intensity of the same Internal Standard in the calibration blank?	[___]	___	___
	If no, was the original sample diluted two fold, Internal Standard added and the sample re-analyzed?	[___]	___	___
	Was the %RI for the two fold diluted sample within the acceptance limits (60-125%)?	[___]	___	___
	ACTION: If no for any of the above, flag detects as "J" and non-detects "UJ" of all the analytes with atomic masses between the atomic mass of the internal standard lighter			

than the affected internal standard, and the atomic mass of the internal standard heavier than the affected internal standard.

A.1.27 **Percent Solids of Sediments**

A.1.27.1 Are percent solids in sediment(s):

< 50%? ___ [___] ___

ACTION:
If yes, qualify as estimated (J) all detects and non-detects of a sample that has percent solids less than 50%(i.e.,moisture content greater than 50%).

NOTE:
Flag(J) only the sample results that were not previously flagged due to other QC criteria.

Inorganic Data Review Narrative

Case# _____ **Site:** _____ **Matrix: Soil** ____

SDG# _____ **Lab:** _____ **Water** ____

Sampling Team: _____ **Reviewer:** _____ **Other** _____

A.2.1 **Data Validation Flags**:
The following flags may have been applied in red by the data validator and must be considered by the data user.

J - This flag indicates the result qualified as **estimated**

R and Red-Line - A red-line drawn through a sample result indicates **unusable** value. The red-lined data are known to contain significant errors based on documented information and must not be used by the data user.

U - This data validation qualifier is applied to sample results ≥ MDL when associated blank is contaminated

Fully Usable Data - The results that do not carry "J" or "red-line" are fully **usable**.

A.2.2 **Laboratory Qualifiers**:
The CLP laboratory applies a contractual qualifier on all

Form I'S and the QC Form when a QC analysis is outside the control limits. These qualifiers are not applied on the Lotus or XLS spreadsheets. These qualifiers and their meanings are as follows:

N: This qualifier indicates the lack of accuracy in the reported result, and is applied when matrix spiked sample recovery is outside the control limits.

E: This qualifier indicates the the presence of interference, and is applied when the ICP serial dilution is outside the control limits.

*****: This qualifier indicate the lack of precision , and is pplied on Fom I'S and Form VI when the Lab Duplicate analysis is outside the control limits.

U: This is a concentration qualifier that laboratory applies to a non-detected result which is essentially less than the Method Detection Limit(MDL). A non-detected result of an analyte is indicated by the Contract Required Quantitation Limit (CRQL) of that analyte suffixed with "U".

J: This is also a concentration qualifier that laboratory applies to a positive result below the CRQL.

NOTE: The laboratory qualifiers are crossed out and replaced with the appropriate data validation qualifiers (J, R or U) by the data validator.

A.2.3.1 **Data Case Description**:

A.2.3.2 **CSF Audit**:

A.2.3.3 **Technical Review:**

A.2.3.4 **Contract-Problem/Non-Compliance:**

HWSS Reviewer: _____ Date:_____
Signature

Contractor Reviewer: _____ Date:_____
Signature

Verified by: _____ Date:_____
Signature

CASE #

SDG #

Contract Laboratory Program
REGION II/LABORATORY COMMUNICATION SYSTEM

Telephone Record Log

Date of Call: _____

ESAT Reviewer/Date: _____

Type of Analysis: ___**Inorganic**_____

Laboratory Name: _____

Lab Contact: _____

Call Initiated By: ___**Laboratory** _X_**Region II**

Inquiry made in reference to data for the following sample number(s):

Summary of Questions/Issues Discussed:

Summary of Resolution:

_____

Signature **Date:** _____

FIELD DUPLICATES

Sample No. **Field Duplicate No.** **Sample Matrix:**

Lab Code: **Case No. :** **SDG No.:**

% Solids Sample: **% Solids Duplicate:**

Concentration Units (ug/l or mg/kg dry weight):

	Action Limit	Sample Concentration	C	Duplicate Concentration	C	RPD	Difference	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									

					YES	NO	N/A		
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Total/Dissolved Concentrations

Lab Code **Case No.** **SDG No.** **Sample Matrix: Water**

Concentration: ug/L

ANALYTE	TOTAL	C	DISSOLVED	C	DIFFERENCE	Q	M
ALUMINUM							
ARSENIC							
BARIUM							
BERYLLIUM							
CADMIUM							
CALCIUM							
CHROMIUM							
COBALT							
COPPER							
IRON							
LEAD							
MAGNESIUM							
MAGNESE							
MERCURY							
NICKEL							

POTASSIUM							
SELENIUM							
SILVER							
SODIUM							
THALLIUM							
VANADIUM							
ZINC							
CYANIDE							

CONTRACT LABORATORY PROGRAM
CLP RAS RE-ANALYSIS REQUEST/APPROVAL RECORD

SECTION A (TO BE COMPLETED BY REGIONAL SENDING OFFICIAL)

Initiated By:

Name, Affiliation, Phone Number

_____

Case Number:_____
! OLM
! OLC
! ILM

Details of Re-Analysis Request:

! Laboratory Name /Contract Number: _____

! Affected Sample Number(s) and Fraction(s): _____

! Reason for Re-Analysis: _____

! Contract Statement of Work Citation*: _____
_____

! Comments:_____

_____

! * PROVIDE SOW CITATION THAT SUPPORTS THIS REQUEST

RE-ANALYSIS Billable ( ) Not Billable ( )

! Approved By: _____ Date: _____

Authorized Regional Sending CLP PO Signature

SECTION B (TO BE COMPLETED BY SMO)

_____

Name of SMO Contact _____ Date:_____

Date of Laboratory Notification (Verbal): _____

Re-analysis Start Date: _____ Data Due Date: _____

_____

Return completed form to:

Sample Management Office (SMO)

Distribtion: (1) CLP PO Copy (2) Regional Sending Official Copy (3) SMO File Copy (4) Laboratory Copy
Final 9/3/99

CLP DATA ASSESSMENT SUMMARY FORM (INORGANICS)

Type of Review: _____ Date:_____ Case# _____SDG#___

Site: _____ Lab Name: _____

Reviewer's Initials:_____ Number of Samples:_____

Analytes Rejected (R) Due to Exceeding Review Criteria

	Holding Time	CRQL Std	Blanks	ICS	Spike Recovery	Dup. Lab.	Dup. Field	LCS	ICP Serial Dilution	% Solids	Internal Std. ICP-MS	Tuning ICP-MS	Total Analytes	Rejection %
ICP-AES														
ICP-MS														
Mercury														
Cyanide														
Total														

Analytes Flagged (J) as Estimated Due to Exceeding Review Criteria

	Holding Time	CRQL Std	Blanks	ICS	Spike Recovery	Dup. Lab.	Dup. Field	LCS	ICP Serial Dilution	% Solids	Internal Std. ICP-MS	Tuning ICP-MS	Total Analytes	Rejection %
ICP-AES														
ICP-MS														
Mercury														
Cyanide														
Total														

APPENDIX E
OFF-SITE LABORATORY QUALITY CONTROL MEMORANDUM AND QUALITY ASSURANCE PLAN

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GUIDING PRINCIPLES

General

- The purpose of laboratory and field QC sampling and testing is to determine whether the sampling and testing process is prone to contamination, matrix effects, and/or laboratory performance problems.
- We must use the data provided to us along with reasonable assumptions as to how the data was generated.
- The quality control criteria discussed within; i.e., LCS, MS/MSD (or MS and laboratory duplicate), and surrogate spike compound recoveries must be considered in total when making a decision as to how to qualify or not qualify results.
- Organic MS/MSD samples will be spiked with the analytes listed in Table 3 of this Technical Scope of Work; LCS blank spikes must be spiked with the full analyte list.

LCS for all methods

If any LCS is outside control limits, the LCS and associated batch samples must be reprepared and reanalyzed. If the lab has a good reason to think that the exceedance is due to the measurement step only, then the LCS extract can be reanalyzed only possibly after some corrective action on the instrument. However, if the reanalysis results are not within QC acceptance criteria, then the LCS must be reprepared and reanalyzed along with all batch samples, and the results must be within QC acceptance criteria.

Surrogate Recoveries for Organic Methods

If surrogate recoveries are not within QC acceptance criteria for a field sample and QC sample surrogates are within criteria, the field sample must be reprepared and reanalyzed to confirm the exceedance. If a QC sample surrogate recovery is outside criteria, the QC sample must be reprepared and reanalyzed and the results must be acceptable.

Calibration – GC/MS

For the initial calibration, all average RRFs must be > 0.05, except for 1,4-dioxane in the 8260B analysis. If an average RRF< 0.05, corrective action (reanalysis) must be performed. If an analyte %RSD is > 90%, the initial calibration must be reanalyzed for that analyte.

For the continuing calibration, all RRFs must be > 0.05; otherwise, correction action (reanalysis) must be performed. If the %D value between the continuing calibration RRF and the initial calibration mean RRF is > 90%, the continuing calibration must be reanalyzed.

Calibration – GC Pesticides

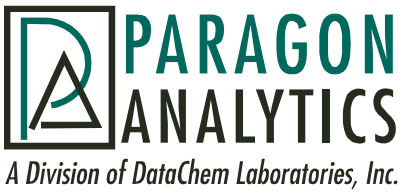
The %RSD from the initial calibration must be less than the allowable limits provided in the Region II SOP HW-44 Validating Pesticide Compounds, Organochlorine Pesticides by 8081B. The %D for each analyte in the continuing calibration must be within ± 20%. If not, the instrument must be recalibrated (5 point initial calibration).

Breakdown Standard/Dual Column Confirmation
The DDT/endrin breakdown standard must be analyzed as per Region II SOP HW-44 Validating Pesticide Compounds, Organochlorine Pesticides by 8081B. Dual column confirmation analysis must also be conducted.

Elements
For elements, the lab must run either a MS/MSD or MS/lab replicate pair with each batch. For the elements calibration, if the correlation coefficient is not > 0.995, then the calibration standards must be reanalyzed. If the continuing calibration is not within the limits provided in Region II SOP HW-2, corrective action (reanalysis) must be taken.

Laboratory Quality Assurance Plan

(LQAP)



ALS Laboratory Group, Environmental Division

– Fort Collins, CO

Note: This document is published annually. Hence, some of the information contained within may be dated. Please contact the laboratory for the most updated information.

(3/9/09 DAS)

Laboratory Quality Assurance Plan (LQAP)

Revision 12c

November 25th, 2008

ALS Laboratory Group, Environmental Division

225 Commerce Drive

Fort Collins, CO 80524

(970) 490-1511 phone

(970) 490-1522 fax

Approved by: *(see page following)*

Ken Campbell
Laboratory Director

Deb Scheib
Quality Assurance Manager

Joel Nolte
Organics Manager

Steve Workman
Radiochemistry, Inorganics Technical Manager

Summary of 2008 LQAP Changes

- All amendments made since 2007 publishing were formally incorporated.
- Minor text additions/clarifications made throughout based on auditor corrective action response.
- Discussion of secondary containment policy augmented in Section 4.9, SOP 023 retired (reference removed).
- Since SOP 300 and SOP 798 were combined upon reissuance, reference to SOP 798 was corrected in Section 7.3.
- Base policy for corrective actions to be completed within 21 calendar days of notification by the QA Department added to Section 11.
- Section 11.2 NCR process updated to reflect LIMS electronic interface.
- Citation iterations updated in Bibliography.

TABLE OF CONTENTS

1. INTRODUCTION

Paragon Analytics (Paragon) is a full service environmental and radiochemistry laboratory located in Fort Collins, Colorado. Paragon is a division of DataChem Laboratories, Inc., and as such, has sister laboratories located in Salt Lake City, Utah; Cincinnati, Ohio; and Everett, Washington. Technical operations at each facility are conducted autonomously.

Paragon performs analyses for organic, inorganic, and radiological constituents in a variety of matrices. Paragon specializes in serving the Department of Energy (DOE), Department of Defense (DoD), and architect-engineering firms. Paragon routinely provides hardcopy data packages and electronic data deliverables that are easily validated by external validators.

The management team at Paragon applies an integrated approach to quality assurance, client service, and efficient operations, that enables Paragon to produce compliant data that meet or exceed all technical and service requirements as prescribed by our clients. This Laboratory Quality Assurance Plan (LQAP) defines Paragon's quality assurance (QA) program, and communicates Paragon's goals, values and policies regarding quality, ethical conduct, data integrity, and optimized operations.

1.1 MISSION STATEMENT

A mission statement is a broad statement that is intended to capture why an organization exists and how it is to serve its shareholders, customers and employees. The mission statement is the pinnacle of what an organization is ultimately striving to achieve. *Paragon's Mission is to provide high quality analytical chemistry and radiochemistry services on time, and to maintain a stimulating workplace that provides personal growth for employees.*

1.2 VISION STATEMENT

A vision statement is a statement intended to capture the one or two things that an organization wants to achieve over the mid- to long-term. It is the integration of an articulated set of longer-range goals. It is that which is just over the horizon. *Paragon's Vision is to be recognized by our peers and clients as the premier analytical chemistry and radiochemistry laboratory in the United States*.

1.3 QUALITY POLICY

Paragon's goal is to produce data of known, documented, and appropriate quality in accordance with applicable Federal or state regulations and requirements, National Environmental Laboratory Accreditation Conference (NELAC) standards, and client-prescribed criteria.

Within this framework, Paragon performs analyses in strict accordance with promulgated methodologies, including:

- USEPA, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods;

- USEPA, Methods for Chemical Analysis of Waters and Wastes (MCAWW);
- USEPA, Methods for Determination of Metals in Environmental Samples;
- American Public Health Association (APHA), Standard Methods for the Examination of Water and Wastewater (SM);
- USEPA, Methods for Determination of Organic Compounds in Drinking Water;
- American Society for Testing and Materials (ASTM), Annual Book of ASTM Standards, Volume 11 – Water and Environmental Technology;
- American Society for Testing and Materials (ASTM), Annual Book of ASTM Standards, Volume 12 – Nuclear Energy;
- USDOE, Environmental Measurements Laboratory (EML), Procedures Manual (HASL-300);
- USEPA, Eastern Environmental Radiation Facility (EERF), Radiochemistry Procedures Manual;
- USDOE, Radiological and Environmental Sciences (RESL), Procedures Manual;
- USEPA, Prescribed Procedures for Measurement of Radioactivity in Drinking Water; and
- US, Code of Federal Regulations (40 CFR).

1.4 STATEMENT ON WASTE, ABUSE AND FRAUD

Paragon is committed to achieving our goals in the most efficient and effective manner possible, thus avoiding wasteful use of resources. This is accomplished by assuring the proper utilization of Paragon's purchased materials and equipment, and time and ability of our personnel. *Any Paragon employee who has any suggestion or concern regarding Paragon's practices, is encouraged to discuss his/her idea or question with their Department Manager, the Quality Assurance Manager, and/or the Laboratory Director*. A means of confidentially reporting concerns anonymously is also available. Grievances and allegations of unethical conduct will be fully investigated, and appropriate actions taken.

Training regarding Paragon's Waste, Abuse and Fraud policies is provided to every new staff member, and to all employees lab-wide as an annual refresher. Paragon's policies regarding waste, abuse and fraud are included in **Appendix A**.

1.5 CODE OF ETHICS AND DATA INTEGRITY STATEMENTS

Paragon is responsible for creating a work environment that enables all employees to perform their duties in an ethical manner. *It is Paragon's expectation that all employees exhibit professionalism and respect for clients and each other in all interactions and tasks.* Paragon requires that each employee abide by the following guidelines:

- Every Paragon employee is responsible for the propriety and consequences of his or her actions. Each employee shall conduct him or herself in a professional manner towards all clients, regulators, auditors, vendors, and other employees. Professional conduct relates to honesty, integrity, respect, and tolerance for cultural diversity.

- Every Paragon employee shall perform all assigned duties in accordance with Paragon's established quality assurance policies and quality control procedures that have been developed to ensure conformance with contractual and regulatory requirements.

- Paragon expects all employees to use professional judgment and to document all situations thoroughly. It is the responsibility of each Paragon employee to consult the Department Manager or Quality Assurance Manager when atypical or unusual situations occur and to disclose and document the decision-making process. Every employee must disclose any instance of noncompliance. Paragon reports all noncompliance issues affecting data to the client.

- It is the responsibility of each Paragon employee to report any suspicion of unethical conduct to the Quality Assurance Manager or the Laboratory Director.

Data integrity procedures provide assurance that a highly ethical approach to testing is a key component of all laboratory planning, training and implementation of methods. The following list provides examples of improper, unethical, or illegal practices that Paragon ***does not*** tolerate:

- Falsification of records to meet method requirements (e.g., sample records, logbooks, sample results, electronic records). This includes intentional misrepresentation of the date or time of analysis (e.g., intentionally resetting a computer system's or instrument's date and/or time to make it appear that a date/time requirement has been achieved); and unwarranted manipulation of computer software (e.g., improper background subtraction to meet ion abundance criteria for GC/MS tuning compounds).

- Improper use of manual integrations performed to meet calibration or method quality control criteria (e.g., peak shaving or peak enhancement

performed solely to meet quality control requirements).

- Selective exclusion of data to meet quality control criteria (e.g., eliminating initial calibration points without technical justification).

- Misrepresentation of quality control samples (e.g., adding surrogates or tracers after sample extraction, omitting preparation steps for quality control samples; over- or under- spiking).

- Reporting results without analyses to support the results (i.e., dry-labbing).

- Notation of matrix interference as basis for exceeding acceptance limits in interference-free matrices.

- Intentional plagiarism or willful misrepresentation of another employee's work as one's own (e.g., Initial or Continuing Demonstration of Capability study (IDOC, CDOC) or Proficiency Testing (PT) study.

Strict adherence to Paragon's Code of Ethics and Data Integrity is essential to the reputation and continued health of our business. All Paragon employees are required to acknowledge their responsibility and intent to behave in an ethical manner by attesting to the requirements described above upon joining the Paragon staff, and annually thereafter. Included in **Appendix A** are the ethics documents that every employee is required to review and attest to.

1.6 REVIEW, REVISION, DISTRIBUTION AND HIERARCHY OF QA DOCUMENTS

Current copies of pertinent quality assurance guidance documents, such as Paragon's LQAP, the NELAC standards, the US DOE Quality Systems for Analytical Services (QSAS), the US DoD Quality Systems Manual (QSM) and others, are posted to the Paragon network so that they are accessible to every employee. Laboratory Standard Operating Procedures (SOPs) and other method references are also posted to the network for lab-wide employee access. Project-specific requirements are disseminated to the laboratory via Laboratory Information Management Systems (LIMS) program specifications (discussed further below).

Paragon recognizes a hierarchy of guidance that provides for comprehensive definition, yet flexible coverage, thus enabling both overall program and site-specific needs to be met. An overview explaining this hierarchy is given below. **SOP 926** provides detailed guidance on the review, revision, and distribution of laboratory-generated controlled documents.

1.6.1 LABORATORY QUALITY ASSURANCE PLAN

The LQAP is an encompassing controlled-document that describes

Paragon's quality assurance program and policies. All systems, policies, and procedures have been developed and implemented in accordance with applicable USEPA requirements, regulations, and guidance; the current NELAC standards; and requirements set forth in various client quality assurance documents and contractual specifications. This document has been prepared in accordance with these referenced documents, as well as others, cited in the attached **Bibliography**. The LQAP is intended to provide a 'quality requirements framework', including quality control (QC) procedures to be followed in the absence of project-specific requirements (note that project-specific requirements are communicated to laboratory staff via LIMS program specifications, which are discussed subsequently).

The Quality Assurance Manager (QAM) bears primary responsibility for ensuring that the LQAP meets industry standards. Proposed revisions to the LQAP are approved by key laboratory personnel (i.e., Laboratory Director, Quality Assurance Manager, and every Technical or Department Manager). Following approval, the QAM posts the revised LQAP to the Paragon network, and distributes attestation notifications to each laboratory Department, which are returned signed to the QA Department, to document implementation of the revised LQAP. Every employee must review the LQAP upon hire and annually thereafter. Archival records of all LQAP iterations are maintained by the Quality Assurance Department.

1.6.2 STANDARD OPERATING PROCEDURES

The second kind of controlled-document in the hierarchy of quality assurance guidance are the Standard Operating Procedures (SOPs). An SOP defines the QA/QC requirements for each method and describes in detail how personnel perform procedures and evaluate data. SOPs pertaining to general practices (e.g., standards, temperature monitoring, etc.), administrative procedures (e.g., procurement of supplies and materials, etc.) and health & safety requirements (e.g., calibration and use of the hand and foot monitor), are also maintained by Paragon. It is Paragon's intent that the information contained in our SOPs are both method-compliant, and accurately reflect actual practice. *Suggestions for SOP content clarification or revision are encouraged.* Although an overall biennial publication schedule is maintained, comments received are addressed as promptly as practicable. *Where SOP directives differ from concepts discussed in the LQAP, the requirements of the SOPs supersede the requirements of the LQAP.*

Every employee must review assigned SOPs upon hire and annually thereafter. Additionally, certain key staff (e.g., Technical and Department Managers), are designated as 'primary authors', whose function is to coordinate and approve updates to the SOPs for which

they have been assigned primary responsibility. The primary author, in conjunction with the QAM, determines if it is appropriate to re-release an SOP without revision (update due date), or to revise the SOP. The primary author and QAM determine the appropriateness of comments received, and revise accordingly. All processing notifications regarding SOPs, as well as plan documents (e.g., LQAP, etc.), are generated through Paragon's SOP and Training Records database. The appropriate Technical Manager, QAM and Laboratory Director perform a final review of the SOP and provide signatures prior to the document's publication. Following approval, the QAM publishes the document and posts it to the Paragon network, and distributes attestation notifications to each laboratory Department, which are returned signed to the QA Department to document implementation of the revised SOP. Dated copies of SOPs are removed from access as new revisions become available. *Laboratory personnel may only refer to current, controlled SOPs while performing procedures.* These practices ensure that the timeframe in which specific SOP iterations were in force is traceable.

Controlled documents that are printed out for reference or review are only valid for 30 calendar days from the date printed. An embedded document header identifies the document, and directs the person printing the document to write-in the date printed, and to discard the printout within 30 days. (3/9/09 DAS)

A list of current SOPs is provided in **Appendix H**. The Quality Assurance Department manages the review, revision and controlled distribution of documents and maintains associated records.

1.6.3 LABORATORY MANAGEMENT INFORMATION SYSTEMS (LIMS) PROGRAM SPECIFICATION

The last and most specific controlled-document in this hierarchy is the LIMS program specification. The LIMS program specification is a distillation of client Quality Assurance Project Plan (QAPjP) or contractual requirements, prepared electronically by the Paragon Project Manager (PM), in collaboration with the QAM and applicable Department Managers. This custom program specification, along with the associated LIMS test code nicknames, contain directives and controls that govern testing and reporting data. The program specification is often limited in scope and addresses only those QA/QC criteria required for a specific project. *When the client's requirements differ from those stated in the SOPs and/or LQAP, the project-specific LIMS program specification requirements supersede the others.* ***It is the responsibility of all personnel who work with samples or data to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of the samples or data.***

2. LABORATORY ORGANIZATION AND RESPONSIBILITIES

This section provides an overview of Paragon's organization and defines key personnel, their responsibilities, and the lines of communication between these employees. An organization chart that illustrates reporting relationships is provided in **Appendix B**.

2.1 GENERAL REQUIREMENTS FOR LABORATORY PERSONNEL

Paragon maintains sufficient personnel to perform analytical services for our clients. Each employee must have a combination of experience and education that enables him or her to demonstrate a specific knowledge of his or her job function, and a general knowledge of laboratory operations, test methods, QA/QC procedures, and records management. *All personnel are responsible for complying with the requirements that pertain to his/her assigned duties.*

2.2 KEY PERSONNEL

Education, experience and skill requirements for these positions are addressed in the **DataChem Career Ladder** document. Functional responsibilities are further discussed below.

In the event of a temporary absence, key personnel must notify other key staff of their absence and reassign their duties to another employee who is qualified to perform the assigned duties. For example, a PM may assign another PM to cover his or her duties; a Department Manager may assign a senior chemist to cover his or her duties within the Department; and the Laboratory Director may assign a Manager to cover his or her duties.

2.2.1 LABORATORY DIRECTOR

The Laboratory Director (and/or designee) is responsible for:

- All laboratory operations, including: business functions such as marketing, sales and financial issues; technical functions such as sample control, preparation, analysis, data management; and quality assurance;
- Providing input and support to proposal processes, including interacting with the Sales, Technical and Quality Assurance staff, to ensure that the laboratory is capable of complying with client and regulatory requirements;
- Supervising all personnel through Management staff, who ensure that QA/QC procedures are being performed and that any nonconformances or discrepancies are documented and remedied properly and promptly;
- Ensuring that corrective actions relating to Findings from internal and external audits are completed in a timely fashion;
- Ensuring that the laboratory has the appropriate resources and facilities to perform analytical services;
- Ensuring that sufficient numbers of qualified personnel are employed to supervise and perform the work of the laboratory;

- Defining the minimum level of education, experience, and skills necessary for all positions in the laboratory;

- Ensuring that only those vendors and supplies that are of adequate quality are used; and

- Directing the performance of the annual Managerial Review.

2.2.2 QUALITY ASSURANCE MANAGER

The Quality Assurance Manager reports to the Laboratory Director and is independent of daily operation and production requirements. Therefore, the QAM is able to evaluate data objectively and perform assessments without production influence. *The QAM has authority to stop work if systems are sufficiently out of control to compromise the integrity of the data generated.*

The QAM shall have documented training and/or experience in QA/QC procedures; knowledge of quality systems as defined by NELAC; and a general knowledge of the analytical test methods for which data review is performed.

The QAM (and/or designee) is responsible for:

- Defining and implementing the quality system;

- Developing and maintaining a pro-active program for prevention and detection of improper, unethical, or illegal practices (e.g., single- or double-blind proficiency testing studies, electronic data audits, maintaining documents that identify appropriate and inappropriate laboratory and data manipulation practices);

- Ensuring continuous improvement of laboratory procedures via training, control charts, proficiency testing studies, internal audits, and external audits;

- Coordinating the laboratory's participation in state and Federal certification programs;

- Scheduling the review and distribution and maintaining distribution records of controlled documents, including plans (e.g., LQAP, etc.) and SOPs;

- Reviewing Requests For Proposal (RFPs) to ensure compliance with required QA/QC practices;

- Facilitating external audits;
- Overseeing or conducting internal audits of the entire operation annually (technical, system, data, electronic);
- Coordinating, preparing and approving external and internal audit responses and corrective actions;
- Managing the laboratory's participation in proficiency testing (PT) studies;
- Reviewing nonconformances and approving corrective actions;
- Reviewing and updating control chart QC limits per established procedures;
- Ensuring that Method Detection Limit (MDL) studies are performed and documented per requirements;
- Managing the reference standards used in the calibration and/or verification of support equipment (e.g., weights, thermometers, balances);
- Revising the LQAP annually in accordance with industry standards;
- Maintaining an archival system for data records; and
- Maintaining technical and quality assurance training records, including employee demonstrations of capability (DOCs).

2.2.3 HEALTH & SAFETY MANAGER/RADIATION SAFTETY OFFICER (RSO)

The Health & Safety Manager/Radiation Safety Officer (RSO) reports to the Laboratory Director. This Manager is responsible for establishing and monitoring adequate systems, procedures and training to ensure that the laboratory staff, facilities and operational activities conducted, function in a manner that minimizes employee risk of illness and injury, is compliant with all applicable regulations pertaining to matters of safety and health, and that limits the financial liability of the corporation as it relates to these matters. As RSO, this Manager is also responsible for discharging the duties and requirements prescribed by Paragon's Radioactive Materials License.

Key responsibilities of the Health & Safety Manager/RSO (and/or

designee) include:

- Ensuring that all employees have sufficient training to perform their job without unnecessary risk of illness or injury, providing health and safety, including radiation safety, training for new employees, and maintaining health and safety-related training records;

- Providing procedural guidance in the form of the Chemical Hygiene Plan (CHP), Radiation Protection Plan (RPP), Respiratory Protection Plan (ResPP), Emergency and Contingency Plan (ECP) and Health and Safety SOPs, and ensuring that these guidances are reviewed annually by laboratory staff;

- Ensuring that the laboratory facilities are maintained and operated in a safe manner, including:

    (a) Performing routine safety inspections of all operational areas;

    (b) Performing routine radiation surveys and managing the radiation dosimetry program; and

    (c) Performing personal monitoring, as indicated, for chemical and other exposures.

- Maintaining the laboratory's Colorado Radioactive Materials License and ensuring compliance with the terms of the license. Included in this responsibility are:

    (a) Procuring and managing radioactive sources and standards;

    (b) Maintaining the laboratory's radioactive materials inventory, which also includes directing prescreen analyses that provide initial characterization of potential sample radioactivity;

    (c) Overseeing permitted low level radioactive materials releases to the sanitary sewer; and

    (d) Ensuring that radioactive materials waste are transported in accordance with all Federal and state regulations, and are transferred only to facilities that possess a radioactive materials license.

2.2.4 FACILITIES/WASTE COMPLIANCE MANAGER

The Facilities/Waste Compliance Manager, reports to the Laboratory Director. This Manager is responsible for day-to-day management of the building and serves as the primary point of contact for all matters related to waste collection and disposal.

The Facilities/Waste Compliance Manager (and/or designee) is responsible for:

- Coordinating heating, ventilation, and air-conditioning (HVAC) systems operation and maintenance;
- Maintaining the uninterruptible power supply (UPS) and coordinating maintenance and repairs to the electrical system;
- Maintaining the in-house vacuum system;
- Coordinating repairs to the building (e.g., doors, locks, windows, cabinetry);
- Maintaining the building's security and fire alarm system;
- Interfacing with fire inspectors; and responding to security and fire alarms on a 24-hour basis;
- Implementing waste reduction procedures;
- Managing the accumulation of radioactive waste in the laboratory;
- Developing and maintaining Satellite Accumulation Areas (SAAs) and 90-Day Storage Areas;
- Overseeing all waste disposal operations performed by Paragon, including (1) ensuring compliance with Federal, state, and local regulations for waste handling and disposal in accordance with RCRA, TSCA, and radioactive waste disposal regulations; (2) managing hazardous waste shipments to Temporary Storage and Disposal Facilities (TSDFs); (3) managing sanitary sewer releases; and (4) managing sample archives and the return of samples and sample residues to clients;
- Training personnel on proper techniques for sample handling and waste disposal, according to standards implemented by Federal, state, and local authorities and maintaining associated

training records; and

- Supervising the Sample Receiving Department.

2.2.5 INFORMATION SYSTEMS MANAGER

The Information Systems (IS) Manager reports to the Laboratory Director. This Manager is responsible for administering the network, maintaining data recovery systems, and for managing personal computing (PC) equipment and peripherals, thus supporting instrumentation and LIMS. The IS Manager (and/or designee) is responsible for:

- Managing and maintaining the laboratory computer system. This function includes determining and purchasing appropriate hardware and verifying that its function meets intended objectives, establishing network server structure, and developing and implementing proper maintenance and backup procedures;

- Procuring, configuring and maintaining all printers and copiers;

- Serving as a technical resource on computer-related issues;

- Documenting related operating procedures through SOPs, manuals or other proprietary documentation;

- Supervising recovery of all systems in the event of a disaster;

- Along with the Laboratory Information Systems Manager, analyzing information flow in the laboratory and suggesting the most effective hardware, applications software, and/or programming changes as solutions to meet long-term customer requirements; also, implementing those changes in data acquisition and management by purchasing hardware or software, where software is not developed internally; and

- Maintaining and implementing existing and future communications systems, including all internet and telephone systems.

2.2.6 LABORATORY INFORMATION MANAGEMENT SYSTEMS MANAGER

The Laboratory Information Management Systems (LIMS) Manager reports to the Laboratory Director, and bears the primary responsibility

for the LIMS, which serves the needs of the technical, business, and management functions of the laboratory.

Key responsibilities of the LIMS Manager (and/or designee) include:

- Designing and developing information systems that relate to data capture and reporting;
- Maintaining and supporting applications that access LIMS and maintaining and supporting database back-end applications used for LIMS;
- Documenting changes and procedures through SOPs, manuals or other proprietary documentation;
- Developing software, as needed, using the appropriate tools, and per industry standard methodologies and validations;
- Overseeing and assisting with the implementation, testing and verification of upgrades made to instrument software;
- Coordinating all efforts to automate and improve electronic systems and processes throughout the laboratory;
- Developing interfaces necessary to achieve the requirements for client-specified electronic data deliverables (EDDs), and managing all deliverable formats provided to clients (hardcopy, electronic); and
- Providing training, as applicable, for all LIMS-related applications.

2.2.7 PROJECT MANAGER

Project Managers report to the Laboratory Director. *The Project Manager serves as the primary point of contact between clients and Paragon.* Each PM (and/or designee) is responsible for:

- Managing and coordinating the laboratory's performance after contract award, by defining technical and service requirements for personnel via LIMS, and interacting with clients and laboratory personnel to ensure that technical criteria and client service needs are met, including monitoring holding times (if appropriate) and deliverable deadlines, for all project sample analyses;
- Reviewing and approving any nonconformances reported by

the laboratory and notifying the client, if appropriate, and communicating with clients pro-actively to ensure that all client service and technical concerns are resolved promptly;

- Reviewing all final reports for completeness, compliance with project requirements, clerical accuracy, and reasonableness;

- Generating, as directed by prompts provided in Paragon's proprietary EDD generator, and transmitting EDDs to their clients as required; and

- Communicating to the Laboratory Director any potential need for new or improved capabilities based on clients' feedback.

2.2.8 TECHNICAL OR DEPARTMENT MANAGER

Technical and Department Managers report to the Laboratory Director. These Managers exercise day-to-day supervision of laboratory personnel, procedures, and reporting of results. They maintain technical expertise in their area of specialization (e.g., organics, inorganics, radiochemistry).

Technical Managers and Department Managers (and/or their designee) are responsible for:

- Providing technical education and training to personnel, certifying that personnel with appropriate educational and/or technical background perform all tests for which the laboratory is accredited, and providing documentation of employee capability and training to the QA Department, and ensuring that training and documentation are up to date;

- Assigning job tasks and prioritizing analyses;

- Developing and implementing a preventive maintenance program for instrumentation in their laboratory, and ensuring that all equipment is maintained, serviced, and properly calibrated;

- Monitoring QA/QC standards of performance, including ensuring that corrective actions are developed, documented, and implemented for all external and internal audit Findings, PT study failures, and other corrective actions;

- Monitoring the validity of the analyses performed and data generated in the laboratory to ensure the production of

compliant data, including, contributing to and/or overseeing data review processes;

- Reviewing and revising (if appropriate) assigned SOPs, at minimum, annually, to ensure that SOPs are compliant with promulgated methodologies and reflect current practice;

- Maintaining current, compliant MDL studies for all methods, matrices, analytes, columns, and instruments;

- Coordinating and approving the purchase of reagents, standards, glassware, and equipment that meet requirements;

- Providing input to the Laboratory Director regarding methodologies, personnel resources, software, and instrumentation; and assisting in the evaluation and/or development of new methods and technologies that improve Paragon's ability to meet clients' needs;

- Reviewing RFPs and assisting in the preparation and submission of proposals; and

- Interacting with the Quality Assurance, Information Systems, and Health and Safety Departments to ensure that the laboratory is capable of complying with client and regulatory requirements.

2.3 GENERAL TECHNICAL PERSONNEL

A chemist (analyst) or technician reports to a Technical or Department Manager. This employee performs work in accordance with Paragon's controlled documents (e.g., SOPs, LQAP, etc.) and project-specific requirements as defined by the applicable LIMS specification. *Paragon believes that quality begins at the bench.* Accordingly, these employees are key contributors to Paragon's success.

A chemist or technician is responsible for:

- Demonstrating proficiency in the analyses for which they are responsible ***before*** analyzing samples (e.g., performing acceptable Initial Demonstration of Capability, IDOC studies), and documenting this demonstration of proficiency, as well as Continuing Demonstrations of Capability (CDOCs), with the QA Department;

- Performing analyses, recording all data accurately, directly, and promptly, and interpreting and reviewing data according to established procedures;

- Performing an annual review of assigned SOPs and plan documents;
- Complying with all QA/QC requirements that pertain to their job function;
- Complying with all health, safety, and waste disposal requirements, as applicable;
- Maintaining and repairing instrumentation;
- Demonstrating good house-keeping practices;
- Disclosing all instances of nonconformances promptly and in writing using the NCR process (**SOP 928**); and
- Participating in training sessions.

3. QUALITY ASSURANCE INDICATORS AND OTHER MEASUREMENT PARAMETERS

Paragon's objective is the development and implementation of policies and procedures that provide results of known, documented, and appropriate quality. This LQAP defines general policies for the analysis, documentation, evaluation, validation, and reporting of data. Specific, detailed procedures for chain-of-custody, calibration of instruments, analysis, reporting, quality control, audits, preventative maintenance, and corrective actions, are provided in SOPs as listed in **Appendix H**.

In order to produce data of known, documented, and appropriate quality, Paragon:

- maintains an effective quality assurance program that measures and verifies laboratory performance;
- provides for a Quality Assurance Department that is independent of the operational groups and that has stop-work authority, and that has the responsibility and authority to audit the laboratory and develop and enforce corrective actions;
- evaluates technical and service requirements of all analytical services requests before accepting samples from a client/project. This evaluation includes a review of facilities, instrumentation, staffing, turnaround times, and any project-specific quality control or reporting requirements;
- provides sufficient flexibility to allow controlled changes in routine methodology in order to achieve client-specific data requirements as prescribed in client documents and contracts;
- documents initial demonstration of capability (IDOC) and continuing demonstration of capability (CDOC) for all methods according to Appendix C of

the NELAC standards;

- performs all analyses according to promulgated methods or methods developed and validated by Paragon and documented in SOPs;

- recognizes as soon as possible and discloses and corrects any factors that adversely affect data quality; and

- maintains complete records of sample submittal, raw data, laboratory performance, and completed analyses to support reported data.

3.1 DATA QUALITY INDICATORS

Data Quality Indicators (DQIs) are qualitative and quantitative statements developed by data users that specify the quality of data from field and laboratory data collection activities in order to support specific decisions or regulatory actions. The DQIs describe *what* data are needed, *why* the data are needed, and *how* the data will be used to address the problem being investigated. DQIs also establish qualitative and quantitative goals that allow the data user to determine whether the data are of sufficient quality for the intended application.

The principal DQIs are **precision**, **accuracy** (bias), **representativeness**, **completeness**, and **comparability** (i.e., the PARCC parameters). The following sections define and describe the application of these parameters. The QA/QC protocols used for the majority of analyses are adopted from SW-846 and 40 CFR methodologies, the USEPA Organics and Inorganics CLP SOWs, and various radiochemistry guidances, which contain detailed descriptions of the quality control measures routinely employed.

3.1.1 PRECISION

Precision is an expression of the reproducibility or degree of mutual agreement among independent measurements as the result of repeated application of the same process under similar conditions. Precision refers to the distribution of a set of reported values about the mean, or the closeness of agreement between individual test results obtained under prescribed conditions. Precision reflects random error and may be affected by systematic error. Precision characterizes the natural variation of the matrix and the contamination that may vary within that matrix. For chemical parameters that do not allow homogenization prior to analysis (e.g., volatile organics analysis), one must review precision values carefully.

Analytical precision is a measurement of the variability associated with duplicate or replicate analyses of the same sample in the laboratory. Analytical precision is determined by the analysis of matrix spike/matrix spike duplicates (MS/MSD), laboratory control sample

pairs (LCS/LCSD), or by unspiked duplicate samples (DUPs). Total precision is a measurement of the variability associated with the entire sampling and analysis process, and is determined by analysis of duplicate or replicate *field* samples, thus incorporating the variability introduced by both the field and laboratory operations.

Precision is independent of bias or accuracy, and reflects only the degree to which the measurements agree *with one another*, not the degree to which they agree with the true or accepted value of the parameter measured. Precision for stable chemistry analyses is typically expressed as relative percent difference (RPD), as defined below:

$$RPD(\%) = \frac{X_1 - X_2}{(X_1 + X_2)/2} \quad (100)$$

where:

RPD = Relative Percent Difference

X_1, X_2 = analyte value of sample 1 and sample 2

Precision, for radiochemical analyses, is typically measured in terms of Duplicate Error Ratio (DER), calculated as follows:

$$DER = \frac{|S - D|}{2 * \sqrt{\sigma^2{}_S + \sigma^2{}_D}}$$

where:

DER = Duplicate Error Ratio

S, D = analyte values of (S)ample and (D)uplicate

σ = One Sigma error value associated with sample result

RPDs or DERs are compared to the control limits established for the analysis method, or other quality control criteria as prescribed in the applicable LIMS program specification. Precision objectives vary per analytical method. Sample homogeneity/non-homogeneity is an important factor that influences the precision of duplicate sample results.

3.1.2 ACCURACY

Accuracy is an expression of agreement between the measured and known or accepted reference values. Accuracy is the measure of the closeness of an observed value to the "true" value (e.g., theoretical or reference value or population mean). Accuracy is influenced by random error and systematic error (bias) that occur during sampling and analytical procedures; therefore, accuracy reflects the total error associated with a measurement. A measurement is accurate when the

value reported does not differ significantly from the known concentration of the spike or standard.

Accuracy is typically measured by determining the percent recovery of known target analytes (i.e., a surrogate or matrix spike) that are spiked into a field sample or reagent water or simulated solid matrix (laboratory control sample). Surrogate recovery is reported and is used to assess method performance for each sample analyzed for volatile and semivolatile organic compounds. For organic and inorganic parameters, the stated accuracy objectives apply to spiking levels at or near the midpoint of the calibration curve. For radiochemical analyses, the spiking levels for the control spikes may vary from five to fifty times the method reporting limit.

Percent recovery is calculated as:

$$R(\%) = \frac{(C_1 - C_2)(100)}{C_3}$$

where:

R% = Spike amount recovered
C_1 = Concentration of analyte in spiked sample
C_2 = Concentration of analyte in unspiked sample
C_3 = Concentration of spike added

Acceptance limits are usually based upon established laboratory performance for similar samples. Other quality control criteria may be prescribed in the applicable LIMS program specification. Recoveries outside the established limits may indicate some assignable cause other than normal measurement error, and the need for corrective action. This corrective action may include reanalysis of the quality control sample, recalibration of the instrument, reanalysis of the affected samples in the batch, re-preparation of samples in the batch, or flagging and qualifying the data as suspect if the problem cannot be resolved. For contaminated samples, recovery of matrix spikes may depend on homogeneity, matrix interference, and dilution requirements for quantitation.

Both accuracy and precision are calculated for each batch and the associated sample results must be interpreted by considering theses specific measures. The quality assurance objectives for precision and accuracy are to achieve the quality control acceptance criteria specified in the appropriate analytical procedure.

For organic analyses, precision and accuracy are determined by using matrix spike and matrix spike duplicate samples and/or surrogate spike compounds and laboratory control samples. For inorganic analyses,

precision and accuracy are determined by using duplicate samples or matrix spike duplicate samples (precision) and matrix spike and laboratory control samples (accuracy). For radiological analyses, precision and accuracy are determined from the results of duplicate samples or matrix spike duplicate samples (precision), laboratory control sample duplicates (precision) and laboratory control samples (accuracy).

Samples identified as field blanks cannot be used for duplicate or matrix spike sample analyses.

QC limits for accuracy and precision may be developed from intra-laboratory historical data or adopted from prescribed limits required by the client. If quality control acceptance criteria do not exist for a given method, then the laboratory may establish advisory control limits derived from a minimum of four data points. Until verified by a statistically significant data population, the control limits will be considered as advisory limits only, and the laboratory will not automatically initiate reanalysis if these limits are not achieved. See Section 9.3 for further discussion of control limits and control charts.

Bias describes the systematic error of a measurement process that causes errors in one direction from the true value. Sources of bias include incomplete homogenization before subsampling and incomplete extraction of target analytes. Calibration drift, which is the nonrandom change in a measurement system over time, is another example of systematic error, and is detectable by the periodic measurement of calibration check standards. *Bias is **not** equivalent to accuracy.*

3.1.3 REPRESENTATIVENESS

Representativeness is a qualitative element. It expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition within a defined spatial and/or temporal boundary.

Sample handling protocols (e.g., holding times, storage, preservation and transportation) have been developed to preserve the representativeness of the samples. Proper documentation establishes that quality control protocols have been followed, and sample identification and integrity are ensured. *Paragon makes every attempt to ensure that the aliquots taken for analysis are homogenous and representative of the samples received.*

3.1.4 COMPARABILITY

Comparability is a qualitative expression of the confidence with which one data set can be compared to another. Comparability is achieved by:

- following established, standardized, and approved sample collection techniques and analytical methods;
- achieving holding times;
- reporting results in common units;
- using consistent detection levels; and
- reporting data according to consistent rules.

See Chapter 10 of this LQAP for further discussion of standard units typically used to report various analytical parameters.

3.1.5 COMPLETENESS

Completeness is an expression of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Completeness is the percentage of measurements that are judged to be usable (i.e., that meet project-specific requirements). Completeness goals are defined in the site sampling and analysis plan, QAPjP or contract, and vary with the size and complexity of the project. Completeness goals of 80-95% are traditionally accepted as realistic. Paragon's objective is 100% completeness for samples unaffected by matrix interferences.

It is recognized that some samples are highly contaminated with target and/or non-target compounds, which necessitate cleanups, multiple analyses, and/or extensive dilutions. In these instances, the internal QC results for a sample help to demonstrate the impact upon recoveries and detection limits due to these atypical situations.

Factors that adversely affect completeness include:

- receipt of samples in which chain-of-custody or sample integrity is compromised in some manner (e.g., broken containers, improperly preserved);
- receipt of insufficient volume to perform initial analyses or repeat analysis if initial efforts do not meet QC acceptance criteria;
- receipt of samples for which more than 50% of the holding time

has expired; and

- receipt of samples that contain high levels of contamination that can cause persistent effects on instrumentation designed for trace-level analyses.

The equation used to calculate completeness is:

$$C\% = \frac{S}{R} (100)$$

where:

C = completeness
S = number of successful analyses
R = number of requested analyses

The USEPA has established that there is a 5% probability that the results obtained for any one analyte will exceed the control limits established for the test as a result of random error, assuming the confidence interval is established at 95% (preamble to 40 CFR Part 136, Vol. 49, No. 209, October 26, 1984). As the number of compounds measured increases in a given sample, the probability for realizing statistical error also increases. The number of compounds present in various methods (e.g., GC/MS Methods SW8260B and SW8270C, ICAP Method SW6010B and Gamma Spectroscopy Method EPA 901.1), increases the probability that one or more analytes will not meet acceptance criteria, to significantly more than the 5% per analyte frequency. The number of target analytes included in these methods can be used to show that a minimum of four to seven target analytes will exceed the control limits established for these methods as a result of the statistical probability for random error. *Establishing quality control criteria that are not consistent with the measurement of the quality objectives for which they are intended is discouraged.*

3.2 TRACEABILITY

Traceability is the extent to which results can be substantiated by hard-copy documentation, electronic or computer-generated data calculations, computer software, and data generation. Traceability documentation exists in two forms: (1) that which links final numerical results to authoritative measurement standards, and (2) that which explicitly describes the history of each sample from collection to analysis. Measurement traceability is further discussed in Chapter 7 of this LQAP.

3.3 SENSITIVITY

The term sensitivity is used in a broad sense to describe the various limits that enable a laboratory to meet project-specific data quality objectives (DQOs).

These limit types include: instrument detection limit (IDL), method detection limit (MDL), method quantitation limit (MQL) or method reporting limit (RL), contract-required detection limit (CRDL), and contract-required quantitation limit (CRQL).

3.3.1 IDL AND MDL

The IDL is a minimum value that addresses the detection capability of the instrument *only*, hence IDL studies are performed on a per analyte per instrument basis. IDL studies are particularly important to metals analyses. These IDL studies must be conducted on a quarterly basis, per method requirements, or whenever there is a significant change in instrument components or reagents.

The MDL is a minimum value that addresses the detection capability for the sample preparation procedures and the instrument. Hence, Paragon performs MDL studies for each preparatory and determinative method combination, matrix, instrument, and analytical column. MDL studies are performed with a frequency that's prescribed by the method, at minimum, annually. Some Wet Chemistry methods require MDL studies to be performed every 6 months. MDL studies are also required for method validation, and whenever the basic chemistry of a procedure changes.

MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are determined from replicate analysis (minimum of seven) of a sample in a given matrix containing the analyte(s). 40 CFR Part 136 Appendix B defines the MDL is defined as:

$$MDL = t(n-1, 1-\alpha, = 0.99) \times \sigma$$

where:

σ = Standard deviation of the replicate analyses

$t(n-1, 1-\alpha, = 0.99)$ = Student's t-value appropriate to a 99% confidence level

An MDL check sample, at a concentration about half that spiked for the MDL study and approximately twice the calculated MDL, is also analyzed with the MDL study (immediately following), to demonstrate that the MDL is valid. Performance criteria is that the MDL check is acceptable if it yields a confident positive detection (i.e., all analytes in the check sample can be identified by method-specified criteria). If MDL check sample results do not support the determined MDL, appropriate corrective actions must be taken (e.g., repeat MDL check sample analysis, repeat MDL study, raise MDL).

An MDL study is not performed for radiological analyses, or any components for which spiking solutions are not available or relevant (e.g., pH, ignitability, etc.). Reporting limits for these kinds of parameters, where applicable, are established based on the laboratory's knowledge of extraction efficiency, instrument sensitivity, and experience with the procedure. **SOP 329** provides additional information about MDL studies.

Although the QA Department provides oversight, each Department Manager is responsible for ensuring that all IDL and MDL studies are conducted and documented as needed.

Results calculated between the MDL and the MQL (RL), see section following, contain a significant amount of error (approximately ±100%). Therefore, values reported between the MDL and MQL (RL) are qualified as estimated – 'J' flagged for organic parameters, 'B' flagged for inorganic parameters. Also, IDL and MDL values are based on an interference-free matrix, and cannot evaluate the effects of sample matrix on the calculated IDL or MDL. Therefore, established IDLs and MDLs may not be achievable in environmental matrices.

3.3.2 MQL, RL

Paragon defines MQL (RL) as the analyte concentration at or above which the laboratory's precision and accuracy requirements can be routinely demonstrated and achieved. The statistical error associated with this region of a calibration curve is significantly smaller than that associated with the region near the MDL. The MQL (RL) values for most analytes reported by Paragon are numbers that are approximately 3 to 5 times the values of the MDL for those analytes. It is Paragon's policy to analyze a calibration standard at or below the MQL (RL) when performing an initial calibration.

The MQL or RL is the lowest level that can be reliably measured by a laboratory with defined limits of precision and accuracy. The USEPA CLP SOW uses the terms CRDL and CRQL to describe *contractually-required* levels of reporting. These reporting terms do not describe instrument sensitivity.

3.4 MINIMUM DETECTABLE CONCENTRATION

The minimum detectable concentration (MDC) is used for radiochemical procedures and is defined as the concentration at which there is a 95% confidence that an analyte signal will be distinguishable from an analyte-free sample.

The general formula for calculating the MDC is based on calculations derived by Curie (Curie, L.A., "Limits for Qualitative Detection and Quantitative

Determination," Analytical Chemistry 40(3); pp. 586-693; 1968) and is calculated as follows:

$$MDC = \frac{(4.65\ X\ \sigma_b) + 2.71}{T * K}$$

where:

MDC = Minimum Detectable Concentration

σb = Standard deviation of the measurement background

T = Sample count time

K = Factor for incorporating efficiency, abundance, aliquot yield, ingrowth and decay, and activity conversion factors

3.5 TOTAL PROPAGATED UNCERTAINTY

Total propagated uncertainty (TPU), is a summation of the various uncertainties present in a measurement process, and is an integral part of every reported radiochemical value. TPU, reported as ±TPU, is the expressed estimated measure of the total uncertainty inherent in that reported radiochemical result.

The components of the TPU are classified as either random or systematic. Random uncertainties, also called counting uncertainties (CU), derive from the statistically random (normally distributed) nature of radioactive decay, and are estimated as the square root of the total number of counts acquired during analysis. In cases where the chemical yield is determined by the analysis of a radioactive tracer, the yield uncertainty (YU) is also a random uncertainty, and is estimated as the square root of the total number of tracer counts acquired. CU and YU are calculated in activity units to afford comparability to the sample result.

Systematic uncertainties are attributable to actual errors in the measurement of a physical quantity. For example, if a balance has an accuracy of $\pm$0.1%, the results of those gravimetric measurements are not normally distributed, but rather are assumed to be biased by that amount. Estimates of systematic uncertainties in laboratory processes are somewhat subjective, but should be supported by empirical data whenever possible. Systematic uncertainties associated with the preparation of a sample are called preparation uncertainties (PU), and are defined based on the number of volumetric and gravimetric measurements, quantitative transfers, etc. Systematic uncertainties associated with the analysis, called instrument uncertainties (IU), include biases associated with sample positioning, standard values, calibration coefficients, etc. PU and IU are typically provided as a percentage of the final result. To afford comparability to sample results, PU and IU are expressed in activity units by multiplying the percentage by the sample activity (A).

All contributions to TPU are considered to be independent of each other, and the individual contributions are combined as the square root of the sum of the squares (see equation below). The final TPU result is expressed in activity units, such as

pCi/g or pCi/L.

$$TPU = \sqrt{CU^2 + YU^2 + (A * PU)^2 + (A * IU)^2}$$

TPU is expressed as a value at a specific confidence interval. The default convention at Paragon is to provide the TPU at the 2-sigma confidence interval. This asserts approximately a 96% confidence level that the actual sample value is within the reported uncertainty range of the calculated result. **SOP 708** provides more information about the calculation and use of TPU.

3.6 QUALITY ASSURANCE PROJECT PLAN (QAPjP) EXCEPTIONS

As a result of the unknown nature of environmental samples prior to analysis, Paragon has minimal control over analytical and quality control complications that result from sample matrix conditions. These conditions may include highly concentrated samples that contain target compounds of interest and/or non-target components; high organic content (both natural and synthetic); and extremes in pH, viscosity, solubility, etc. Each of these conditions may require a different approach.

Analysis for some samples may be achieved through the use of reduced aliquot sizes. Some sample matrices may require the laboratory to use cleanup and/or dilution techniques in order to analyze the sample by the desired protocol. Unfortunately, reduction of analysis aliquot or diluting a sample necessitates raising reporting limits (RLs) or MDCs, and often adversely impacts the calculation of surrogate, tracer, and matrix spike compound recoveries.

Paragon has the responsibility to identify matrix interferences that preclude the generation of 'compliant' data. This determination may be made by demonstrating reproducibility (i.e., reanalysis of the affected sample) to show that the quality control measurement failure resulted from sample matrix conditions beyond the laboratory's control and not as a result of analytical error. For example, if the surrogate or tracer recoveries are outside of control limits, then samples may be re-extracted and/or reanalyzed. Repeated non-compliant results indicate that sample matrix probably prevented the laboratory from reporting results deemed compliant.

Analytical projects containing particularly "dirty" samples (i.e., highly contaminated with target compounds and/or matrix co-extractives) will often fail to meet pre-established completeness goals (set forth in the QAPjP), when prior site history does not reveal the matrix constituents issues. Although the laboratory performs all analytical testing and cleanup procedures by the prescribed protocols, the results obtained may not meet validation criteria as a result of elevated reporting limits or the frequency at which surrogate, internal, tracer, or matrix spike recoveries fail to meet acceptance limits. In cases where the laboratory is unable to meet quality control criteria as a result of sample

matrix complications, results that are qualified by data validation guidelines may still be useful to the end user of the data.

Paragon is committed to adhering to the method requirements and quality control procedures prescribed by our clients. Paragon strives to produce compliant data, however, uncertainties associated with environmental samples may preclude the laboratory's ability to generate fully compliant data. Paragon will not assume responsibility for conditions beyond our reasonable control, that directly impact the "validity" versus the usability of the associated analytical data generated by the laboratory.

4. SAMPLE CONTAINERS, PRESERVATION, HANDLING, HOLDING TIMES

Defining the magnitude and nature of an environmental problem, and developing an appropriate solution, requires the collection of representative samples for laboratory analysis and data evaluation. The objective of field sampling is to remove a small portion of an environment that is representative of the entire body. *Analytical methods have been standardized, but the results of analyses are only as good as the sampling protocol and the sample preservation and handling methods.* Defining sampling procedures and the quality elements applicable to environmental testing is beyond the scope of this document, and beyond the responsibility of the laboratory.

Although the laboratory is not responsible for sample collection, it is responsible for maintaining the integrity of the sample after receipt. After the sample has been collected, the constituents of the sample must remain as close as possible to the field condition (i.e., degradation must be prevented). The length of time that these constituents will remain stable is related to their character and the preservation method used. Preservation is accomplished by the addition of chemical preservatives and/or storage at a controlled temperature, and by the strict observation of prescribed maximum holding time allowances. **Appendix C** lists sample container types, preservation requirements, and holding times.

4.1 FIELD SUPPORT

Unless not required by the client, sample kits are prepared at the laboratory to provide the client with all of the sample containers, preservatives and documentation needed for the analyses needed for a project. Paragon provides shipping containers, custody documents, custody seals, clean sample bottles, labels, applicable high-purity chemical preservatives for water samples, trip blanks, and, upon request, "blue ice" packs to support field-sampling events. Hard-sided, insulated, "picnic" coolers are typically used to transport samples from the field to the laboratory. These coolers meet or exceed all protocol requirements (i.e., USDOT, USEPA, ASTM) for shipping. Paragon **SOP 205** provides further information on sample kits.

4.2 SAMPLE CONTAINERS

Paragon provides certified clean (I-Chem 300™, Eagle Pitcher Level 1, or equivalent) sample bottles for sample collection. Used sample bottles are never used by the laboratory. The Sample Receiving Department maintains certificates

of cleanliness that are provided by the vendor for all sample bottles. These certificates are provided to the client upon request. Containers are stored in clean areas, away from laboratory processes, to prevent exposure to fuels, solvents, and other contaminants.

4.3 SAMPLE PRESERVATION AND HOLDING TIMES

Paragon provides the required chemical preservatives for water samples and, upon request, "blue ice" packs, for thermal preservation during transport. Typically, high quality reagent grade chemical preservatives (i.e., acids, solutions, etc.) are added to individual sample bottles, as appropriate per method and US Department of Transportation (DOT) requirements. Only trace metals grade nitric acid is used for preservation of metals or radiochemical samples, as applicable. It is the responsibility of those collecting the samples to properly use these materials (e.g., don't rinse or overfill container such that the preservative is washed out), and to ensure that chemical preservation requirements are met, and proper preservation techniques (chilling) are performed. Holding times begin with the collection of samples and continue until analysis is complete. See **Appendix C** for a summary of container, preservation and holding time requirements specific to various analyses and matrices.

4.4 SAMPLE RECEIPT SCHEDULE

Paragon receives samples six days of the week, Monday through Saturday. Paragon requests that clients ship samples for delivery within one day of collection, and give advance notice to the laboratory regarding shipment of RUSH samples or samples with short hold time requirements. Shipping containers received at the laboratory on holidays or after business hours are placed in a walk-in refrigerator and opened on the next business day, unless other arrangements are made in advance.

4.5 CHAIN-OF-CUSTODY

Chain-of-custody (COC) documentation begins with field sampling and continues through laboratory analysis and disposal. A chain-of-custody record that identifies all individuals who handle the sample is used to establish an intact, continuous record of the physical possession, storage, and disposal of collected samples, including their aliquots, extracts or digestates. The chain-of-custody record is initiated in the field by field personnel who complete a COC form listing all samples. This form contains the following information and remains with the samples during transport:

- client project name and project location;
- field sample number/identification;
- date and time of sample collection;
- matrix;
- container type and number of containers for each sample;

- preservative;
- analysis requested;
- sampler's remarks and signature;
- signature of person relinquishing samples and date and time relinquished;
- custody seal number (if applicable); and
- designation of matrix spike/matrix spike duplicate (MS/MSD) samples (optional).

  Note that contingent upon the sample matrix and analysis to be performed, additional sample volume may need to be submitted to accommodate MS/MSD analyses.

All transfers of samples, except directly between commercial couriers, must be recorded on the chain-of-custody form via the "relinquished" and "received by" sections. All information, except signatures, should be clearly printed.

The USEPA National Enforcement Investigations Center (NEIC) defines evidence of custody as:

- in one's actual possession, or
- in one's view, after being in one's physical possession, or
- having been in one's possession and then locked or sealed to prevent tampering, or
- kept in a secure area, restricted to authorized personnel only.

To ensure that sample custody objectives of traceability are achieved for every project, the chain-of-custody initiated in the field, is continued and maintained internally throughout the laboratory per the requirements specified in **SOP 318.** Internal chain-of-custody begins with sample acceptance and login (**SOP 202**), is maintained as samples are distributed for use throughout the laboratory (further discussed in LQAP Section 4.10), and concludes with final sample disposition (i.e., return to the client or disposal). Paragon applies a unique barcode to each sample bottle received, and maintains several scanners and PCs throughout the laboratory to document and assist with sample, aliquot, extract and digestate movement throughout the facility. This electronic process is accomplished through LIMS, which retains records of all sample and fraction transactions made.

4.6 SAMPLE ACCEPTANCE POLICY

Paragon's sample acceptance policy requires that a sample meet the following conditions:

- The sample shall be completely documented (sample identification,

location, date and time of collection, collector's name, preservation type, sample type, any special remarks concerning the sample);

- The sample shall be identified by a unique identifier using durable labels completed in indelible ink;
- The sample shall be collected in adequate volume;
- The sample shall be collected in an appropriate container;
- The sample shall be delivered to the laboratory with at least one-half the holding time remaining;
- The sample shall not exceed allowed radioactivity levels; and
- The sample shall not show signs of contamination, breakage, or leakage.

Sample receipt discrepancies are documented by Sample Receiving Department personnel on the Condition of Sample Upon Receipt, Form 201 (**Appendix D**), which is forwarded to the Project Manager as part of the workorder folder. Where samples do not meet the criteria stated above, the Project Manager requests information from the client before proceeding. If the client can provide the information and, in cases of compromised sample integrity, directs the laboratory to proceed, then data acquired from the sample(s) analysis is reported and the problems noted during sample receipt are disclosed in the narrative of the final data report.

In support of the protection of employee health and of Paragon's radioactive materials license, Paragon observes prescreening protocols that designate or determine samples with radioactive content. Detailed procedures for conducting radiological survey of incoming sample packages are given in **SOP 008**, further details regarding prescreening protocols are given in **SOP 703**.

4.7 SAMPLE RECEIPT PROTOCOLS

Upon receipt of the field samples at the laboratory, personnel ensure that sample bottles are maintained according to storage requirements, and in a manner that does not contaminate the samples (see section 4.9 for further details).

Ascension numbers that increment serially each month of the year are applied as workorder number assignments. Following sample arrival and initial screen for USDOT compliance and removable radioactivity, sample receiving personnel inspect the sample and record any discrepancies using Form 201 (**Appendix D**). The following information is documented:

- client and project name, as applicable;
- presence/absence and condition of (i.e., intact, broken) custody seals on the shipping containers;
- presence/absence of chain-of-custody and completeness;

- sample condition (intact, broken, leaking);
- presence/absence of removable sample tags;
- agreement/non-agreement between the sample labels, tags, chain-of-custody, and any other client documentation;
- receipt of adequate sample volume;
- sample temperature, where applicable;
- presence/absence of headspace in VOA and ^{222}Radon vials; and
- chemical preservation, where applicable.

Sample temperature is verified upon receipt by measuring the temperature of the temperature blank (if available) or by measuring the temperature of a representative samples(s) with an infrared (IR) temperature device. See **SOP 210** for instructions and procedures related to IR temperature guns. Samples that require thermal preservation are considered acceptable if the temperature upon arrival is between just above freezing to 6ºC. Samples that require thermal preservation but are hand-delivered to the laboratory immediately after collection, may not meet the temperature requirement. If the hand-delivered sample is packed in ice, then Sample Receiving personnel record its temperature and note that the chilling process was initiated.

4.8 SAMPLE LOGIN POLICIES AND PROCEDURES

After completing sample receipt procedures, the following sample information and analytical requests are entered into LIMS under the unique workorder number assigned:

- client name, contact, address, phone number;
- Paragon Project Manager;
- date and time of sample receipt;
- unique laboratory identifier for each sample;
- sample description, including date/time of collection;
- analyses requested (LIMS calculates holding times for each analysis);
- program specification or other special instructions, if applicable; and
- due date.

In general, a group of received samples is assigned one workorder number in LIMS. Each sample container is assigned a unique Paragon identifier (barcode) that is placed on each container. This unique identification includes all samples, subsamples, and subsequent extracts and/or digestates.

See **SOPs 201 and 202** for additional information about sample login and

distribution.

4.9 SAMPLE STORAGE

Samples requiring thermal preservation are stored in designated refrigerated storage areas that are maintained just above freezing to 6ºC, centered at 4±2ºC. Freezer storage areas are maintained at freezing to ⁻20ºC, centered at ⁻15±5ºC. The temperature of refrigeration units is monitored continuously using electronic min/max thermometers and recorded each business day, near to the beginning of the work shift. If the temperature exceeds the prescribed range, then corrective action is taken and documented immediately, and the client notified, if appropriate; see **SOP 326** for further details. Directives for corrective action pertaining to catastrophic failure of cooling units (as well as laboratory ovens, etc.) are included in Paragon's Emergency and Contingency Plan (ECP).

Samples are stored away from all standards, reagents, food and other sources of contamination. Samples are stored in such a manner as to prevent cross-contamination. For example, pure product or potentially contaminated samples are tagged as "hazardous" and stored within a secured area, separate from other samples. Paragon provides designated sample storage areas according to the following parameter groups: metals, inorganics (WetChem), semivolatile organics, volatile organics, fuels, and radiochemical analyses.

Samples having suspected radioactive activity and scheduled also for stable chemical analyses are refrigerated. Samples to receive tritium analyses are refrigerated. Samples designated for radiochemistry analyses *only*, with the exception of tritium, are segregated and maintained at ambient temperature.

To effectively monitor the storage and potential contamination of volatile organic samples, Paragon observes a refrigerator blank program (detailed in **SOPs 511, 512**).

To provide for the safe containment of sample material that could be released as a result of sample container failure, all samples are stored in secondary containment bins. These secondary containment bins are of a sturdy and inert nature, and are sufficient in size to fully contain the sample(s) in the event of a spill, leak or breakage. The bin(s) may be uniquely identified (labeled) to assist in locating samples via the chain-of-custody system. The bins are thoroughly cleaned between uses.

4.10 SAMPLE ACCESS

It is Paragon's policy that neither samples nor data may be released to unauthorized personnel. In order to ensure that this policy is maintained, the laboratory facilities are maintained under controlled access and are restricted to authorized personnel only (see **SOP 132** for further details pertaining to building security).

As discussed previously in this section, Paragon personnel follow strict sample handling and internal chain-of-custody procedures to ensure the integrity of all data generated. Limited access electronic controls in LIMS further protect the validity of the data results. Samples are scanned and transacted in LIMS when they are removed from a storage area for preparation or analysis. The sample ID, analyst, date, time, and location are recorded with each transaction. Likewise, the samples are scanned and transacted in LIMS upon their return to the storage unit. Barcode scanning and LIMS transaction is also observed for the return of sample remainders to the client, and for disposal (see LQAP Section 4.13). Paragon **SOP 318** contains internal chain-of-custody details; procedures for sample return to the client are described in **SOP 027**.

4.11 SAMPLE HOMOGENIZATION AND SUBSAMPLING

Obtaining a representative aliquot of sample for testing is critical to the representativeness of the analytical results obtained. Proper subsampling techniques, particularly for solid matrices, are a component of each bench employee's technical instruction. Sample homogenization procedures prior to radiochemical analysis are prescribed in **SOP 721**. Representative subsampling procedures for stable chemistry analyses, may be discussed in individual preparatory SOPs, and additional guidance, "Subsampling Soils and Sediments", is also posted to the Paragon network for ready reference. Client-specified procedures for homogenization or aliquotting may also be defined in the applicable LIMS program specification.

4.12 SUBCONTRACTING ANALYTICAL SERVICES

Paragon strives to identify the need to subcontract specific analytical procedures during the bid response process. Analyses may also need to be subcontracted, however, in cases of emergency where the ability to meet sample holding time criteria is endangered. In these instances, Paragon compiles a list of qualified subcontract laboratories that are suitable to perform the needed analyses, then submits the list to the client for selection and approval. If NELAC certified analyses are to be subcontracted, the subcontract laboratory must also hold NELAC certification for the analyses that are to be conducted. The same concept regarding subcontract laboratory qualifications may apply for other program samples (e.g., DOD laboratory approval status is required for the analyses to be conducted in the case of DOD samples that must be subcontracted for analysis). Note that for subcontracted DOD sample analyses, the subcontract laboratory must receive project-specific approval from the DOD client before any samples are analyzed.

Paragon's Project Manager must receive permission from the client, in writing, before the subcontract laboratory can be procured and samples forwarded to the laboratory. At a minimum, the specific terms of the subcontract laboratory agreement must include:

- analytical method required (e.g., SW-846, 40 CFR, etc.);

- number and type of samples expected;
- project-specific quality control requirements;
- deliverables required (hardcopy, electronic);
- laboratory certifications required;
- price per analysis; and
- turnaround time requirements.

See **SOP 103** for guidance on evaluating a subcontract laboratory's qualifications. Detailed procedures pertaining to submitting samples to a subcontract laboratory are provided in **SOP 207**.

4.13 SAMPLE DISPOSAL

After completion of sample analysis and submission of the project report, unused portions of samples are retained by the laboratory for a minimum of 90 days from date of invoice. Samples are disposed or returned to the client according to the nature of the samples and the client's specifications. Paragon documents and retains all conditions of disposal and correspondence between all parties concerning the final disposition of the sample.

Samples, digestates, leachates, extracts, and process waste that are characterized as hazardous, radioactive, or mixed waste are disposed in accordance with Federal and state laws and regulations. Paragon maintains records to demonstrate that all disposal efforts were conducted in compliance with these laws and regulations. This documentation includes the unique sample identity, date of disposal, nature of disposal (e.g., sample depleted, sample disposed in hazardous waste facility, sample disposed in mixed waste facility, sample returned to client); and name of the individual responsible for disposal.

5. LABORATORY FACILITIES

Appendix E contains a diagram of the Paragon laboratory facility. Paragon maintains constant and consistent test conditions throughout the facility (e.g., temperature, air purification, lighting). All entrances and exits are wired to a laboratory-wide security system that is monitored continuously. Access to the laboratory area from the front offices is restricted by means of keypad locks requiring numeric security code entry. Visitors must sign in at the front desk and must be escorted at all times (some vendors are allowed access without continuous escort, in order to facilitate repairs or deliveries). Further details pertaining to building security are provided in **SOP 132**.

The following sections highlight areas of the laboratory that are involved with sample receipt, handling, preparation, and analysis of samples.

5.1 SAMPLE RECEIPT AREAS

Paragon's sample receiving area consists of a large dedicated room of more than

500 ft^2. It contains two fume hoods and radiation survey equipment to safely handle incoming radioactive and mixed waste samples. There is an outside access door to facilitate sample delivery and shipping of sample kits. Adjacent to the sample receiving area is the bottle storage room and the radioactivity prescreening lab.

5.2 SAMPLE STORAGE AREAS

Paragon's sample receiving area has a walk-in cooler and a freezer that are used for temporary storage of samples that require thermal preservation. In addition, there are several designated sample storage locations throughout the laboratory that are used to store samples scheduled for specific analyses (see section 4.9 for further details).

5.3 SAMPLE PREPARATION AREAS

The laboratory has nine sample preparation/extraction/digestion areas. These areas are divided as follows: six radiochemistry preparation laboratories; two organics extraction laboratories; and one metals digestion laboratory. The total floor space of these six laboratories is approximately 4500 ft^2.

Laboratory preparation procedures are segregated as much as possible to minimize the potential for contamination, maximize processing efficiency, and maintain analytical integrity. Rigorous cleaning of glassware (**SOPs 334** and **720**) and apparatus ensures that cross-contamination is minimized. Each laboratory area has a dedicated or locally shared HVAC system that continuously exchanges the laboratory air with filtered and conditioned outside air. There are 34 laboratory hoods in the six sample preparation areas, and each sample preparation area has at least one hood that is capable of maintaining an average face velocity of 100 feet per minute.

5.4 STANDARDS PREPARATION AREAS

A dedicated radiochemical standards preparations room, and an organics standards preparation area are maintained. Metals and inorganic standards are stored independently from sample storage areas and are prepared in their respective laboratory areas.

5.5 ANALYTICAL LABORATORIES

The Paragon facility houses a volatile organics analysis (VOAs) laboratory that is on an upper level of the building, away from all other laboratory operations. The Paragon facility also houses one general chemistry (WetChem) laboratory, two radiochemical counting rooms, a total organic carbon (TOC) laboratory area, two gas chromatograph (GC)/high performance liquid chromatography (HPLC) labs, a semivolatile organic compounds (SVOCs) laboratory, and a metals laboratory that contains separate inductively coupled plasma (ICP), mercury, and inductively coupled plasma/mass spectrometry (ICP/MS) rooms.

5.6 OTHER LABORATORY AREAS

Other areas of the Paragon facility include a tank room for compressed gasses, several waste management areas, telephone and computer storage rooms, staff offices, Reporting Group and Reports Management data processing rooms, and various scanning/reproduction and supply storage areas.

5.7 DEIONIZED WATER SYSTEM

Within the laboratory, there are two main deionized (DI) water distribution systems available for glassware cleaning, bulk reagent preparation, and general use. One system is located in the janitor's area and serves the radiochemistry side of the facility (ASTM Type II water generated). The other system is located adjacent to the metals laboratory area and serves the stable chemistry side of the facility (ASTM Type I water generated). These DI water systems are capable of continuously delivering water that meets the requirements specified for the ASTM water type, and are monitored and documented each business day to ensure that the water meets these criteria. Paragon also maintains a third treated water system that is used to support washing of stable chemistry laboratory glassware.

DI water is defined as municipal tap water that has been treated by passing it through a particulate filter, activated carbon unit, cation exchange resin, anion exchange resin, mixed bed resin, and a final "polishing" cartridge. This water contains no detectable heavy metals or inorganic compounds of interest, and is free of organic compounds of analytical interest above Paragon's routine reporting limits. Additionally, a benchtop Millipore Synergy 185™ unit is available for laboratory use should further finishing be desired.

SOP 319 provides detailed information pertaining to Paragon's DI water systems, including discussions of independent monthly testing to verify that electronic readouts of water quality are accurate, maintenance by a vendor contractor, and corrective measures to be taken should water quality degrade to below acceptable limits.

6. ANALYTICAL PROCEDURES

Paragon is capable of analyzing various matrices, including surface and groundwater, drinking water, soil, sediment, vegetation, tissue, filter and aqueous and solid wastes. Paragon does not routinely perform analyses on air (non-particulate), however, analysis of these matrices may be available through our sister laboratories. Analyses are performed using promulgated methodologies as requested by the client and their regulators, and as required by Paragon's certifying authorities. *New iterations of established methodologies are evaluated on an ongoing basis and implemented as client needs dictate.* Analytical procedures are conducted in strict adherence with SOPs that describe the preparation, analysis, review and reporting of samples. In some cases, these SOPs may also describe proprietary methods developed by Paragon and used per the client's request. A list of Paragon's analytical capabilities is presented in **Appendix C.** A list of Paragon's SOPs is provided in **Appendix H**. References for analytical procedures used are presented in the

attached **Bibliography**. Paragon also, upon request, develops and validates procedures that are more applicable to a specific client objective.

6.1 ANALYTICAL METHODS

Selection of the appropriate method is dependent upon data usage and regulatory requirements. Paragon may modify existing methods in order to:

- achieve project-specific objectives;
- incorporate modifications or improvements in analytical technology;
- address unusual matrices not covered in available methods; and
- provide analytical capabilities for an analyte for which there are no promulgated methodologies.

Paragon discloses method modifications to our clients by providing the appropriate SOP for review.

6.2 METHOD COMPLIANCE

Compliance is the proper execution of recognized, documented procedures that are either approved or required. Strict adherence to these procedures is necessary to provide data acceptable to a regulatory body of competent jurisdiction in a specific regulatory context.

Compliance is, however, separate from, but not inconsistent with, technical scientific quality. Paragon understands that the expectations of our clients commonly include the assumption that data and reports will satisfy a regulatory purpose and will be found acceptable and compliant with regulatory requirements.

6.2.1 UNDERSTANDING THE REGULATORY FRAMEWORK

Compliance is not likely to be achieved in the absence of an understanding of the regulatory framework. Upon receipt of a statement of work (SOW), Paragon attempts to ascertain, prior to accepting samples:

- what regulatory jurisdiction pertains to a project (USEPA, State Department of Health, etc.)
- within the regulatory jurisdiction, what body of regulations has primacy (RCRA, SDWA, CWA, etc.); and
- within this context, what QA/QC protocols are required (DOE, DoD -- AFCEE, NFESC, etc.).

Paragon works with our clients to achieve a mutual understanding of all

requirements and makes the following commitments:

- Paragon will proactively attempt to identify and understand the regulatory context of client's needs.
- Paragon will strive to be expert in understanding and executing the regulatory requirements for compliance.
- Paragon will ensure that we have the capabilities, resources and facilities to perform the requested analyses.
- Paragon will identify and disclose to clients instances of non-compliance in a forthright and timely fashion.

6.2.2 RESOLVING COMPLIANCE CONTRADICTIONS

Multiple regulatory jurisdictions may overlap for a specific project, which may cause uncertainty or contradictions to arise. Similarly, methods and protocols may be prescribed in a scope of work or QAPjP that either will not achieve stated or implied DQOs, or that conflict with the regulatory requirements. Paragon will attempt to detect these inconsistencies and contradictions and will disclose them to clients in a timely fashion. Paragon voluntarily accepts a responsibility to provide information to our clients; however, the primary responsibility for resolving inconsistencies with regulators remains with the client.

6.2.3 DISCLOSURE OF NON-COMPLIANCE

As previously stated, it is Paragon's policy to disclose in a forthright manner any detected non-compliance that may affect the usability of data produced by Paragon. It is not within our expertise to predict the manner in which a specific regulator or regulatory body will interpret the rules governing analysis; therefore, Paragon is unable to guarantee compliance. It is Paragon's policy that our responsibility begins with a bona-fide and competent attempt to evaluate potential compliance issues, and ends with disclosure of any findings that may enable our clients to make an informed decision.

Procedures for documenting non-compliances and applying corrective actions are given in **SOP 928**. A copy of Paragon's Nonconformance Report (NCR) is provided in **Appendix F**.

6.3 NON-STANDARD METHOD VALIDATION

When a non-promulgated method (i.e., methods other than EPA, ASTM, etc.) is required for specific projects or analytes of interest, or when the laboratory develops a procedure, the laboratory must establish the validity of the method prior to extracting or analyzing a client's samples. *Validity is established by*

meeting criteria for precision and accuracy. Method development and validation must include the following:

- Initial Demonstration of Capability (IDOC) for each analyst performing the method;
- MDL studies or MDC determination, as applicable, for every analyte, matrix, instrument, and column (if applicable);
- validated extraction and analytical criteria; and
- SOP generation and approval per established processes.

7. MEASUREMENT TRACEABILITY AND CALIBRATION

Paragon follows a well-defined calibration routine for all instruments and equipment. Calibration may be performed by laboratory personnel using certified reference materials traceable to NIST or equivalent certified materials, or by external calibration agencies or equipment manufacturers. The discussion in this section of the LQAP is general in nature because the requirements for calibration are instrument or equipment and method specific. Details of calibration procedures and requirements can be found in Paragon's standard operating procedures (SOPs), analytical methods and operations manuals.

A list of all major instrumentation available at Paragon is provided in **Appendix G**. The Quality Assurance Department maintains this list.

7.1 TRACEABILITY OF CALIBRATION

Paragon's program of calibration and/or verification and validation of equipment must ensure that, wherever possible, measurements performed by the laboratory are traceable to national standards of measurement. Paragon requests and maintains calibration certificates (e.g., weights, thermometers, balances) that demonstrate traceability to national standards of measurement. If traceability to national standards of measurement is not available or applicable, then Paragon provides evidence of correlation of results (e.g., verifying an in-line resistivity meter by reading the system's output with a conductivity meter; participating in a PT studies).

7.2 REFERENCE STANDARDS OF MEASUREMENT

Paragon uses reference standards of measurement (such as Class S weights or NIST-traceable thermometers) for calibration verification purposes only (i.e., these reference standards are not available to laboratory staff for general use). Reference standards of measurement are calibrated or verified by a qualified vendor that must provide, where possible, traceability to a national standard of measurement. Thermometer Masters are independently recertified annually, weight masters are independently recertified every five years. Certificates of vendor calibration/verification for the reference standards recertifications are maintained by the Quality Assurance Department.

The certified reference standards are then used to annually verify other measurement devices (e.g., laboratory thermometers, laboratory weight sets) in-house. The in-house verification efforts are managed by the Quality Assurance Department. All items so verified are tagged with a sticker indicating the unique identity of the device, the date of verification and the initials of the technician who performed the verification, and the date the verification is valid through. Procedures for the in-house verification of thermometers are given in **SOP 923**. Procedures for the verification of weight sets are given in **SOP 901**.

7.3 TRACEABILITY OF STANDARDS, SOLVENTS AND REAGENTS

Paragon purchases the highest quality standards, solvents, and reagents appropriate to the analytical methodologies employed. The vendor must supply a Certificate of Analysis, Certificate of Purity, or equivalent. These certificates are maintained by the Department who uses the materials.

With the exception of extraction solvents, each Department documents the date of receipt, date opened and an expiration date for all standards and reagents by labeling the original container, or certificate and/or by entering this information into Paragon's Standards and Reagents database. Because of the quantity of solvents consumed in a short time frame, solvents are labeled only with the date received.

Each Department is responsible for the preparation, documentation, storage and disposal of its chemicals. Standards preparation information is documented by entry in a Paragon's Standards and Reagents database. The following information, needed to maintain traceability of the standard, is recorded for each standard:

- date of receipt of reference standard;
- unique internal identification number and traceability to purchased stock or neat compounds, as applicable (i.e., vendor/lot numbers; unique Paragon identifier);
- date of preparation;
- name of preparer;
- amount of reference material used;
- volume/identity of reagents and solvents used;
- final volume;
- concentration;
- expiration date of the stock and prepared standards.

See **SOP 300** for additional information about standards preparation, storage, and expiration. Verification (re-verification) of radiochemical standards is also

addressed in SOP 300.

7.4 GENERAL REQUIREMENTS FOR CALIBRATION

Each calibration is dated and documented to ensure that it is traceable to the method, instrument, date of analysis, analyte, concentration, and response. Sufficient information must be documented to permit reconstruction of the calibration. Acceptance criteria for calibrations must comply with method requirements.

7.5 INSTRUMENT CALIBRATION

This section defines the essential elements of initial instrument calibration (ICAL) and continuing instrument calibration verification (CCV). These procedures ensure that the data will be of known, documented, and appropriate quality for a given application. *Samples yielding concentrations that exceed the upper limit of the calibration curve shall be diluted and reanalyzed, if possible, to bring the results within the calibrated range. Results of samples outside the known calibration range, above or below, must be reported as qualified values and discussed in the case narrative.*

Initial instrument calibration is used for quantitation and continuing instrument calibration verification is used to confirm the validity of the initial calibration. The following items are required of both initial and continuing instrument calibrations:

- The details of the instrument calibration procedures, including evaluation and acceptance criteria, and corrective measures to be taken in the event that these acceptance criteria are not met, must be included or referenced in the test method SOP.

- Sufficient raw data records must be retained to allow reconstruction of the instrument calibration (e.g., calibration date, test method, instrument, date of analysis, name of analyst, concentration of standard(s), response, response factor).

Additional essential elements of initial as well as continuing instrument calibrations are discussed below.

7.5.1 INITIAL INSTRUMENT CALIBRATION

The following items are essential elements of initial instrument calibration:

- Samples must be quantitated from the ICAL, unless the reference method states otherwise.

- The initial calibration range must consist of at least the minimum number of calibration points specified by the

reference method. If the reference method does not specify the number of calibration standards, then the minimum number is two, not including blanks or a zero standard. Exception: multi-component analytes, such as chlordane, toxaphene or Aroclors, may be analyzed using a one-point calibration, per SW-846 guidance, if so requested by the client.

- The lowest calibration standard must be above the detection limit (MDL) and at or below the RL (i.e., the method reporting limit must be within the calibrated range of the method).

- Calibration standards must include concentrations at or below the regulatory limits, if these limits are known to the laboratory.

- Criteria for the acceptance of an initial instrument calibration must be established (e.g., RSD, correlation coefficient, etc.).

- If ICAL results are outside acceptance criteria, then corrective action must be performed, and the instrument recalibrated before analyzing samples.

- Exclusion of initial calibration points without technical justification is not allowed (poor injection or power failure are valid reasons to exclude a calibration point).

- All reported target analytes and surrogates must be included in the initial calibration.

- The ICAL must be verified (see section 7.5.3) before samples can be analyzed.

7.5.2 CONTINUING INSTRUMENT CALIBRATION

A continuing calibration verification (CCV) standard must be analyzed with the frequency prescribed in the reference method, or as dictated by the applicable LIMS program specification (typically within every 12hr time period). For example:

- When an ICAL is not performed on the day of analysis, then validity of the initial calibration must be verified with an acceptable CCV prior to sample analysis.

- A CCV must be repeated at the beginning and end of each analytical sequence. (For GC/MS methods that use an internal standard, only one CCV must be analyzed before each

analytical sequence). Some methods additionally prescribe that a CCV must be analyzed after every 10 (or 20) samples analyzed.

The following items are essential elements of continuing instrument calibration:

- With the exception of multi-component analytes, all reported target analytes must be included in the continuing instrument calibration standard.
- Criteria for the acceptance of a CCV must be established (e.g., %D, %Drift, from the initial calibration).
- If the CCV results exceed acceptance criteria, then corrective actions must be performed. If routine corrective action procedures do not produce a second consecutive CCV within acceptance criteria, then a new calibration must be performed and successfully verified.

Additional aspects of calibration verification are discussed below.

7.5.3 CALIBRATION VERIFICATIONS

All ICALs must be verified with a ***second source*** standard obtained from a different manufacturer/vendor and traceable to a national standard, when available. If a different manufacturer/vendor is not available, the laboratory must request a different lot number of the standard.

In most cases, a second-source initial calibration verification (ICV) standard is analyzed immediately after the ICAL and before any samples are analyzed. However, analysis of an ICV is not required, if the continuing calibration verification (CCV) standard is from a second source.

The concentrations of the calibration verification standards must be varied within the established calibration range. At least one of the standards must fall below the middle of the calibration range. Paragon usually accomplishes this criterion by analyzing the ICV at a different and lower concentration than the CCV. Acceptance criteria for an ICV are usually the same as those for a CCV.

Sample data associated with an unacceptable calibration verification standard may be reported as qualified data in the following cases:

- When the acceptance criteria for the CCV is exceeded high (i.e., high bias), and only non-detects were determined for the

affected analyte(s) in associated samples, then those non-detects may be reported.

- When the acceptance criteria for the CCV is exceeded low (i.e., low bias), then these sample results may be reported if they exceed a maximum regulatory limit.

- When the acceptance criteria for the CCV are exceeded (high or low), and the effect on the system from previous sample analysis is substantiated (e.g., by reanalysis or sample response characteristics on a different detector), then the sample results may be reported.

Other levels of concentrations and frequencies of analysis for calibration checks (ICVs, CCVs) may be required by specific client programs. These requirements, which supercede method, SOP or LQAP requirements otherwise stated, are communicated to the laboratory staff via LIMS program specifications.

8. PREVENTIVE MAINTENANCE AND REPAIR OF EQUIPMENT

Paragon maintains an organized maintenance program that is broader than the particular instruments or devices a specific employee may operate or is familiar with. The objective of Paragon's equipment maintenance program is to provide a structure of care that prevents quality control failures and minimizes lost productivity that results from equipment malfunction or failure. Within this program are provisions for corrective actions, maintaining spare parts, and a contingency plan in the event of catastrophic failure (e.g., loss of power for a significant period of time).

See Appendix G for a comprehensive list of Paragon's equipment.

Paragon's maintenance program is based on equipment manufacturer's recommendations, operator training guidance, and other considerations (e.g., sample throughput). The established maintenance program applies to all laboratory primary instrumentation, as well as support equipment (see Section 8.6 for a definition of what constitutes support equipment). Provisions for documenting all routine and non-routine instrument equipment maintenance and repairs is also established within the maintenance program.

Responsibilities for applying Paragon's maintenance program rests with the Department that utilizes the equipment, the Quality Assurance Department bears responsibility for certain support equipment such as balances, ovens, refrigerators, freezers, and temperature measurement devices. Only authorized personnel are permitted to perform maintenance.

Culturally, Paragon makes a distinction between 'operational' and 'routine' maintenance, that external parties generally do not. Paragon considers the normal/typical things that operators do to keep the equipment functioning properly (e.g., septum replacement, reagent refill, etc.), as 'operational' maintenance, and does not generally view these tasks as routine

maintenance events that require specific documentation in a dedicated maintenance log. Paragon's view is that the fact that the equipment is performing properly and yielding acceptable QC results, evidences that these maintenance tasks were performed as needed. Paragon's maintenance system does, however, provide for attestations that this maintenance was performed, where applicable. In contrast, Paragon defines routine maintenance as those things done in-house only periodically (i.e., that are beyond what is performed as usual 'operational' maintenance), that are short of vendor repair (e.g., annual GFPC drawer evaluation).

Documentation requirements are discussed further in Section 8.4 below.

Note that Paragon does not consider 'priming', or analysis of solvent blanks, which generally get recorded in the instrument run log, as maintenance.

8.1 MAINTENANCE SCHEDULES

With the exception of certain support equipment that is maintained by the QA Department, each Department Manager is responsible for developing procedures and schedules for maintaining the equipment utilized within their Department, and for delegating specific maintenance responsibilities to employees.

In general, Paragon performs maintenance as needed (including preventive considerations). Certain aspects of routine maintenance are considered to be 'operational', and are performed each time the instrument is run. Other maintenance is performed 'periodically' (e.g., roughly monthly, contingent upon sample throughput). Each instrument operator is responsible for the performance of their own instrument, and may perform maintenance duties at their discretion. For these reasons, Paragon's culture is not one of 'scheduled' maintenance, in the traditional (calendar) sense. Consequently, although the Department Manager provides oversight, it is not necessary or practicable to create formal maintenance schedules, or to have maintenance performance synchronized within the Department.

Paragon maintains service contracts for most major analytical equipment, including gas and high-performance liquid chromatographs, mass spectrometers, liquid scintillation counters, and cold vapor atomic absorption and inductively coupled plasma spectrophotometers. Preventive maintenance is included in most of these service contracts. Service contracts that include preventive maintenance are also retained for Paragon balances and the DI water system.

8.2 SETTINGS

Paragon's equipment list (Appendix G) depicts the following information: a) the identity and type (i.e., manufacturer and model number) of equipment (including its configuration) and its software; b) the equipment's serial number or other unique identification; c) the current location; d) the date received and date placed in service (if available); and e) the condition when it was received (e.g., new, used, reconditioned).

While it is true that some settings (e.g., detector wavelength) may be stipulated in reference methods, most instrument settings are not specifically prescribed, as they are instead, dictated by acceptable outcome (e.g., peak resolution, etc.). In a similar vein, Paragon provides typical instrument settings in the associated determinative SOP, but actual settings may vary contingent upon instrument performance and contributing factors, such as ambient conditions and operator subjectivity.

For the most part (i.e., not applicable to some types of equipment), instrument configuration and settings information is captured electronically by the instrument's 'method' files. Typically there is an 'acquisition' method file and a 'quantitation' method file that together, control the manner in which the data are obtained and subsequently calculated. These instrument files are archived via established laboratory electronic backup protocols (Form 159 – IS / LIMS Policy Statement), and are retrievable, thus providing for the reconstruction of data. The utilization of proper settings is evidenced by analytical data and QC results that meet performance criteria.

8.3 TRENDS

The dominant focus of trending contained in pertinent guidance documents relates to the generation of acceptable 'at on-set' and 'continuing' method QC checks. Concurrent with these requirements, Paragon's culture for trending observation labwide consists of ensuring that acceptable instrument checks are generated, and that the system is not producing any artifacts at levels of concern, prior to analyzing sample sets.

The expertise of the operator is a major component in effective equipment operation. Experienced operators develop an intuitive sense as to how their instrument is performing. Generally this sense is not based on a specific indicator, as there may be many contributing factors to that particular indicator, but rather on an accumulation of ques (similar to those factors that would be considered during the troubleshooting process). Because this type of expertise does not lend itself well to documentation, Paragon emphasizes cross-training to ensure consistent data generation, and the retention of 'corporate knowledge'.

8.4 EQUIPMENT DOCUMENTATION REQUIREMENTS

Analysts are responsible for maintaining calibration/verification and maintenance records of all instruments and equipment involved in the creation of the analytical data they generate. Considerations of maintenance, settings and trends, and their documentation, vary widely contingent upon the type of equipment, how automated it is, and the degree of sample throughput. Documentation can be accomplished by various means, electronically and via hardcopy. For example, ICP, ICP/MS and CVAA routine maintenance is entered into the instrument's PC and printed out in the raw data header, while service contract maintenance and repair are documented in hardcover logbooks. Labwide, dedicated hardcover maintenance logbooks are assigned to each piece of major Paragon

instrumentation, however, the manner is which equipment documentation is recorded, is at the discretion of the Department Manager. It is not Paragon's intent to unify or centralize maintenance information.

Although the manner of record keeping varies, in order to provide a clear and complete history of repairs and maintenance associated with the instrument, each entry must include the following elements:

- the date of the maintenance or repair:
- the reason for the maintenance or repair (e.g., was this action taken to correct a problem or was this action routine instrument maintenance);
- a full description of the maintenance or repair conducted;
- the name of the analyst or vendor who performed the maintenance or repair;
- reference that it was verified that the equipment is operating properly before being placed back in service (SOP 317), and where this information can be found; and
- the initials of the analyst making the entry and date of entry.

Where applicable, the identity of the reference material used as an instrument check must also be recorded, and where applicable, a statement as to the calibration's expiration must also be made.

Details regarding equipment documentation are also provided in SOP 303. Note that maintenance logs are included in monthly logbook review.

Table 8.1 (Maintenance Snapshot) following provides a brief summary of laboratory equipment, an overview of associated maintenance performed, and comments regarding how associated maintenance documentation is accomplished.

8.5 CORRECTIVE ACTIONS, SPARE PARTS, CONTINGENCY PLAN

8.5.1 CORRECTIVE ACTIONS

Corrective measures for failed QC checks are given in the associated determinative SOP. General procedures for removing equipment from service and placing new or repaired equipment into service, are provided in SOP 317. Detail regarding corrective measures and repair for support equipment failures (e.g., ovens, cooling units, pipets, DI water system), are discussed in SOPs 320, 326, 321 and 319, respectively. Actions to be taken in the event of catastrophic failure are discussed in Section 8.5.3 below.

Paragon maintains service contracts (preventive maintenance, repair) for most major analytical equipment. Some equipment (particularly some support equipment) does not lend itself to repair and would likely be replaced instead, per requirements given in SOP 127.

8.5.2 SPARE PARTS

An adequate inventory of spare parts is required to minimize equipment downtime. This inventory should include those parts and supplies that:

- are subject to frequent failure;
- have limited useful lifetimes, or
- cannot be obtained in a timely manner should failure occur.

Department Managers are responsible for maintaining an adequate inventory of necessary spare parts for all major instruments and equipment items. Examples of spare parts maintained for major instrumentation include: septa, inserts, columns, tube fittings, filaments, source parts, and traps.

8.5.3 CONTINGENCY PLAN

In the event of a catastrophic instrument failure, Paragon will make every effort to analyze samples within holding times by alternate means. If the redundancy in instrumentation is insufficient to handle the affected samples, then the Department Manager will notify the Project Manager immediately. In turn, the PM will notify the client to discuss options that will ensure successful completion of the project.

Paragon will also take appropriate mitigating steps and notify the client should significant power, cooling unit, etc. failures occur that create circumstances which could adversely impact the client's sample results. An automated system is in place to notify the IS Manager and Laboratory Director should a power outage of significant duration occur. However, any employee who notes an outage or unit failure is responsible for contacting the Department Manager or Laboratory Director, who will in turn direct the necessary actions. The specific course of action taken is dependent upon the nature and extent of the failure. General procedures to be followed in the event of catastrophic failure are provided as an appendix to Paragon's Emergency and Contingency Plan (ECP).

8.6 SUPPORT EQUIPMENT

Paragon defines support equipment as all those devices which are not the primary determinative instrument defined by the analytical method, which support laboratory operations. Support equipment includes balances, ovens, refrigerators,

freezers, water baths, temperature measurement devices, and mechanical (e.g., Eppendorf ™ pipets. Per Paragon's definition, support equipment also includes: desiccators; centrifuges; vortex mixers; sonicators; homogenizers (including ball mills, riffle splitters and shatter boxes); pressure filters; vacuum pumps; zero headspace (ZHE) extractors; tumbling devices; platform shakers; water baths; chillers; heating blocks, mantles, hot and stir plates; evaporators; muffle furnaces; kilns and cleanup apparati.

Additionally, Paragon's deionized (DI) water systems (SOP 319) and health physics equipment (Appendix G) and are also considered to be support equipment.

Requirements pertaining to glassware are given in SOPs 334 and 720. Procedures for maintaining computers and other electronic devices (e.g., printers, backup devices, etc.) are developed, implemented and maintained by the IS Department (Form 159, et. al.)

Support equipment must be calibrated or verified, typically annually, within the applied range of use. NIST-traceable references must be used when available, and the results of the calibration/verification must be documented and within the specifications required of the application for which the equipment is intended.

All support equipment must be maintained in proper working order, and records must be retained to document the equipment's performance, maintenance, and repair. *Each business day, near to the beginning of the work shift, the proper functioning and calibration of the following equipment must be verified: balances, ovens, refrigerators, freezers*. Water bath temperatures must be verified each day of use. Additional monitoring must also be performed and documented, if so prescribed by a test method (e.g., recording the temperature of a water bath during digestion).

Per **SOP 321**, the volumes dispensed from mechanical pipets are verified prior to each use, as these volumes are critical measurements. Because automatic dispensing devices used to deliver solvents or reagents (e.g., for sample preservation and extractions) are not used to deliver critical volumes, these devices are exempt from daily verification.

Where necessary, in-house verifications are performed to document the capability of graduated laboratory glassware (e.g., records are on file in the Quality Assurance Department that document the capacity of the cyanide Midi-Dist sample tube glassware).

Certificates of Accuracy are acquired from the manufacturer and are retained on file within each Department for glass microliter syringes.

The following SOPs provide additional information about calibration and

Table 8.1 Maintenance Snapshot

Extractions - GPC (Gel Permeation Cleanup) Apparatus Column flow 5.0 (+/-0.1)mL/min (stipulated in SOP) SOP 641. Maintenance discussed sufficiently in SOP (adequate MeCl2 supply; proper flow rate; no leaks, all connections tight). Maintaining hardcover log.	**Extractions - Ignitability Apparatus** SOP 629. Operation and checks discussed sufficiently in SOP (Procedures). If not functioning properly, most likely replace. No maintenance log required.
Extractions Support - Kilns Desired setting given in SOP. Unit either works or doesn't. Vendor repair possible contingent upon problem, most likely replaced. No maintenance log required.	**Extractions Support - Recirculating Chillers** Setting = sufficient water flow, stated in SOP. Either works or doesn't. Vendor repair possible contingent upon problem, most likely replaced. No maintenance log required.
'Extractions Support - Lunar Lander Pressure Filter SOP 608, 609, 666. No special considerations, either works or doesn't. Most likely replace rather than repair. No maintenance log required.	**Extractions Support - Rotary Tumbler** SOPs 603, 608, 609, 666, 668. Desired setting given in SOP. Device either works or doesn't. Vendor repair contingent upon problem (replaced). No maintenance log required.
'Extractions Support - Mixer, Homogenizer No special considerations, either works or doesn't. Most likely replace rather than repair. No maintenance log required.	**Extractions Support - Sonicators** (handheld) (bath, hand-held) - SOPs 665, 673. Temperature requirement and recording directives given in SOPs, as applicable. Specific setting does not need documented (aside from temperature which is evidenced by acceptable reading, setting not critical). Maintenance log not required, unit either works or doesn't (replaced).
'Extractions Support - Nitrogen Evaporator SOPs 637, 665. Desired setting given in SOP. Unit either works or doesn't. Vendor repair not likely, replaced. No maintenance log required.	**Extractions Support - Steam Generator & Evaporator** SOPs 607, 672. Desired setting given in SOP (i.e., value open & flowing). Unit either works or doesn't. Vendor repair not likely, replaced. No maintenance log required.
Extractions Suppot - RapidVap Concentrator Various SOPs. Unit either works or doesn't. Vendor repair not likely, replaced. No maintenance log required.	**Extractions Support - Zero Headspace Extractors** SOPs 608, 669. Detailed operation/maintenance contained in SOP. Benchsheet attestation.
Metals - ICP Analyzer, Autosampler, includes ICP/MS SOPs 807, 827, 834. Maintenance tasks are discussed sufficiently in the SOPs (check gas pressures and supply; for ICP/MS, verify that cooling water for instrument is flowing; check filters on rear of instrument and vacuum monthly; check pump tubing (replace when necessary); check drainage bottle (empty if necessary). Routine maintenance is documented via run data headers, which are e-files maintained on the instrument PC. Settings are included in calibration report printout. Hardcover maintenance logs are being kept for repair documentation.	**Metals - Mercury Analyzer (CVAA)** SOP 812; does not presently contain maintenance text in Procedures Section, SOP will be revised accordingly per established publication schedule (make sure lamp life is adequate; clean window; replace Nafion cartridge as necessary; check adequate reagent supply; replace tubing, tighten fittings as necessary). Routine maintenance is documented via run data header, which is an e-file maintained on the instrument PC. Settings are included in calibration report printout. Hardcover maintenance log is being kept for repair documentation.
Organics - Gas Chromatograph, (Autosampler), Purge & Trap (includes sample heators); all detectors (including MS) GC SOPs: 402, 406, 407, 409, 424, 425, 434, 438, 444 GC/MS SOPs: 506, 525. ECDs (SOP 016 for leak/wipe tests), FPD (detector considerations), FIDs (periodic cleaning, jet replacement - indicated by instrument performance), PIDs (adequate lamp, clean window), others?. Instrument injection port and seal maintenance (liner cleaning/replacement, septum replacement, etc.); front portion of column clipped off; splitter cleaned, where applicable; check adequate gas flow and reserves (columns & detectors); replace traps (including Vocarb) as needed; use of column and trap bake cycles; tubing clean; fittings tight. Autosampler maintenance essentially means operate with adequate flushes. Maintaining maintenance logs/headers.	**Organics - TOC Analyzer, Autosampler** SOP 670. Routine maintenance discussed as Section 8.1 (check adequate gas pressure and supply; make sure 8-port valve connections are tight; check adequate reagent supply; check halogen scrubber and gas/liquid separator; check mist trap and drain if necessary). Maintaining hardcover log.

Table 8.1 Maintenance Snapshot

Organics - HPLC & Components, includes LC/MS-MS SOPs 404, 408, 439, 446, 447, 336 Maintenance discussed sufficiently in SOPs (check that eluent supply and pressure are adequate; replace column frits/guard columns/columns as necessary; all fittings tight; empty and refill HPLC water supply; replace detector lamp as necessary). Maintaining hardcover log.	
RAD - Alpha Spectrometer (towers & octetes) Operationally discussed sufficiently in SOP. Certain practices, like detector segregation (U/Th vs Am/Pu) could be considered preventive maintenance; also, use of the 'thin film' method for Polonium. Daily vacuum pressure check; weekly cleaning. Periodic maintenance provided for in established instrument training modules. Detectors are placed 'off-line' rather than repaired (either cleaned or changed out). Some repair can be done in-house (replace octet tubing, check connections), otherwise via vendor. Hardcover maintenance log is being kept. Detectors are tracked so that trend information can be ferreted out if needed.	**RAD - Liquid Scintillation Counters** SOP 704. Operationally discussed sufficiently in SOP. LSC operation is more about being optically clean. Instrument is checked annually (alignment, etc.) under service contract. In-house repair is really not applicable. Hardcover maintenance log is being kept.
RAD - Gamma Spectrometers SOP 713. Operationally discussed sufficiently in SOP. Check N2 tank and fill as necessary; hose and fittings checks; clean detectors, shields weekly. Periodic maintenance provided for in established instrument training modules. Some repair can be done in-house, otherwise maintenance is provided under contract. Hardcover log being maintained.	**RAD - Scaler w/ Lucas Cell Counter** Operationally discussed sufficiently in SOP, although a lot of expertise is involved and that expertise/knowledge is primarily obtained by demonstration, not via an operator's manual (each use, make sure cell and tubing are clean and that fittings are tight). Cells are good for 20 runs, then CCV checked. If not acceptable, run CCV again. If still not acceptable, take cell out-of-service per SOP 317. Photomultiplier is cleaned monthly. Plateau is verified annually. Periodic maintenance provided for in established instrument training modules. Hardcover log is being maintained.
RAD - Gas Flow Proportional Counter (Counting Room, PreScreen) SOP 724. Operationally discussed sufficiently in SOP (daily tank pressure check and flow to instrument). Periodic puck maintenance; planchet holder and slides cleaning also performed; provided for in established instrument training modules. Detectors are put 'off-line' rather than repaired. A drawer evaluation is conducted annually. Paragon is considering putting the GFPCs under a maintenance contract. A hardcover log is being maintained.	
RAD Support - Ball Mill SOP 336. Operation/maintenance defined sufficiently in SOP. Device either works or doesn't. Since performance doesn't vary, no maintenance log required.	**RAD Support - Riffle Splitter** SOP 336. Operation/maintenance defined sufficiently in SOP. Device either works or doesn't. Since performance doesn't vary, no maintenance log required.
RAD Support - Platform Shakers SOP 336. Operation/maintenance defined sufficiently in SOP. Device either works or doesn't. Since performance doesn't vary, no maintenance log required.	**RAD Support - Shatterbox** SOP 336. Operation/maintenance defined sufficiently in SOP. Device either works or doesn't. Since performance doesn't vary, no maintenance log required.
Support - Balances SOP 305. Vendor serviced (cleaned, certified) annually (records maintained by QA Dept.). Daily use checks (e.g., level, pan/chamber clean, etc.) and calibration verification defined in SOP (performed by Department). Logbooks (Form 301) that contain acceptance limits and corrective action directives are kept & subject to monthly review.	**Support - Ovens & Muffle Furnaces** SOP 320. Assigned verified thermometers (muffle furnaces rough-checked with thermistor). Daily performance check defined in SOP, performed by Department. Logbooks (Form 312) that contain acceptance limits and corrective action directives kept & subject to monthly review. Problems usually thermometer-related (managed by QA Dept.), when necessary, appliance vendor contacted for servicing (records maintained by Facilities or QA). Departmental staff make minor setting adjustments when necessary (documentation of setting not required, proper setting evidenced by acceptable readings). 'Return to Service' actions defined in SOP, recorded in logbook.

Table 8.1 Maintenance Snapshot

Support - Centrifuges Desired setting given in SOP, but performance not critical. Unit either works or doesn't (vendor repaired if possible, replaced).	**Support - Thermometers** (glass, electronic, IR) - SOP 923. Annual verification and records managed by QA Dept. Directives to notify QA if malfunction given in SOPs 320, 326, 210. Corrective measures, return to service discussed in SOP 923.
Support - Cooling Units (Refrigerators, Freezers) SOP 326. Assigned verified thermometers. Continuous electronic monitoring discussed in SOP. Logbooks (Form 347) that contain acceptance limits and corrective action directives kept Departmentally & subject to monthly review. Problems usually thermometer-related (managed by QA Dept.), or defrost needed (managed by Dept.). When necessary, appliance vendor contacted for servicing (records maintained by Facilities or QA). Departmental staff make minor setting adjustments when necessary (documentation of setting not required, proper setting evidenced by acceptable readings). 'Return to Service' actions defined in SOP, recorded in logbook	**Support - Vacuum Pumps** (instrument, independent) - Organic, Inorganic, RAD. Those affiliated with instruments are included in instrument maintenance practices/documentation. Potential oil change for stand-alones. Managed by Facilities. Not capital equipment. No maintenance log required.
Support - Dessicators Tight seals on unit, for indicating DrieriteTM, replace when pink (can be 'recharged'). SOP directives are sufficient.	**Support - Vortex Mixers** No real setting, technique driven (training). Device either works or doesn't. Vendor repair not likely, replaced. No maintenance log required.
Support - Heating Mantles / Hot Plates / Stir Plates Desired setting given in SOP, not critical, so long as monitored temperature can be sustained. Unit either works or doesn't. Vendor repair unlikely, replaced. No maintenance log required.	**Support - Water/Sonic Baths** Complete unit, or device on top of hot plates. Temperature requirement and recording directives given in SOPs. Specific setting does not need documented (evidenced by acceptable temperature). Should not leak. Maintenance log not required, unit either works or doesn't (vendor repaired if possible, replaced).
Support - Millipore Water System SOP 319. Monitoring (Departmental), acceptance criteria, corrective actions discussed in SOP. Context with larger resin units also discussed. Logbooks (Form 712) subject to monthly review maintained. Independent monthly check also discussed. If needed, unit repair may be attempted in-house, most likely unit would be replaced (discussed in SOP); SOP 127 requirements. Documentation of setting not required, proper setting evidenced by acceptable readings. 'Return to Service' criteria = acceptable readings must be maintained.	
WetChem / Metals - pH Meter / ISEs / Conductivity Meter SOP 1126, 1128, several others. Care & feeding of probes is adequately addressed as Procedures in SOPs. Probe/instrument manuals are listed in the SOPs Reference Section.	**WetChem - Ion Chromatograph, Autosampler** SOPs 1113, 1125. Maintenance considerations need to be added to the beginning of SOP Section 9 (check that eluent supply and pressure are adequate; replace column frits/guard columns/columns as necessary; check that gas supply and pressure are adequate; all fittings tight; empty waste container as necessary). Consider adding detector maintenance detail as well. Settings are included in calibration report printout. Instrument is not networked, still subject to IS backup protocols. Hardcover repair log is being maintained.
WetChem - Cyanide Distillation Apparatus SOP 1110. Necessary detail already in SOP.	**WetChem - UV Spectrophotometer** Various SOPs. Performance mostly involves optically clean and matched cuvettes. Sufficient operational maintenance detail is given in the SOPs. Hardcover maintenance log kept.
WetChem - Flow Injection Analyzer SOPs 1127, 1129, 1123. Sufficient operational detail in Sections 11-14 of SOP)adequate reagent supply; clean, unclogged tubing; fittings tight). Software methods stored in instrument PC, subject to IS back-up protocols (no printout). Hardcover repair log is maintained.	

verification of support equipment:

- **SOP 305** -- balance calibration and verification
- **SOP 320** -- monitoring and recording of oven temperatures
- **SOP 326 --** monitoring refrigerator and freezer temperatures.

9. QUALITY CONTROL PROCEDURES

Paragon's quality control program provides a systematic process that enables the laboratory to evaluate and control the validity of analytical results, by measuring and monitoring accuracy and precision by method and matrix; by developing control limits and using these limits to detect errors or out-of-control events; and by requiring corrective actions to prevent or minimize the recurrence of these events. Paragon observes QC procedures to ensure that sample data meet laboratory and client quality objectives.

The purpose of preparing and analyzing QC samples is to demonstrate accuracy and precision of the sample data and efficacy of the method for the target analytes being investigated. Acceptance criteria may be dictated by reference methods or by project requirements. All assessments of QC data are performed after all rounding and significant figure truncations have been performed.

For all analyses performed by Paragon, the QC concepts and samples described in the following sections are mandatory. Determinative SOPs contain a Table that summarizes the types and frequency of QC samples, acceptance criteria, and corrective actions required. Observation of maximum holding time allowance is discussed in LQAP Chapter 4.

9.1 DEFINITION OF BATCH

9.1.1 PREPARATION BATCH

A preparation batch consists of as many as 20 field samples of the same or similar matrix, that are prepared together by the same analyst(s) within a limited or continuous time period, following the same method, and using the same kind of equipment and same lots of reagents. Each batch must contain the appropriate number and kind of method control samples (e.g., MB, LCS) and matrix-specific QC samples (e.g., MS/MSD, DUP). Cleanup procedures may be included as part of the preparation batch. All field and QC samples in the batch should be subjected to the same preparation and cleanup procedures.

9.1.2 ANALYSIS BATCH

The analysis batch (or sequence) consists of samples that are analyzed together within the same or continuous time period, on the same instrument, and processed using the same calibration. Each analysis sequence must contain the appropriate number and kind of standards and samples as defined by the method. If samples from a preparation

batch are analyzed in multiple analysis batches, extended method control and matrix-specific QC samples need not be analyzed with every analysis batch.

Where no sample pre-treatment (such as extraction or digestion) is required prior to analysis (e.g., analysis of volatile organic compounds, anions analysis by ion chromatography, etc.), the preparation batch and analysis sequence are equivalent.

9.2 PREPARATION BATCH QC SAMPLES AND STANDARDS – DEFINITION AND USE

The results of quality control samples provide an estimate of accuracy and precision for the preparation and analysis steps of sample handling. The following sections describe the QC information provided by each of these analytical measurements.

9.2.1 METHOD BLANK

A method blank (MB) consists of an aliquot of well-characterized, controlled, or certified matrix (e.g., reagent water, Ottawa sand, solid reference material, boiling chips) that is processed through the entire sample preparation, cleanup, and analysis procedure. For radiochemical analyses, a suitable blank solid matrix has not been identified; therefore, reagent water is routinely used for the blank for most solid matrices. The volume or weight of the blank must be approximately equal to the sample volume or weight processed for sample analyses.

The purpose of the MB is to demonstrate that interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, are known and minimized. A method blank should not contain target analytes at or above the reporting limit, unless otherwise permitted in the method. Other maximum blank contamination control criteria may apply, as indicated in the associated LIMS program specification.

While some methods may require background correction, sample results are typically not corrected for blank contamination.

9.2.2 LABORATORY CONTROL SAMPLE

A Laboratory Control Sample (LCS) consists of an aliquot of well-characterized, controlled, certified matrix (e.g., reagent water, sand, solid reference material, Teflon^{TM} chips) that is spiked with analytes of interest and processed through the sample preparation, cleanup, and analysis procedure.

The purpose of the LCS is to provide an estimate of bias based on recovery of the compounds from the clean, controlled matrix, and to demonstrate that the laboratory is performing the method within accepted guidelines without potential non-matrix interferences.

Where sample pretreatment is not required, such as with ion chromatography or gamma spectroscopy analysis, or the analysis of volatile organic compounds, the ICV standard or other appropriate control standard may be employed as the LCS.

An LCS for methods with extensive lists of analytes that may interfere with one another may include a limited number of analytes, but the analytes included must be representative of as many analytes as is practical.

Other client-specific QC requirements may be prescribed in the applicable LIMS program specification. The requirements set forth in the LIMS program specification supercede those stated in the method, SOP or LQAP.

9.2.3 MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A matrix spike (MS) or matrix spike duplicate (MSD) is a field sample to which known concentrations of target analytes are added before the sample is processed. The purpose of MS/MSD samples is to assess the performance of the method for a particular matrix and to provide information about the sample's homogeneity. Results of the MS/MSD samples are evaluated in relation to the method QC samples to determine the effect of the matrix in regards to accuracy and precision. Sample results are not corrected for MS/MSD excursions.

To generate MS/MSD pairs for any analysis, there must be an adequate volume/weight of field sample available. Inadequate sample volumes preclude the possibility of generating this pair of QC samples. Paragon asks clients to designate the sample to be used for MS/MSD analysis to ensure that adequate sample volumes are collected.

For some analyses, changing the composition of the sample in any way invalidates the analysis to be performed (e.g., hardness, alkalinity, pH). Therefore, an MS/MSD pair cannot be generated for these analyses. Normally, duplicate sample aliquots are analyzed in order to generate an estimate of the method's precision.

Other client-specific quality control requirements may be prescribed in the applicable LIMS program specification. The requirements set forth in the LIMS program specification supercede those stated in the method, SOP or LQAP.

9.2.4 SAMPLE DUPLICATE

A sample duplicate (DUP) is a second representative portion of sample that is carried through the preparation, cleanup and analysis process. Results for the duplicate sample are compared to the initial sample analysis results as a means of evaluating precision. For organic analyses, the MS/MSDs fulfill this function. The degree of sample homogeneity directly impacts the integrity of the sample duplicate analysis.

Precision criteria for sample duplicate analyses are those prescribed in the reference method and/or SOP, unless otherwise superceded by client-specific requirements contained in the applicable LIMS program specification.

9.2.5 SURROGATES

Surrogates are organic compounds that are similar to the target analytes, but are unlikely to be present in actual field samples. They are introduced into all field and QC samples in a batch prior to sample preparation, and provide an estimate of bias based on recovery of similar compounds, for a given extraction technique and analysis method combination. Sample results are not corrected for surrogate recoveries.

Acceptance criteria for surrogates are those prescribed in the reference method and/or SOP, unless otherwise superceded by client-specific requirements contained in the applicable LIMS program specification.

9.2.6 CHEMICAL YIELD MONITORS OR ISOTOPIC TRACERS

Chemical yield monitors are used in radiochemical analyses and provide information similar to the surrogate spikes discussed above. The primary difference between a chemical yield monitor and a surrogate is that sample results are corrected for chemical yield recoveries and not corrected for surrogate recoveries. A chemical yield monitor is a substance that has similar chemical characteristics as the parameter being measured. It is introduced into all field and QC samples in a batch during the preparation procedure. Chemical yield monitors provide information regarding the performance of a method on a sample-by-sample basis.

Chemical yield monitors are evaluated against established laboratory control limits. These Paragon default control limits may be superceded by other quality control criteria specified in the applicable LIMS program specification.

9.3 CONTROL CHARTS

Control charts are a tool that can assist the laboratory in evaluating method control and assessing trends. Control charts can clarify the routine performance expectations for a method, and can give warning before a measurement system drifts into an out-of-control situation. Information such as radiochemical calibration parameters, results of daily efficiency checks, etc. can be documented in control charts. Accuracy control charts, discussed further below, that contain method LCS (and surrogate, as applicable) performance information, are managed through LIMS. Although the QAM is responsible for periodically (at minimum, semi-annually), reviewing the control-charted LCS information, and adjusting established QC limits as appropriate or necessary, this control-charted LCS information is accessible to *all* bench personnel through LIMS.

Further discussions of control charts and control limits and other considerations such as outlier rejection and trend evaluation follow below.

9.3.1 ACCURACY CONTROL CHARTS

Accuracy (recovery) for a batch can be evaluated by plotting the individual percent recovery points for analytes on a control chart and comparing the values against the current control limits. If the spike recovery values for the current analytical batch meets the acceptance criteria for that method, then the data point (and batch) are accepted.

Accuracy control charts are generally maintained for each method that utilizes an LCS. For methods that cannot use LCS samples (e.g., pH, flashpoint, conductivity), other tools are used to assess method control. If fewer than 20 data points for a method, matrix, and analyte combination are acquired, then control charts yield scant information.

9.3.2 CONTROL LIMITS

Control limits for each controlled analyte are calculated, and can be updated, using Paragon's LIMS. The recovery values from all data processed within a specified date range, are used to calculate the control limits and compile the control chart.

The upper and lower control limits of the control chart are designated as the value equal to the average recovery plus or minus three times the standard deviation (i.e., 99% confidence interval).

The upper and lower warning limits for the control chart are designated as the value equal to the average recovery plus or minus two times the standard deviation (i.e., 95% confidence interval).

The average recovery, standard deviation, minimum value, maximum value, and population are displayed on each control chart.

Control limits are updated as needed (e.g., acquisition of a sufficient number of data points to establish meaningful control limits for a newly implemented method; if deemed appropriate as a result of a corrective action investigation; etc.). The frequency with which control limits are updated may vary for different methods. Generally, intra-laboratory historical control limits are not updated more than once per year.

9.3.3 OUTLIER REJECTION

For the generation of control charts, and other quality control data that monitor the laboratory's performance, it is essential to prevent spurious or erroneous data from being incorporated. It may be necessary to reject data as an outlier to prevent an adverse effect on the values being calculated. In every case, the cause of the outlier rejection must be clearly understood before any data point is manually rejected.

For the purposes of statistically determining whether a data point is an outlier or not, Paragon may use the procedures discussed in the Dixon Rank Sum Test or the Grubbs Test. If a data point is determined to be an outlier, it will not be incorporated into the dataset when updating QC limits.

9.3.4 TREND EVALUATION

Trend analysis techniques can be applied to control charts as a preventive tool to help indicate conditions that could cause an analysis to become out of control. In evaluating control charts, a trend is recognized if one or more of the following situations exist:

- A series of seven successive points occur on the same side of the mean;
- A series of five successive points occur going in the same direction;
- Two consecutive points occur between the warning and control limits;
- A single value occurs outside of control limits.

Corrective action investigation should be employed for every trend identified. Items to be considered upon investigation may include, but are not limited to, the following:

- Has there been a change in instrumentation or personnel?
- Has instrument maintenance been properly performed?

- What conditions have changed since the trend began?
- Have standard or spike solutions changed?

9.4 SECOND COLUMN OR SECOND DETECTOR CONFIRMATION

Second column or detector confirmation is performed for several GC and HPLC methods. Whenever two dissimilar chromatography columns or two detectors of a different nature are available for a given method, the laboratory performs second column or second detector confirmation analysis to confirm the identity of target analytes in field samples. When second column analysis is performed for any chromatography technique, the following policies apply:

- Every attempt will be made to calibrate the second (confirmatory) column in the same manner as the quantitative (primary) column. The same initial and continuing calibration standards will be analyzed on the confirmation column in the same manner as the quantitation column. The purpose of this dual calibration requirement is to allow the possibility of reporting quantitative results from the confirmation column if interferences on the primary column prevent accurate target analyte quantitation.

- For chromatographic techniques, the determination of target analytes in a sample depends solely on peak retention times observed in both primary and secondary column chromatograms. If target analyte peaks are present at the proper retention times in both confirmation and quantitation column chromatograms at levels above the MDL, then Paragon considers this analyte to be confirmed.

- In general, Paragon reports the higher value of the two columns per SW8000 guidance (e.g., 8011, 8081, 8082, 8141, 8151, 8021). It is also Paragon's policy to report the higher value of the two columns for other EPA methods (e.g., 608, 615).

  If no interferences are present, and an analyte's value from either the primary or secondary column is greater than the reporting limit but between the MDL and the reporting limit on the other column, then Paragon reports the higher value that is greater than the reporting limit for that analyte.

- Paragon customarily reports the value from the primary column for methods SW8330 and SW8332. Co-elutions or interferences are frequently observed on the secondary column for these HPLC methods.

- Other reporting rules may apply as dictated in the applicable LIMS program specification. The rules of the LIMS program specification

supercede standard Paragon policy.

9.5 MANUAL RE-INTEGRATION POLICIES AND PROCEDURES

Many data collection systems allow the analyst to reprocess data, thereby allowing for the manual re-integration of analyte peaks. Paragon makes every attempt to optimize peak integration parameters; however, manual reprocessing of data must be performed to correct a data system's integration error (e.g., incorrect or missed peak assignment, over- or under-integration of area). Manual re-integrations may not be performed solely to meet initial or continuing calibration criteria or any QC criteria (e.g., tuning, or surrogate or spiking compound recovery).

Whenever a manual integration is performed, the analyst performing this process must include a hardcopy of the original and re-integrated peak in the final data report. In addition, the analyst must initial and date the re-integrated page and document the reason for re-integration on the printout. The re-integration must be documented in the case narrative.

Further details regarding manual integration procedures are given in **SOP 939**.

10. DATA REDUCTION, VALIDATION AND REPORTING

Data transfer and reduction are essential functions in summarizing information to support conclusions. It is essential that these processes are performed accurately and are followed by multiple reviews before data are submitted to the client. All analytical data generated by Paragon are extensively reviewed for accuracy and completeness. The data validation process consists of data generation, reduction, and multiple levels of review, as described below.

10.1 DOCUMENTATION OF RAW DATA

Where possible, raw data are captured and processed electronically using verified software programs (see **SOPs 709 and 1400** for further information regarding software verification).

To facilitate manual documentation of raw data (where suitable LIMS benchsheet interfaces do not yet exist), Paragon creates custom logbooks comprised of forms or benchsheets that are tailored to contain the information required to adequately document the process being performed, and the associated data. The Quality Assurance Department controls these forms and benchsheets, and issues bound and paginated logbooks to the laboratory as needed via controlled distribution.

As applicable, hardcover, bound laboratory notebooks (most frequently used for instrument maintenance logs or Project Manager notebooks) are also issued via controlled distribution to laboratory staff as needed.

The manually recorded raw data are entered into the laboratory logbook directly, promptly, and legibly in indelible ink. All raw data entries must, at a minimum, contain the following information:

- the initials of the individual who performed the process;
- the date the process was performed;
- the methodology used; and
- the identity of all samples or standard solutions that were employed in carrying out the process.

Raw data must be maintained as part of the laboratory's records. Raw data not only includes instrument outputs, but sample preparation, standard materials documentation, and equipment maintenance information as well. Raw data may be archived electronically or as hardcopy.

10.2 CORRECTION OF ERRORS IN DOCUMENTS

During the course of processing and reviewing sample preparations and analysis results, it may be necessary to correct documentation errors. Detailed requirements for the correction of manual documentation errors are prescribed in **SOP 303**; the correction of electronic information is governed by LIMS controls and audit trails. In summary, manual entries may not be obliterated by erasure, use of correction fluid, or other means. In order to maintain the integrity of the documentation generated by the laboratory, changes to hardcopy documentation must be made in the following manner:

- A single line must be struck through the error so that the original text remains legible;
- As applicable, a corrected entry must be made adjacent to the error; and
- The person making the change must initial and date the corrective entry.

If not clearly evident, the reason for the data change must be indicated.

10.3 DATA REDUCTION

Paragon's analysts perform data reduction. This process consists of interpreting instrument results and verifying calculated concentrations in samples from the raw data. The complexity of the data reduction is dependent on the specific analytical method and the number of discrete operations involved in obtaining a measurement (e.g., digestions, dilutions, cleanups, concentrations). The analyst calculates the final reportable values from raw data or enters all necessary raw data into the LIMS so that the LIMS can calculate the final reportable values.

Data are reduced according to protocols described in SOPs and method-specific review checklists. Computer software used for data reduction is validated before use and verified regularly by manual calculations. All information used in calculation is recorded in order to facilitate reconstruction of the final results (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, sample response, and blank or background-correction protocols). Information about the preparation of the samples is maintained in order to facilitate reconstruction of the final results (e.g., weight or volume, percent moisture for solids, extract volume, dilution factor).

Copies of all raw data and the calculations used to generate the final results, as recorded in hardbound laboratory notebooks, spreadsheets, electronic data files and LIMS record files, are retained in the project file to allow reconstruction of the data reduction process.

10.4 REPORTING OF SAMPLE RESULTS

Sample results are reported either on an "as-received" basis, or in units of dry-weight measure. The number of significant figures reported is consistent with the limits of uncertainty inherent to the analytical method. In most cases, results are reported to no more than two or three significant figures. Analytical problems, and/or any modifications of referenced methods are noted in the data package case narrative.

Standard units appropriate to the analytical method are used to report all sample results. Measurements for radiochemical analyses are reported in units of activity such as:

- picocuries per liter (pCi/L), aqueous; or picocuries per gram (pCi/g), solid matrix samples.
- disintegrations per minute per liter (dpm/L) or disintegrations per minute per gram (dpm/g).
- Becquerels per liter (Bq/L) or Becquerels per gram (Bq/g).

It should be noted that one (1) Curie is equal to 2.22×10^{12} dpm; and is also equal to 3.7×10^{10} Bq.

Standard units for inorganic and organic analyses are units of mass per volume (aqueous samples), or mass per weight (solid matrix samples). For example, Wet Chemistry parameters such as hardness, total organic carbon (TOC), etc., are typically reported in milligrams per liter (mg/L) or milligrams per kilogram (mg/kg). Metals results for liquid samples may be reported as mg/L or as micrograms per liter (µg/L). Some methods have specific reporting units mandated by their analysis technique. For example, pH is reported as pH units, and specific conductance is reported as milli-Siemens (mmho/cm) or micro-Siemens (µmho/cm).

10.5 DATA REVIEW

Paragon employs multiple levels of data review. All data generated and reduced follow review protocols specified in laboratory SOPs (such as **SOPs 052** and **715**), and method-specific checklists. The preparatory technician and analyst who generates the analytical data perform a **Level 1** review of the data for correctness and completeness. This data review verifies that:

- the appropriate SOPs have been followed;
- any special sample preparation or analytical requirements that were communicated to the laboratory via the LIMS program specification have been met;
- all sample preparation information is correct and complete;
- all analysis information is correct and complete;
- QC samples meet criteria for frequency, accuracy and precision;
- all calculations, conversions, and data transfers are accurate;
- all documentation is present and complete, including benchsheets and/or run logs, any applicable NCRs, and documentation and presentation of manual integrations per SOP 939, as applicable.

Procedures for handling unacceptable data are discussed subsequently (LQAP Section 10.6).

Following completion of the Level 1 Review, the analyst then forwards the data to the Department Manager or another qualified reviewer whose function is to provide an independent **Level 2** review of the data. In addition to the elements evaluated in the Level 1 review described above, the Level 2 reviewer verifies that:

- the calibration data are scientifically sound, appropriate to the method, and completely documented;
- qualitative identification of target analytes is correct;
- quantitative results are correct.

The Level 2 reviewer selects a sample and verifies it to the benchsheet. If no errors are found, then the review is considered complete. If any problems are discovered, then additional samples are verified to the benchsheet with the process continuing until no additional errors are found or until the data package has been reviewed in its entirety. The Level 2 review is documented by recording

the date and initials of the reviewer on the checklist employed. This sign-off signifies that the data are approved for release and a final report is prepared.

Once the final report is prepared, an additional overall technical review is performed before it is routed to the Project Manager for a **Level 3** review. The intent of this review is to verify that the report is complete and that the data meet the overall objectives of the project.

Each step of the review process involves evaluation of data quality based on both the results of the QC data and the professional judgment of those conducting the analysis and/or review. This application of technical knowledge and experience to the evaluation of the data is essential in ensuring that data produced are consistently of known, documented, and appropriate quality.

10.6 PROCEDURES FOR HANDLING UNACCEPTABLE DATA

All QC information is recorded in the same format, with the same units, as that of the associated sample results. It is the analyst's responsibility to evaluate QC data against applicable prescribed limits. When an analysis of a QC sample (e.g., MB, LCS, CCV, etc.), indicates that the associated samples do not meet requirements, the analyst must immediately notify the Department Manager. The Department Manager then consults with the PM (and QAM, as applicable) to determine whether or not the affected samples must be re-prepped and/or re-analyzed, and/or if specific corrective action needs to be taken before additional analysis may proceed. A Nonconformance Report (NCR) as discussed in Chapter 11 of this LQAP, is initiated per **SOP 928**, as applicable. If the non-compliant data cannot be corrected, then the affected results must be flagged as discussed below, and the discrepancy disclosed in the data package case narrative. The completed NCR Form is included in the data report.

10.7 DATA REPORTING

Data reports contain final sample results, the methods of analysis used and limits of detection, and QC data. The extent of supportive data included (e.g., benchsheets, run logs, calibration data, instrument raw data printouts, etc.), is contingent upon the type of report contracted by the client.

Results of subcontracted data are clearly indicated as subcontract laboratory results when incorporated into the final data package report.

10.7.1 FACSIMILE OR IMAGED REPORTS

For projects that require rapid turnaround of sample analysis results, the laboratory may provide a facsimile or imaged e-mail attachment to the client, followed by the full data report at a later date. If the analysis results provided by facsimile or imaged e-mail attachment have undergone the same review processes followed for final data packages, then this forwarded report indicates that the sample analysis results are

final. However, if the accelerated turnaround time requirements preclude a full review/validation of the sample data, then the report is marked as "PRELIMINARY" to indicate that results may change as the review process is completed.

10.7.2 HARDCOPY DATA PACKAGES

The format and content of a data report is dependent upon project specifications, and it is beyond the scope of this document to describe project-specific report requirements. In the absence of client-specified data package deliverables, the following sections describe the items that must be included in all data reports.

10.7.2.1 COVER LETTER

Items contained in the cover letter include:

- the client's name and address;
- Paragon's name and address, name of contact and telephone number;
- a tabular presentation of field/client sample ID, Paragon Sample ID, date received, matrix, and date collected. This item is typically presented as an attachment, the Sample Cross Reference Table;
- a list of each analysis performed and total number of pages for each analytical report;
- identification of all test data provided by a subcontract laboratory;
- a discussion of previously submitted or partial reports that pertain to the samples discussed in the current report; and
- the signature of Paragon's Project Manager or designee.

10.7.2.2 REPORT FORMAT

Analysis reports are presented in tabular format, and consistent significant figures and units of measurement are used. The following information is included in each report:

- laboratory name, client name, project name and/or number;
- client/field sample ID and Paragon sample ID;

- date of sample receipt, date and time of sample collection, and date/time of sample preparation and/or analysis;
- sample matrix;
- reporting units and identification of whether the sample results are reported on an "as-received" or dry weight basis;
- method reference for the parameter analyzed and method reporting limits;
- identification of numerical results with values below the method reporting limit;
- case narrative that identifies test methods, describes any deviation from the method or contractual requirements, additions or exceptions to the SOP, and discloses any conditions that may affect the quality of the results;
- identification of sample results that did not meet sample acceptance criteria;
- footnotes or qualifiers referenced to specific data (as applicable) and explanations or keys to flags and abbreviations used;
- surrogate and tracer recoveries, where applicable;
- where applicable, a statement of the estimated uncertainty of the test result; and
- a signature and title, or equivalent electronic identification, of the personnel who accepts responsibility for the content of the report, and the date of issue.

If a report is reissued, the amendments must clearly state that the report is reissued. The cover letter and case narrative must describe why the report has been reissued and which sample results have been reissued.

10.7.2.3 QC REPORTS

Each final report includes QC reports that summarize results from the associated LCS, MB, and matrix QC samples. Additional QC samples may be prepared and reported to comply with project-specific requirements.

10.7.2.4 DATA QUALIFIERS – FLAGGING CODES

Whenever the data quality objectives of the LQAP are not met, the associated sample results must be flagged with the appropriate flagging codes. These codes are applied only in the event that the laboratory cannot generate (through reanalysis) fully compliant data. If sample values are reported outside the calibration range of the method or unreliable interferences exist in the sample, then descriptive codes are applied to the result.

Data qualifiers are added by the laboratory prior to reporting the analysis results. The laboratory appends data qualifiers to each environmental field sample based on an evaluation of all available QC information (e.g., MS/MSD samples, laboratory blanks, LCSs, calibration verification standards, etc.). Analytical batch comments are added to the narrative section of each data report to explain any nonconformance or other issues.

Other flagging practices may be observed if so dictated by the applicable LIMS program specification.

10.7.3 ELECTRONIC DATA DELIVERABLES (EDDS)

The electronic data deliverables generated by the laboratory are project-specific and are produced in a format specified by the client. *Information presented in corresponding fields of the hardcopy report and EDD are identical as both are generated from LIMS.* Before submitting the EDD file, the Project Manager or designee verifies that the EDD is complete and meets the client's format requirements. All EDDs are submitted to the client on computer disks or are transmitted electronically.

10.8 RECORDS AND DATA STORAGE

Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussion concerning laboratory results. These records, particularly those that are anticipated to be used as evidentiary data, provide the historical evidence needed for later review and evaluation. Records must be legible, identifiable, and retrievable. They must be protected against damage, deterioration, fire, theft, vermin, and loss. Though only 5-year retention is required by NELAC, Paragon retains all records for a minimum of seven (7) years, or as otherwise specified per the client's contract.

Laboratory records include the following kinds of documentation:

- personnel qualifications, experience, and training;

- correspondence between Paragon and clients;
- quality assurance records (e.g., retired SOPs and LQAPs, PT study results, internal and external audit reports and responses);
- contents of laboratory logbooks;
- equipment maintenance records;
- traceability of standards, solvents and reagents;
- instrument checks and calibrations;
- raw data;
- final data reports; and
- sample management records (e.g., sample login, field and internal chain-of-custody, storage, disposal).

10.8.1 ELECTRONIC RECORDS

Paragon employs a multi-level system that addresses both the frequent backup of sample results (in LIMS) and the periodic backup of raw data (from both networked and non-networked instruments). Additionally, the software that Paragon uses for these backups, contains a disaster recovery module that allows for the complete recovery of the backup database, in its entirety. In short, Paragon's LIMS is backed up hourly, and, along with all network servers, is additionally backed up to tape each business day. As indicated in the IS and LIMS Policy Statement (**Appendix A**), instrument backups are performed approximately monthly. Contingent upon the volume of analysis, the frequency of backup might vary.

Backup of the instrument computers is done centrally by the IS Manager if the instrument computer is on the network. It is the responsibility of the operator\user to coordinate a convenient time for both the IS Manager and the user for non-network instrument backup. The instruments that are not on the network are backed up using portable devices. These devices, as well as media, are checked out from the IS Manager, then are returned to the IS Manager for safe storage.

An electronic archive for maintaining final project reports was implemented in 2001. Upon completion of a workorder, all data reports are scanned to create image files that are catalogued and saved to a dedicated server that is backed up daily as described above. The scanned images remain available on the network for review should any questions regarding the data arise. Retention of hardcopy data reports prior to 2001 is discussed below.

10.8.2 HARDCOPY RECORDS

Prior to electronic compilation and storage, Paragon created paper copies of project reports. These hardcopy data archives are retained off-site by a records storage contractor. The QAM maintains a database inventory of all records that are stored at the contractor's facility. The contractor is responsible for the maintenance and protection of these records. Access to the records is limited to only designated individuals. If any records need to be retrieved from the storage site, the requestor must fill out an archive request form (Form 136) and submit it to the Quality Assurance Department. E-mail requests directed to the QAM are also acceptable. The QA Department then requests the records from the contractor, who retrieves the records and delivers them to the laboratory on the next business day.

Hardcopy originals of records that have been imaged and verified may be destroyed confidentially (i.e., shredded). Detailed procedures for archiving records and submitting archive requests are provided in **SOP 069**.

As of this writing, no provisions have been made to permanently destroy any records generated by Paragon. Should Paragon permanently destroy any records, written notification will be provided to all clients affected.

In the event that the laboratory changes ownership, the responsibility for the retention of records in accordance with the guidelines established in this LQAP, is conferred to the new owner. Should Paragon go out of business, Paragon will inform our clients in writing of this business decision, and will transfer records at the client's request.

10.9 CLIENT INQUIRIES/COMPLAINTS

The focal point of contact with the client is the Paragon Project Manager. If a complaint or any circumstance raises doubt concerning Paragon's compliance with its policies or procedures, or with the requirement of a method or quality system, it is the Project Manager who initiates investigation and follows through to resolution. The QAM, Department Managers, and Laboratory Director are made aware of, and involved in, the resolution process as needed. Documentation of the complaint and its resolution are maintained as part of the project records. Where resubmission of data is required and/or implementation of preventive measures is necessary, an NCR Form (**Appendix F**) is used and processed (**SOP 928**), through the QAM. Paragon will respond to all complaints in a timely fashion.

10.10 CONFIDENTIALITY

All laboratory results and associated raw data are confidential and may not be released to or discussed with any party other than the client who requested the analytical services. Access to laboratory records and LIMS is limited to laboratory personnel, on a restricted basis, based on need (i.e., job function). Records are available for an accrediting authority's on-site review, and records specific to the client (as well as quality system records) are available to the client for client audits. Paragon expects that auditors will honor our clients' and Paragon's confidentiality requirements, and will not discuss any results, documents, or records viewed during the course of an audit.

Confidentiality is included as a component of Paragon's ethics training, which is provided to each person as they join the Paragon staff, and annually, as a refresher training, thereafter.

11. CORRECTIVE ACTIONS

Corrective action is necessary when any measurement system fails to meet the requirements of this LQAP, the appropriate SOP or project-specific instructions, or whenever an error is detected. Items that may need corrective action range from a minor problem such as an analyst failing to initial a form, to a major problem such as a chemist preparing a sample using the wrong reference method.

Corrective actions fall into two general categories: short-term and long-term. Short-term corrective actions are those that can be applied immediately. Examples include: having an analyst initial a form where the initial was missed, or correcting an error in a logbook entry per procedures described in SOP 303. Long-term corrective actions are those that require a clarification of practice or a change in policy in order to effectively resolve the problem. Corrective actions must be completed by the date designated by the QA Department (i.e., within 21 calendar days or less, unless otherwise provided for). Associated SOPs may need to be revised and republished for long-term corrective actions, laboratory staff must be re-trained in accordance with the updated procedures.

11.1 RESPONSIBILITIES FOR CORRECTIVE ACTION INITIATION

The type of corrective action taken is coordinated by the Department, Quality Assurance and applicable Project Managers. A controlled Nonconformance Report (**Appendix F**) is used to document the corrective action. *Any* individual who notes a problem or deviation is responsible for initiating the NCR in a timely manner.

It is the responsibility all personnel who work with samples to note any discrepancies or nonconformances that occur with sample handling. It is the responsibility of the chemists who prepare samples for analysis to document any problems that are noted during sample preparation. It is the analyst's responsibility to monitor the proper functioning of the analytical system prior to, during and following sample analysis. To accomplish this, various DQIs as

discussed in Chapter 3 of this LQAP are monitored and evaluated against laboratory established or project-specific QA/QC requirements. If the evaluation reveals that any of the QC acceptance criteria are not met, then the analyst must immediately correct the problem. When an acceptable resolution cannot be achieved and/or data quality is negatively impacted, the analyst must notify the Department and Project Managers and must initiate an NCR (**SOP 928**) immediately. Per the guidance contained in SOP 928, the laboratory shall notify all affected clients of potential data quality issues in a timely manner, and corrective actions taken to resolve the issue shall be completed in a reasonable timeframe, with documentation submitted to the client.

11.2 PARAGON'S CORRECTIVE ACTION PROCESS

Non-conformances are reported (documented) electronically through a LIMS interface that is available to all staff. The individual who discovered the problem or deviation is responsible for initiating the next sequential NCR in LIMS. Note that in addition to documenting laboratory sample or test issues, NCRs are also used to address client inquiries, and to investigate Performance Test (PT) sample failures.

Documented on the NCR are the initials of the initiator and descriptions of the method, workorder(s) and samples affected; the type, content and extent of the problem noted; the probable cause and the root of the problem (if known); measures taken to prevent recurrence; the specific corrective actions taken and their outcome; and the final disposition/resolution of the data.

As described in **SOP 928**, the processing of the NCR flows from the initiator, to their immediate Supervisor and/or Department Manager and the relevant Project Manager(s), and finally to the Quality Assurance Manager. In this manner, a consensus is achieved as to what specific corrective actions are to be taken. The Project Manager, at his or her discretion, may or may not contact the client to discuss options based on the nature of the nonconformance. Whether or not the client is contacted is noted on the NCR, if the client is contacted, the Project Manager documents who was contacted and when. The Project, Department and Quality Assurance Managers electronically sign and date the NCR, documenting their final approval and verification of the disposition of the data. The LIMS provides for delegation of signature authority as needed to cover key staff outages.

The LIMS, which is subject to Paragon's frequent backup protocols, maintains an archive of all NCRs generated. In this manner, NCRs are retained as part of the laboratory's electronic records. Also, contingent upon the level of data deliverable specified by the client, a copy of the associated NCR report is included in the analytical data package. Corrective actions that require follow-up, including those initiated by internal or external auditors, are catalogued in a separate LIMS Table that tracks audit findings. This LIMS Audit Findings Table

is managed by the QA Department but is available to all staff on a read-only basis.

12. AUDITS

12.1 INTERNAL AUDITS

Periodic evaluations conducted by the Quality Assurance Department and the analysis of Proficiency Test (PT) samples are two types of internal audits used to assess and document the performance of laboratory staff and processes. Audit documentation constitutes a permanent record of the conformance of Paragon's measurement systems to quality system requirements.

Internal audits include both technical and systems audits, and are performed periodically per an annual schedule developed and maintained by the Quality Assurance Department. Considerations taken into account in developing the internal audit schedule include, but are not limited to, requests made by the Laboratory Director; the scheduled occurrence of external audits; as needed to support a specific project's requirements; to verify the continued effectiveness of corrective actions previously taken; or in response to an identified need to evaluate compliance in any area of laboratory operations. The intention of the internal audit schedule is to provide for the evaluation of each laboratory area or system at least once annually, thereby providing an overview of laboratory operations. Form 168 or other audit questionnaire may be used as a guide to conduct and document internal audits. Each year, the internal audits conducted are compiled into the annual Quality Systems Audit (QSA), which is discussed subsequently (LQAP Section 12.1.3).

All internal audits are conducted by QA staff or designees who, by experience, are deemed to be knowledgeable in the area assessed. The assigned auditor identifies the scope, time frame and expected duration of the audit, and communicates this information to the applicable Department Manager. The auditor reviews relevant information such as regulations, contract requirements, published procedures, SOPs, etc., prior to the audit. The criteria set forth in these applicable guidances establish the basis of the audit. These reference materials may also be used as auditor's aids.

The audit is conducted in an efficient and professional manner. Findings, Observations and comments are communicated to the Department Manager.

Short-term corrective actions may be taken at the time an item is noted, or an appropriate long-term corrective action plan may be developed. An audit is considered to be closed-out when deficiencies have been satisfactorily corrected.

An audit report summarizing the Determinations made and the corrective actions taken or planned is compiled; the original auditor's notes are customarily included

as an attachment of the audit report. The outcome of the audit is communicated to the Laboratory Director. Internal audit corrective actions requiring follow up are tracked in a LIMS Table that is available for viewing to all laboratory personnel. The QAM oversees satisfactory completion of corrective measures taken. Internal audit records are maintained by the Quality Assurance Department.

See **SOP 937** for additional information pertaining to internal audit procedures.

12.1.1 INTERNAL TECHNICAL AUDITS

Departmental functions that may be reviewed during a technical audit may include, but are not limited to:

- Adherence to SOPs and compliance with promulgated method requirements during sample preparation and analysis;
- Maintenance of internal chain-of-custody;
- Proper preparation, storage, use and documentation of standards;
- Performance and documentation of instrument maintenance;
- Performance and documentation of data review;
- Evaluation of documentation practices pertaining to benchsheet and logbook entries, Nonconformance Report (NCR) generation and analyst demonstration of capability.

12.1.2 INTERNAL SYSTEM AUDITS

Examples of elements that may be reviewed as a system audit may include, but are not limited to:

- An assessment of the SOP process, including procedures for submitting and approving revisions, update and distribution of SOPs, tracking of employee SOP assignments and sign-offs, SOP electronic file management, and archiving of older SOP iterations and records.
- LIMS data capture and reporting processes.
- Sample handling, storage and disposal practices, including maintenance of sample storage areas, sample tracking and internal chain-of-custody documentation, duration of retention, and disposal designation and documentation.
- Use of Paragon's Standards and Reagents database.

- Performance and documentation of laboratory logbook review.

12.1.3 ANNUAL QUALITY SYSTEMS AUDIT

A lab-wide review of conformance to Paragon's quality system is conducted annually by the QA Manager or designee(s) as required by Section 5.5.3.1 of the NELAC Standard. The annual Quality Systems Audit (QSA) shall be managed, conducted and reported according to the audit procedures described above. Inputs to the QSA may include, but are not limited to, summaries of the following: Nonconformance Reports (NCRs), Proficiency Testing (PT) study results, deficiencies noted during data review, internal audit Determinations, and Determinations made via external audits.

12.1.4 PROFICIENCY TESTING STUDIES

Paragon participates in agency studies and/or contracts approved vendors to provide PT samples in accordance with a schedule developed and maintained by the Quality Assurance Department. Participation in PT studies enables Paragon to demonstrate capability for continued accreditation, competency in a newly developed method, or the effectiveness of corrective actions taken.

Paragon participates in the following inter-laboratory proficiency testing studies:

- Water Supply (WS) -- twice annually
- Water Pollution (WP) -- twice annually
- Soil/Hazardous Waste and UST -- twice annually
- Radiochemistry -- twice annually
- US Department of Energy (USDOE) Mixed Analyte Performance Evaluation Program (MAPEP) -- twice annually

These PT studies support various regulatory programs (SDWA, CWA, RCRA) and require that the laboratory perform analyses per various methodologies (e.g., EPA 600 series, MCAWW, ASTM, SW-846), matrices and analytes. Analyte lists include: volatile organics, semivolatile organics, organochlorine pesticides, polychlorinated biphenyls, organophosphorous pesticides, phenoxyacid herbicides, high explosives, petroleum hydrocarbons, metals, minerals, nutrients and radionuclides. The analyses of PT samples are conducted in-house, in the manner prescribed by the provider, and within the turnaround time stipulated. The PT samples are distributed to the laboratory and are

processed by qualified analysts who routinely perform the analytical method.

PT study results are evaluated by the Quality Assurance Department and the applicable Department Manager as they become available. The NCR and corrective action process as described in Chapter 11 of this LQAP, is used to address any deficiencies that are noted. An archive of PT study reports, maintained by the QA Department, is posted to the network for lab-wide access.

12.1.5 ANNUAL MANAGERIAL REVIEW

A lab-wide Managerial Review is performed annually as required by Section 5.5.3.2 of the NELAC Standard. The Managerial Review assesses operational effectiveness in terms of meeting Paragon's business goals. It is a tool used to document and facilitate the consideration and introduction of needed operational changes and improvements.

The Managerial Review is performed by a designee under the direction of the Laboratory Director. The general techniques of scoping, assessment interview, reporting and follow-up as described in the internal audit procedures discussed above and outlined in SOP 937, are used to conduct the annual Managerial Review. The contents of the annual Managerial Review are considered to be confidential. A confidential footer must, therefore, appear as a component of the annual Managerial Review report.

Inputs to the Managerial Review may include, but are not limited to the following: a snapshot summary of product generated (i.e., number of samples analyzed and the types of analyses performed), various business assessment reports (e.g., TAT, on- time delivery), output from the annual QSA (i.e., problem areas identified), interview of laboratory staff, and presentation of items discussed during strategic planning sessions and/or Manager's meetings.

12.2 EXTERNAL AUDITS

External audits may be performed by a state or Federal agency or a client as part of an ongoing certification process. Items evaluated by external assessors may include, but are not limited to, reviews of the following: analytical capabilities and procedures; COC procedures; document control; quality systems; and QC procedures. Blind PT samples may be submitted to the laboratory as a form of external audit.

See **Appendix I** for a list of Paragon's state and Federal certifications. Should Paragon drop or lose an accreditation, the PMs must notify all clients that may be affected in a timely manner.

13. PERSONNEL TRAINING

The selection of well-qualified personnel is a factor that contributes to Paragon's success. Therefore, qualifications of personnel are based upon education and experience. In order to maintain qualified staff, provide personnel advancement within the laboratory, and to provide for personnel's ongoing awareness of potential hazards and protective measures, Paragon follows a formal documented program of orientation and training. Records of Health & Safety and waste training are maintained by the Health & Safety Manager/RSO and Facilities/Waste Compliance Manager. Technical training records are forwarded to the Quality Assurance Department for retention.

13.1 ORIENTATION

Before working in the laboratory, new employees receive a four-part orientation as described below:

- Human resources -- involves matters of immediate personal concern, such as benefits and company policies

- Quality assurance -- addresses topics related to ethical conduct, good laboratory practices and ongoing documentation of employee capability demonstrations. Required readings (SOPs, LQAP) are assigned at this time.

- Health & safety -- provides for a review of Paragon's various safety program documents (Chemical Hygiene Plan, CHP; Radiation Protection Plan, RPP; Emergency and Contingency Plan, ECP; Respiratory Protection Plan, ResPP; Waste Management Plan, WMP); as well as other safety and security training.

- Department functional orientation -- focuses on the new employee's basic understanding of their role within the Department and the overall role of Operations within the structure of Paragon. The Departmental training expands upon the employee's scientific background and work experience to provide the employee with a level of competence that enables the individual to successfully function within the defined responsibilities of his/her position.

Temporary employees receive the same orientation as regular staff, with the exception of the human resources orientation.

SOP 143 details information regarding quality assurance orientation and training for new employees.

13.2 TECHNICAL TRAINING

Chemists (analysts) and technicians are qualified to perform specific analytical procedures and methods. The qualification process, at a minimum, consists of

background/theory training, on-the-job training, and demonstration of proficiency. Additional training may include further individualized instruction, programmed learning, conferences and seminars, and specialized training by instrument manufacturers.

Department Managers are responsible for providing documentation of analytical training and proficiency for each employee in their group(s) to the Quality Assurance Department for retention.

13.2.1 INITIAL DEMONSTRATION OF CAPABILITY (IDOC)

New analysts and technicians are trained by Department Managers according to the following guidelines:

- The new employee reads the SOP(s) pertinent to the analytical method being learned, and receives background/theory instruction, as applicable.

- The new employee observes the procedure in which the analytical method and required process documentation is demonstrated by trained personnel. Job requirements are outlined and quality control measurements are defined. For most methods, the trainee performs an Initial Demonstration of Capability (IDOC) by preparing and/or analyzing four (4) blank spike samples under the supervision of the Technical or Department Manager, or an analyst proficient in that method.

- The results of the new employee's preparation and/or analysis are evaluated and problems and corrective actions are discussed. If the blank spike recovery and precision data meet quality control criteria for that method, the employee is deemed to have demonstrated proficiency and is allowed to work on client samples. If the values generated are outside acceptance limits, then training continues until the trainee can consistently meet the acceptance criteria for the method.

- After the certification process has been successfully completed, the Department Manager forwards the documentation to the Quality Assurance Department for retention.

13.2.2 CONTINUING DEMONSTRATION OF CAPABILITY (CDOC)

Paragon's personnel are required to demonstrate their proficiency upon hire and annually thereafter for the methods they perform. Results from four (4) laboratory control sample (LCS) spikes performed by the chemist (analyst) or technician may be compiled to serve as the employee's Continuing Demonstration of Capability (CDOC).

Alternately, MDL studies and reports from PT sample analysis may be used to demonstrate an employee's CDOC.

13.2.2.1 METHOD DETECTION LIMIT (MDL) STUDIES

Most of the analytical methods employed at Paragon require the periodic generation of MDL data. The generation of acceptable MDL values requires a thorough understanding of the total analytical process and is a rigorous test of the proficiency of the analytical staff that performs the analysis. An analyst's or technician's performance in an MDL study that generates values that are consistent with past performance may be used to demonstrate initial and/or continuing proficiency in a method. This MDL information may be used in lieu of other demonstrations of proficiency, except where a regulatory promulgated method explicitly requires specific procedures to be followed for the initial demonstration of proficiency.

13.2.2.2 PROFICIENCY TEST (PT) SAMPLES

As discussed in Chapter 12 of this LQAP, Paragon participates in several proficiency testing programs. These programs typically submit single-blind standards to the laboratory and return a performance summary after results have been evaluated by the sponsoring agency or qualified vendor. Successful participation in these PT study programs by personnel is a rigorous demonstration of the staff's ability to perform routine analytical procedures. Records of successful participation in these programs may be used to demonstrate that an employee has been adequately trained in the methods that he/she performs. This IDOC/CDOC information may be used in lieu of other demonstrations of proficiency, except where a regulatory promulgated method explicitly requires specific procedures to be followed for the initial demonstration of capability.

13.3 TRAINING RECORDS

Technical and quality assurance training records are maintained by the Quality Assurance Department. Health & Safety training records are managed and retained by the Health & Safety Manager/RSO. Waste management training records are managed and maintained by the Facilities/Waste Compliance Manager. Employee training record files may contain, but are not limited to, the following:

- signed annual Ethics training documents
- resume or personnel qualifications form
- transcript or diploma
- QA training and signature/initial on file
- documentation of annual assigned SOP readings
- documentation of annual LQAP reading
- IDOC/CDOC documentation
- PT study results
- MDL study results
- off-site training certificate

14. GLOSSARY, ACRONYMS AND SYMBOLS

14.1 GLOSSARY

TERM	DEFINITION
Acceptance Criteria:	Specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQ)
Accreditation:	The process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory. In the context of the National Environmental Laboratory Accreditation Program (NELAP), this process is a voluntary one. (NELAC)
Accrediting Authority, Primary:	The agency or department designated at the Territory, State, or Federal level as the recognized authority with responsibility and accountability for granting NELAC accreditation for a specified field of testing. (NELAC) [1.5.2.3]
Accuracy:	The degree of agreement between a observed value and the accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations. (QAMS)
Aliquot:	A discrete, measured, representative portion of a sample taken for analysis. (EPA QAD)
Ambient:	Usual or natural surrounding conditions, e.g. ambient temperature – the natural, uninfluenced temperature of the surroundings. (NIRP Glossary)

TERM	**DEFINITION**
Analyte:	The specific chemicals or components for which a sample is analyzed; may be a group of chemicals that belong to the same chemical family and that are analyzed together. (DoD QSM)
Audit:	A systematic evaluation to determine the conformance to quantitative and qualitative specifications of some operational function or activity. (EPA-QAD)
Background:	Ambient signal response recorded by measuring instruments that is independent of radioactivity contributed by the radionuclides being measured in the sample. (DOE QSM)
Batch:	Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one to twenty environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An **analytical batch** can include prepared samples originating from various environmental matrices and can exceed 20 samples. (NELAC Quality Systems Committee)
Bias:	The deviation of a single measured value of a random variable from a corresponding expected value, or a fixed mean deviation from the expected value that remains constant over replicated measurements within the statistical precision of the measurement (Synonyms: deterministic error, fixed error, systematic error). (DOE QSM)
Blank:	A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, or analysis. The blank is subjected to the same analytical and measurement process as the associated samples. Blanks include: Equipment blank: a sample of analyte free media which has been used to rinse common sampling equipment to check effectiveness of decontamination procedures. (NELAC) Field blank: a blank prepared in the field by filling a clean container with pure deionized water and appropriate preservative, if any, for the specific sampling activity being undertaken. (EPA OSWER) Trip blank: Contaminant free water, or appropriate matrix, which accompanies bottles and samples during shipment to assess the potential for sample contamination during shipment. Trip blanks are

TERM	**DEFINITION**
	not opened in the field, and are required for Volatile Organic Analysis only. (NIRP) Instrument Blank: A clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (EPA-QAD) Method blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all the steps of the analytical procedures. (NELAC) Reagent blank: a sample consisting of reagent(s), without the target analyte(s) or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps. (QAMS)
Blind Sample:	A sub-sample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample, but not the composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process. (NELAC)
Calibration:	To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. See Initial Calibration. (NELAC)
Calibration, Continuing:	The process of analyzing standards periodically to verify the maintenance of calibration of the analytical system.
Calibration Curve:	The graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. (NELAC)
Calibration, Initial:	The process of analyzing standards, prepared at specified concentrations, to define the quantitative response, linearity and dynamic range of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a continuing calibration do not conform to the requirements of the method in use or at a frequency specified in the method. See Calibration.
Calibration, Initial Check/Verification	Verification of the ratio of instrument response to analyte amount, a calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a

TERM	**DEFINITION**
(ICV):	stock solution which is different from the stock used to prepare calibration standards. (NIRP Glossary)
Carrier:	Carriers are typically non-radioactive (e.g. natural strontium, barium, yttrium) elements. They follow similar chemical reactions as the analyte during processing and are added to samples to determine the overall chemical yield for the analytical preparation steps. The yield of the carrier is typically determined gravimetrically or by ICP and is used to correct radiochemical results for acceptable losses occurring during the preparation process. (DOE QSM)
Chain-of-Custody (COC) Form:	Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers, the mode of collection, preservation, and requested samples. (NELAC)
Confidential Business Information (CBI):	Information that an organization designates as having the potential of providing a competitor with inappropriate insight into its management, operation or products. NELAC and its representatives agree to safeguarding identified CBI and to maintain information identified as such in full confidentiality. (NELAC)
Confirmation:	Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to: second column calibration, alternate wavelength, derivatization, mass spectral interpretation, alternative detectors, or additional cleanup procedures. (NELAC)
Conformance:	An affirmative indication or judgment that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements. (ANSI/ASQC E4-1994)
Control Chart:	A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control.
Control Limit:	A range within which specified measurement results must fall to signify compliance. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that nonconforming data be investigated and flagged.
Corrective Action:	The action taken to eliminate the causes of an existing

TERM	DEFINITION
	nonconformity, defect, or other undesirable situation in order to prevent recurrence. (ISO 8402)
Counting Efficiency:	The ratio of the net count rate of a radionuclide standard source to its corresponding known activity. (DOE QSM)
Counting Uncertainty (Poissonian):	A statistical estimate of uncertainty in a radiochemical measurement due to the random nature of decay. Every radiochemical result is reported with an associated counting uncertainty, usually at the 95% confidence interval.
Data Quality Indicators:	The qualitative or quantitative statements that specify the quality of data required to support decision for any process requiring chemical or physical analysis.
Data Reduction:	The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form. (EPA-QAD)
Daughter:	A nuclide formed by radioactive decay of a parent radionuclide.
Deficiency:	An unauthorized deviation from acceptable procedures or practices, or a defect in an item. (ASQC)
Demonstration of Capability (DOC):	A procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC)
Detection Limit, Analyte:	The lowest concentration or amount of the target analyte that can be identified, measured, and reported with confidence that the analyte concentration is not a false positive value. See Method Detection Limit. (NELAC)
Detection Limit, Instrument (IDL):	The concentration of an analyte that produces an output signal twice the root mean square of the background noise, or the parameter determined by multiplying by three the standard deviation obtained of three to five times the desired IDL on three nonconsecutive days with seven consecutive measurements per day. IDL is only required for the metals and analysis. (DOE QSM)
Detection Limit, Method (MDL):	The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It may be determined using replicate spike samples prepared by the lab and taken through all steps of the method. The detection limit is calculated using the appropriate student's t-parameter times the standard deviation of a series of spiked samples. (Ref. 40 CFR Part

TERM	**DEFINITION**
	136, Appx. B)
Digestion:	A process in which a sample is treated (usually in conjunction with heat) to convert the sample into a more easily measured form. (DoD QSM)
Dilution Factor:	The factor by which the dilution level of the sample differs from that of a predefined method blank. The method blank is prepared within the prescribed parameters of the method, and has a dilution factor of one. The dilution factor does not include a dryness factor. (DOE QSM)
Document Control:	The act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly, and controlled to ensure use of the correct version at the location where the prescribed activity is performed. (ASQC)
Dry Weight:	The weight of a sample based on percent solids. The weight after drying in an oven at $105 \pm 5^{o}C$.
Duplicate, Replicate Analysis:	The analyses or measurements of the variable of interest performed identically on two sub samples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation, or storage internal to the laboratory. (EPA-QAD)
	The measurements of the variable of interest performed identically on two or more sub-samples of the same samples within a short time interval. (NELAC)
Duplicate (Replicate) Error Ratio (DER/RER):	A measure of precision used to assess agreement between radiochemical duplicates (replicates) that compares the discrepancy between two measurements to the associated uncertainties.
Duplicate, Replicate Sample:	A second aliquot of the same sample that is treated the same as the original sample in order to determine the precision of the method.
	A second, separate sample collected at the same time, from the same place, for the same analysis, as the original sample in order to determine overall precision.
Eluent:	A solvent used to carry the components of a mixture through a stationary phase. (DoD QSM)
Elution:	A process in which solutes are washed through a stationary phase by

TERM	DEFINITION
	the movement of a mobile phase. (DoD QSM)
Energy Calibration:	The correlation of the multi-channel analyzer (MCA) channel number to decay energy, obtained from the location of peaks from known radioactive standards. (DOE QSM)
False Negative:	An analyte incorrectly reported as absent from the sample, resulting in potential risks from their presence. (DoD QSM)
False Positive:	An item incorrectly identified as present in the sample, resulting in a high reporting value for the analyte of concern. (DoD QSM)
Finding:	An assessment conclusion that identifies a condition having a significant effect on an item or activity. An assessment finding is normally a deficiency and is normally accompanied by specific examples of the observed condition. (NELAC)
Half Life ($T_{½}$):	The time required for 50% of a radioactive isotope to decay. (DOE QSM)
Holding Time (Maximum Allowable):	The maximum times that samples may be held prior to analysis and still be considered valid or not compromised. (40 CFR Part 136)
Homogeneity:	The degree to which a property or substance is evenly distributed throughout a material.
Interference, Spectral:	Occurs when particulate matter from the atomization scatters the incident radiation from the source or when the absorption or emission of an interfering species either overlaps or is so close to the analyte wavelength that resolution becomes impossible. (DoD QSM)
Interference, Chemical:	Results from the various chemical processes that occur during atomization and later the absorption characteristics of the analyte. (DoD QSM)
Internal Standards:	A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method. (NELAC)
Isomer:	Generally, any two chemicals with the same chemical formula but with a different structure. (DoD QSM)
Isotope:	A variation of an element that has the same atomic number of protons but a different weight because of the number of neutrons. Various isotopes of the same elements may have different radioactive behaviors, some are highly unstable. (NIRP Glossary)

TERM	**DEFINITION**
Lot:	A quantity of bulk material of similar composition processed or manufactured at the same time.
Matrix:	The substrate of a test sample. **Field of Accreditation Matrix:** these matrix definitions shall be used when accrediting a laboratory: Drinking Water: any aqueous sample that has been designated a potable or potential potable water source. Non-Potable Water: any aqueous sample excluded from the definition of Drinking Water matrix. Includes surface water, groundwater, effluents, water treatment chemicals, and TCLP or other extracts. Solid and Chemical Materials: includes soils, sediments, sludges, products, and by-products of an industrial process that results in a matrix not previously defined. Biological Tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin. Air and Emissions: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device. (NELAC) Non-aqueous Liquid: any organic liquid with <15% settleable solids.
Minimum Detectable Activity (MDA, Lower Limit of Detection):	The minimum detectable activity is the smallest amount (activity or mass) of an analyte in a sample that will be detected with a probability beta of nondetection (Type II error) while accepting the probability alpha of erroneously deciding that a positive (non-zero) quantity of analyte is present in an appropriate blank sample (Type I error). For the purposes of this standard, the alpha and beta probabilities are both set at 0.05 unless otherwise specified. (ANSI N 13.30 and ANSI N42.23)
Minimum Detectable Concentration (MDC):	The Minimum Detectable Activity expressed in concentration units.
National Voluntary Laboratory Accreditation Program (NVLAP):	A program administered by NIST that is used by providers of proficiency testing to gain accreditation for all compounds/matrices for which NVLAP accreditation is available, and for which the provider intends to provide NELAP PT samples. (NELAC)

TERM	DEFINITION
Negative Control:	Measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results. (NELAC)
Nonconformance:	An indication or judgment that a product or service has not met the requirements of the relevant specifications, contract or regulation, also the state of failing to meet the requirements. (DoD QSM)
Performance Based Measurement System (PBMS):	A set of processes wherein the data quality needs, mandates, or limitations of a program or project are specified and serve as criteria for selecting measurement processes which will meet those needs in a cost effective manner. (NELAC)
Positive Control:	Measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects. (NELAC)
Precision:	The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms. (NELAC)
Proficiency Test Sample:	A sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (QAMS)
Qualitative:	Analysis without regard to quantity or specific numeric values. (NIRP Glossary)
Quality Assurance:	An integrated system of activities involving planning, quality control, quality assessment, reporting, and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)
Quality Control (QC):	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of the users. (QAMS)
Quality Control Sample:	An uncontaminated matrix spiked with known amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system. (EPA-QAD) Laboratory Control Sample (LCS): (However named, also Laboratory Fortified Blank, Blank Spike, or QC Check Sample): A

TERM	DEFINITION
	sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias, or to assess the performance of all or a portion of the measurement system. (NELAC)
	Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently. (NELAC)
	Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency. (QAMS)
Quantitation Limits, Practical (PQL):	Levels, concentrations, or quantities of a target variable (e.g. target analyte) that can be reported at a specified degree of confidence. (NELAC) The value at which an instrument can accurately measure an analyte at a specific concentration (i.e. a specific numeric concentration can be quantified). These points are established by the upper and lower limits of the calibration range. (DoD clarification)
	The lowest concentration where the 95% confidence interval is within 20% of the true concentration of the sample. The percent uncertainty at the 95% confidence level shall not exceed 20% of the results for concentrations greater than the practical quantitation limit. (DOE QSM)
Quantitative:	Analysis with regard to quantities or specific numeric values. (NIRP Glossary)
Radioactive Decay:	The process by which a spontaneous change in nuclear state takes place. This process is accompanied by the emission of energy and subatomic particles. (DOE QSM)
Radiation Yield:	The amount of radiation of the type being measured that is produced per each disintegration, which occurs. For gamma spectrometry, this is commonly called gamma abundance. (DOE QSM)
Raw Data:	Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study.

TERM	DEFINITION
	Raw data may include photography, microfilm, or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g. tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted. (EPA-QAD)
Reagent Water:	Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method. (NELAC)
Region of Interest (ROI):	In radiochemical analysis, the Multi-channel Analyzer region defining the isotope of interest displayed in terms of energy or channels. (DOE QSM)
Relative Percent Difference (RPD):	A measure of precision between two duplicate (replicate) results expressed as the percent difference between the results relative to the average of the results.
Reliability Check (Daily):	A periodic check of the Continuing Calibration of an instrument used for radiochemical measurements.
Reporting Limit:	The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the statistically determined MDL, but may be higher based on any of the above considerations. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.
Retention Time:	The time between sample injection and the appearance of a solute peak at the detector. (DoD QSM)
Rounding Rules:	If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded to 11.44. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded to 11.45. If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded to 11.44, while 11.425 is rounded to 11.42. If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

TERM	DEFINITION
Sample:	A single container or series of containers identified by a unique number comprised of material drawn from a single location or a composite of locations during a fixed period representative of that location (s) and time period(s) for the purpose of analytical testing or physical evaluation. (DOE QSM)
Selectivity:	(Analytical chemistry) The capability of a test method or instrument to respond to a target substance in the presence of non-target substances. (EPA-QAD)
Sensitivity:	Capability of method or instrument to discriminate between measurement responses representing different levels (e.g. concentrations) of a variable of interest. (NELAC)
Signal-to-Noise Ratio:	The signal carries information about the analyte, while noise is made up of extraneous information that is unwanted because it degrades the accuracy and precision of an analysis and also places a lower limit on the amount of analyte that can be detected. In most measurements, the average strength of the noise is constant and independent of the magnitude of the signal. Thus, the effect of noise on the relative error of a measurement becomes greater and greater as the quantity being measured (producing the signal) decreases in amplitude. (DoD QSM)
Split Sample:	A portion or subsample of a total sample obtained in such a manner that is not believed to differ significantly from other portions of the same sample.
Standard Operating Procedure (SOP):	A written document which details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing routine and repetitive tasks. (QAMS)
Reference Material:	A certified reference material produced by the U.S. National Institute of Standards and Technology or other equivalent organization and characterized for absolute content, independent of analytical method. (EPA-QAD) A reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO Guide 30 – 2.2)
Standard (Spike) Addition:	In radiochemistry, the addition of a known quantity of a radiotracer to a sample and to a split or splits of a sample. Both the sample and split(s) are then processed through the method and the difference in response between the samples used to correct for overall bias

TERM	**DEFINITION**
	resulting measurement bias and from losses during preparation. This method of internal calibration is used in radiochemical determinations where isotopic differentiation between target analyte and tracer is not possible.
Statistical Minimum Significant Difference (SMSD):	The minimum difference between the control and a test concentration that is statistically significant, a measure of test sensitivity or power. The power of a test depends in part on the number of replicates per concentration, the significance level selected, and the type of statistical analysis. If the viability remains constant, the sensitivity of the test increases as the number of replicates is increased. (NELAC)
Surrogate:	A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes. (QAMS)
Target Analytes:	Identified on a list of project-specific analytes for which laboratory analysis is required.
Tolerance Chart:	A chart in which the plotted quality control data is assessed via a tolerance level (e.g. +/-10% of a mean) based on the precision level judged to be acceptable to meet overall quality/data use requirements instead of a statistical acceptance criteria (e.g. +/- 3 sigma) (applies to radio bioassay laboratories). (ANSI)
Total Propagated Uncertainty (TPU):	An estimate or approximation of the total error associated with a measured value by propagation of individual (preparation, determination) uncertainties.
Traceability:	The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons. (VIM-6.12)
Tracer:	A traceable internal standard, usually a unique isotope of the element being determined, added to each sample in known amount which enables quantitation of analytes of interest independent of external means of calibration.
Tracer Chemical Recovery:	The percent yield of the recovered radioisotope after the sample/tracer aliquot has undergone preparation and instrument analysis. (DOE QSM)
Tune:	An injected standard required by the method as a check on instrument performance for mass spectrometry. (DoD QSM)
Validation:	Confirmation by examination and provision of evidence that specified

TERM	DEFINITION
	requirements have been met. (EPA-QAD)
Verification:	Confirmation by examination and provision of evidence that specified requirements have been met. (NELAC) NOTE: In connection with the management of measuring equipment, verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification peculiar to the management of the measuring equipment. The result of verification leads to a decision either to restore in service, to perform adjustment, to repair or downgrade, or declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.
Warning Limits:	The limits (typically 2 standard deviations either side of the mean) shown on a control chart within which most results are expected to lie (within a 95% probability) while the system remains in a state of statistical control.

14.2 ACRONYMS

TERM	DEFINITION
AA	Atomic Absorption
AFCEE	Air Force Center for Environmental Excellence
ANSI/ASQ	American National Standards Institute/American Society for Quality
APHIS	USDA Animal and Plant Health Inspection Service
API	American Petroleum Institute
ARAR	Applicable or Relevant and Appropriate Requirement
ASCII	American Standard Code Information Interchange
ASTM	American Society for Testing and Materials
BFB	Bromofluorobenzene
BNA	Base-Neutral and Acid Extractable Organic Compounds

TERM	DEFINITION
BS	Blank Spike
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
°C	Degrees Celsius
CAS	Chemical Abstract Service
CCC	Calibration Check Compound
CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CDPHE	Colorado State Department of Public Health and the Environment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CF	Calibration Factor
CFR	Code of Federal Regulation
CLLE, CLE	Continuous Liquid-Liquid Extractor
CLP	Contract Laboratory Program
COC	Chain of Custody
CVAA	Cold Vapor Atomic Absorption Spectroscopy.
CWA	Clean Water Act
D	Drift or Difference
DBCP	1,2-Dibromo-3-chloropropane
DCM	Dichloromethane
DENIX	Defense Environmental Management Information Exchange
DER	Duplicate Error Ratio
DFTPP	Decafluorotriphenylphosphine
DI	Deionized
DOC	Demonstration of Capability
DoD	Department of Defense
DOE	Department of Energy

TERM	DEFINITION
DOT	Department of Transportation
DPM	Disintegrations per Minute
DQI	Data Quality Indicator
DRO	Diesel Range Organics
ECD	Electron Capture Detector
EDB	Ethylene Dibromide
EDD	Electronic Data Deliverable
EERF	Eastern Environmental Radiation Facility
EMSL	Environmental Monitoring Systems Laboratory
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
GALP	Good Automated Lab Practice
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GFAA	Graphite Furnace Atomic Absorption
GFPC	Gas Flow Proportional Counting
GPC	Gel Permeation Chromatography
GRO	Gasoline range organics
HECD	(Hall) Electrolytic Conductivity Detector
HEM	Hexane Extractable Material
HDPE	High-Density Polyethylene
HPGe	High Purity Germanium Gamma Spectrometer
HPLC	High-Performance Liquid Chromatography
IC	Ion Chromatography
ICAP-AES	Inductively Coupled Argon Plasma -Atomic Emission Spectroscopy

TERM	DEFINITION
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICS	Interference Check Standard
ICV	Initial Calibration Verification
IDL	Instrument Detection Limit
IPC	Instrument Performance Check
IPN	Incoming Project Notice
IRPIMS	Installation Restoration Program Information Management System
IS	Internal Standard
ISO/IEC	International Standards Organization/International Electrotechnical Commission
KD	Kuderna Danish
LCS	Laboratory Control Sample
LD	Laboratory Duplicate
LFB	Laboratory Fortified Blank
LFM	Laboratory Fortified Matrix
LIMS	Laboratory Information Management System
LLRW	Low Level Radioactive Waste
LQAP	Laboratory Quality Assurance Plan
LRB	Laboratory Reagent Blank
LSC	Liquid Scintillation Counting
LUFT	Leaking Underground Fuel Tank
LUST	Leaking Underground Storage Tank
MAPEP	Mixed Analyte Performance Evaluation Program
MCAWW	Methods for Chemical Analysis of Waters and Wastes

TERM	DEFINITION
MDA	Minimum Detectable Activity
MDC	Minimum Detectable Concentration
MDL	Method Detection Limit
MEK	Methyl Ethyl Ketone (2-Butanone)
MIBK	Methyl Isobutyl Ketone
MSA	Method of Standard Additions
MSD	Matrix Spike Duplicate
MSDS	Material Safety Data Sheet
MTBE	Methyl tert-butyl ether
N/A	Not applicable
NIST	National Institute of Standards
NCR	Nonconformance Report
ND	Non Detect
NEIC	National Enforcement and Investigations Center
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
NEPA	National Environmental Policy Act
NFESC	Naval Facilities Engineering Service Center
NIRP	Navy Installation Restoration Program
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NVLAP	National Voluntary Laboratory Accreditation Program
OSHA	Occupational Safety and Health Administration
PAH	Polynuclear Aromatic Hydrocarbon
PARCC	Precision, Accuracy, Representativeness, Completeness, Comparability
PBMS	Performance Based Measurement System

TERM	**DEFINITION**
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PEG	Polyethylene Glycol
PEL	Permissible Exposure Limit
PETN	Pentaerthrite tetranitrate
PID	Photoionization Detector
PM	Project Manager
PNA	Polynuclear Aromatic Hydrocarbon
PQL	Practical Quantitation Limit
psi	pounds per square inch
PT	Proficiency Testing
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QAPjP	Quality assurance project plan
QASS	Quality Assurance Summary Sheet
QC	Quality Control
QIP	Quench Indicating Parameter
r^2	Correlation Coefficient
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RFP	Request for Proposal
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
RL	Reporting Limit
ROI	Region of Interest

TERM	DEFINITION
RPD	Relative Percent Difference
RPM	Revolutions Per Minute
RRT	Relative Retention Time
RSD	Relative Standard Deviation
RSO	Radiation Safety Officer
RT	Retention Time
RTW	Retention Time Window
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
SMSD	Statistical Minimum Significant Difference
SOP	Standard Operating Procedure
SOW	Statement of Work
SPCC	System Performance Check Compound
SPLP, SLP	Synthetic Precipitation Leaching Procedure
SVOC	Semivolatile Organic Compound
TAL	Target Analyte List
TCLP	Toxicity Characteristic Leaching Procedure
TCMX	Tetrachlorometaxylene
TCL	Target Compound List
TDS	Total Dissolved Solids
TIC	Tentatively Identified Compound
TLV	Threshold Limit Value
TOC	Total Organic Carbon
TPH	Total petroleum hydrocarbon
TPU	Total Propagated Uncertainty
TRPH	Total Recoverable Petroleum Hydrocarbons

TERM	DEFINITION
TSCA	Toxic Substances Control Act
TSDF	Treatment, Storage, and Disposal Facility
TSS	Total Suspended Solids
TVPH	Total Volatile Petroleum Hydrocarbons
USACE	United Stated Army Corp of Engineers
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UST	Underground Storage Tank
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
WET	Waste Extraction Test
ZHE	Zero Headspace Extraction

14.3 SYMBOLS

LENGTH	DEFINITION	SYNOMYM
um	micrometer	10^{-6} meter
mm	millimeter	10^{-3} meter
cm	centimeter	0.01 meter
dm	decimeter	0.1 meter
m	meter	

WEIGHT	DEFINITION	SYNOMYM
pg	picogram	10^{-12} gram
ng	nanogram	10^{-9} gram
ug	microgram	10^{-6} gram
mg	milligram	10^{-3} gram
g	gram	
kg	kilogram	10^{3} gram

VOLUME	DEFINITION	SYNOMYM
uL	microliter	10^{-6} Liter
mL	milliliter	10^{-3} Liter
dL	deciliter	0.1 Liter
L	Liter	

CONCENTRATION	DEFINITION
ng/uL	nanograms per microliter
ug/L	micrograms per liter
ug/kg	microgram per kilogram
ug/g	microgram per gram
ug/mL	microgram per milliliter
mg/kg	milligram per kilogram
mg/L	milligram per liter
ug/m^3	microgram per cubic meter
ppb	part per billion
ppm	part per million

TIME	DEFINITION	SYNOMYM
s or sec	second	1/60 minute
m or min	minute	60 seconds, 1/60 h
h	hour	60 minutes

TEMPERATURE	DEFINITION
^oC	Degrees Celsius
^oF	Degrees Fahrenheit
^{o} K	Degrees Kelvin

ACTIVITY	DEFINITION	SYNOMYM
Bq	Bequerels	Disintegration/s
Ci	Curie	3.7×10^{10} Bq
dpm	Disintegrations per minute	

ELECTRICAL	**DEFINITION**
V	Volt
A	Ampere
EV	Electron Volt
F	Farad
Ω	Ohm
S or mho	Siemens
W	Watt

PREFIXES	**NUMERIC AMOUNT**
tera	10^{12}
giga	10^{9}
mega	10^{6}
kilo	10^{3}
hecto	10^{2}
deca	10
deci	0.1
centi	10^{-2}
milli	10^{-3}
micro	10^{-6}
nano	10^{-9}
pico	10^{-12}
femto	10^{-15}

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Appendix A

Ethics Documents
(Forms 159, 162, 166)

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Information Systems (IS) Policies

All employees of Paragon Analytics are expected to comply with each of the following policies and/or procedures. Attempts to circumvent these policies and controls are subject to disciplinary action, including immediate termination.

Local Area Network Policies

1. Users of the Paragon network are given a password that is *not* to be shared with anyone else, other than the IS Department, for *any* reason. All work performed is to be done using your own unique account and password identification. Your password shall be changed every 90 days, and the same password cannot be used more than once in a 2-year period. You will be prompted by the system when your password is about to expire. Contact the IS Manager as soon as possible to arrange a new password. Do not attempt to change your password yourself.
2. Training is provided and access is granted to users dependant on their job function.
3. Each user has a drive mapping to H: which is their own secure area. Storage of more than 10 megabytes should be approved by the IS Manager as there are space restrictions.
4. Creation of directories in the existing network structure should be done by IS Department personnel only. Please send requests via e-mail or contact the IS Manager or staff directly. This prevents multiple entries as well as maintenance problems.
5. Any malicious deletion of files or directories can result in termination.
6. There is an external e-mail system that should be checked *daily* as that is how company information is most often conveyed. You can check your mail from any computer as it is web based. All current employees have been trained in its use. If you have questions please contact the IS manager. E-mail is property of Paragon Analytics and no expectation of privacy exists.
7. When you leave your computer or any computer you are logged in to for an extended period of time (like lunch), you are expected to log out from the network. When you leave the building, you are expected to log out from the network. There are only a few exceptions, like some of the instrument computers.

Hardware Policies and Software Policies

1. There is not to be *any* hardware or software brought into Paragon for installation on company computers. This includes screensavers. If, as a part of your job function, you require either hardware or software, please request it via e-mail or in person from the IS Manager.

   Screensavers should be used sparingly. They have been known to cause computer problems especially on instrument computers. The best ones to use are either the 'Blank Screen' or the 'Starfield Simulation'.
2. Paragon computers are not to be used for games.

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Virus Protection Procedures

1. In the event of a virus detection, contact the IS Manager immediately. **Do not do anything further. Do not reboot the computer under any circumstance.**
2. All floppies or CDs brought in from outside that you may have been using to do company work at home, must scanned by IS staff prior to inserting them into any computer. Failure to do so could result in termination. Virus signatures are updated daily in most cases, but new viruses are launched at any time.
3. Do not open any mail from anyone you do not know. Especially be wary of e-mails with attachments. Best practice is to keep your preview pane closed at all times to limit the possibility of self-extracting viruses.

Computer Failures Procedures

1. You are to contact the IS Department if you have hardware or network failures. You are not to try and 'fix' them yourselves without first calling IS staff.
2. Please report consistent failures like computer lockups to the IS Manager either by e-mail, voice mail, or in person.

Backup Procedures

1. The entire network is backed up daily between 1 AM and 5:30 AM. Users are not allowed on the network during these hours.
2. Backup of the instrument computers is done centrally by the IS Manager if the instrument computer is on the network. It is the responsibility of the operator\user to coordinate a convenient time for both the IS Manager and the user for backup. The instruments that are not on the network are to be backed up using portable devices. Those devices as well as media are to be checked out from the IS Manager at a convenient time for the operator\user and then returned to the IS Manager for safe storage. Backups should be done on the average of once a month. In some instances, depending on the volume of analysis, the frequency of backup might vary.

Telephone Systems

1. For those people with personal extensions, please contact the IS Manager for instructions on configuring the greetings and voice mail.
2. Each extension is password protected for voice mail. In the case of a Department phone where everyone needs access to messages, the password may be shared. In all other cases, the password should be kept confidential.
3. Please contact either the Office Manager or the IS Manager for instructions on all other operations concerning the phone system.

In the case of an emergency, the IS Manager can be contacted 24 hours/day by cell phone. The number is listed on the computer laboratory door.

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Laboratory Information Management System (LIMS) Policies

Paragon's Laboratory Information Management System (LIMS) is a data management system, which is used to track, manage, and report data to our clients. Throughout this process, it is the responsibility of Paragon Analytics and its employees to maintain *strict client confidentiality* regarding the handling of client's data and their samples. Consequently, because the LIMS is used as a tool to handle and process all data through the laboratory, it is imperative that all employees follow the basic LIMS operating guidelines listed below. **Note that these policy statements are not intended as a substitute for proper LIMS training - LIMS training is conducted by authorized personnel on topics that are related to the job function of each employee.**

1. Prior to using LIMS, employees must have received proper training in all LIMS processes that are required to help them perform their job. The training schedule will be coordinated between individual Department Managers and the LIMS Manager.
2. Employees must have a user account assigned to them by the LIMS Manager (Mark Roche') before they are allowed to use the LIMS. 'Sharing' or using another person's account is *strictly prohibited.* Similarly, employees are prohibited from performing any work in LIMS while another user is logged on. Additionally, to prevent unauthorized access to restricted areas in LIMS, all employees are required to log off the system before they leave their PC for any extended period of time.
3. All changes to any validated data contained within LIMS must have prior approval by the Department Manager—**unauthorized changes are a serious violation of employee conduct and may result in disciplinary action, including immediate dismissal**. Accidental changes or errors in data entry should immediately be reported to the Department and LIMS Managers.
4. Because of the sensitive nature of our business, LIMS has been equipped with a full set of security and auditing features. Employees are assigned to groups and they are given specific permissions to access menus and operations in LIMS, which are pertinent to the tasks they are required to perform. **Any employee who attempts to circumvent these features in any way will be subject to disciplinary action, including immediate dismissal**.
5. Invariably, in the course of LIMS operations, errors may occur in the application. Some of these errors can lead to extensive data loss, system downtime and, therefore, rework. **When these errors occur, it is the employee's responsibility to immediately notify the LIMS Manager so that data loss may be avoided or minimized**.

Some processes in LIMS may require the system to access thousands or, even hundreds of thousands of records at a time. Therefore, some operations in LIMS may take several minutes to complete. During this processing time, it may appear as if your computer is locked up or not responding. Although there are times when it may be appropriate to forcibly shutdown LIMS when this occurs, employees should seek assistance from the LIMS Manager prior to attempting this shutdown process if they are unsure of the consequences. Improper shutdown of LIMS may result in *extensive data loss, system downtime, and rework*.

Please contact the IS and/or LIMS Managers if you have any questions regarding the policies set forth in this document.

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By my signature below, I acknowledge that I have read, understood and agree to abide by Paragon's Information Systems (IS) and Laboratory Information Management System (LIMS) Policies, while employed by Paragon:

_____
Printed Name

_____
Signature

_____
Date

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Ethics and Data Integrity Policies

The intent of this policy statement is to highlight and clarify Paragon's requirements and expectations for behavior in the work place. Paragon requires that all employees conduct themselves with honesty and integrity at all times. It is Paragon's expectation that all employees exhibit professionalism and respect for clients and each other in all interactions and tasks. To this end, Paragon requires that every employee abide by the following guidelines:

- Every Paragon employee is responsible for the propriety and consequences of his or her actions.
- Every Paragon employee is required to conduct him or herself in a professional manner toward all clients, regulators, auditors, vendors, and other employees. Professional conduct relates to honesty, integrity, respect, and tolerance for cultural diversity.
- Every Paragon employee must perform all assigned duties in accordance with Paragon's established quality assurance policies and quality control procedures, which have been developed in substantial conformity with contractual and regulatory requirements.
- Every employee must disclose any instance of noncompliance. Employees are expected to use professional judgment, and to document all situations thoroughly. It is the responsibility of each Paragon employee to consult the Department Manager or Quality Assurance Manager when atypical situations occur, and to fully disclose and document the decision-making process utilized. Paragon reports all noncompliance issues to the client, if data are affected by the noncompliance.
- It is the responsibility of each Paragon employee to report any suspicion of unethical conduct or fraudulent activities to the Department and/or Quality Assurance Manager, or the Laboratory Director.

Following are examples of improper, unethical, or illegal practices that will <u>not</u> be tolerated by Paragon:

- Improper use of manual integrations performed to meet calibration or method quality control criteria (e.g., peak shaving or peak enhancement performed solely to meet quality control requirements).
- Intentional misrepresentation of the date or time of analysis (e.g., intentionally resetting a computer system's or instrument's date and/or time to make it appear that a date/time requirement has been achieved).
- Falsification of records to meet method requirements (e.g., sample records, logbooks, sample results, LIMS records).
- Reporting results without analyses to support the results (i.e., dry labbing).
- Selective exclusion of data to meet quality control criteria (e.g., eliminating initial calibration points without technical justification).

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- Misrepresentation of laboratory performance by presenting calibration data or quality control limits within data reports that are not relevant to the results being reported.
- Notation of matrix interference as basis for exceeding acceptance limits in interference-free matrices.
- Unwarranted manipulation of computer software (e.g., improper background subtraction to meet ion abundance criteria for GC/MS tuning compounds; chromatographic baseline manipulations).
- Improper alteration of analytical conditions from standard analysis to sample analysis (e.g., modifying EM voltage, changing temperature or eluent profiles to shorten analytical run time).
- Misrepresentation of quality control samples (e.g., adding surrogates or tracers after sample extraction, omitting preparation steps for quality control samples; over- or under-spiking).
- Reporting results from the analysis of one sample for another (file substitution).
- Intentional plagiarism or willful misrepresentation of another employee's work as one's own (e.g., DOC or PT study).

Any unethical conduct, such as willful falsification, concealment, or alteration of a material fact or the false, fraudulent or fictitious statement or representation made by any person performing work may subject that person to prosecution and punishment in accordance with applicable Federal statutes. Any breach of ethics will result in disciplinary action, up to and including termination, according to Paragon's disciplinary guidelines.

By my signature below, I acknowledge that I have read, understood and agree to abide by Paragon's Ethics and Data Integrity Policies, while employed by Paragon:

_____

Printed Name

_____

Signature

_____

Date

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Waste, Abuse and Fraud Notification

The DataChem/Paragon quality policy states that we are committed to 'generating accurate and reliable data in accordance with contractual and regulatory requirements; and to performing work in the most efficient manner possible, thus avoiding waste of resources.' Hence, it is against corporate policy to improperly manipulate or falsify data, to engage in unethical conduct, or to tolerate wasteful practices that abuse resources.

Additionally, as a Federal contractor, per DOE Order 221.1a, all DataChem/Paragon employees are instructed that 'whosoever is aware of any case of fraud, data manipulation/ falsification, waste or misuse/abuse of resources, corruption, mismanagement or other unethical practice or misconduct, is obligated to inform the appropriate Department Manger.' Alternately, the Quality Assurance Manager or Laboratory Director may be contacted.

Furthermore, a Confidential Reporting Procedure page is posted on the DCL intranet. This page explains that in the event of an allegation, the facility Laboratory Director and QA Manager will conduct a confidential investigation using qualified technical and management personnel. The investigation may include interviews, data audits, internal method audits, and surveillance to determine inappropriate practices. All records of the investigation are kept strictly confidential. Client contact and data recall is initiated as applicable.

Note that an anonymous electronic reporting form that may be used by any employee who wishes to report improper laboratory practices is available on the Confidential Reporting Procedure web page. This electronic form goes to the corporate QA office and is then sent to the facility Laboratory Director and QA Manager so that a confidential investigation as previously described can be conducted.

Per the USDOE General Provision DEAR 952.203.70 "Whistleblower Protection for Contractor Employees" policy, to which Paragon also adheres, the Office of the Inspector General (OIG) of the USDOE or USEPA may be contacted where the allegation pertains to DOE or EPA programs, operations, facilities, contracts, or information technology systems. Contact information for these offices are provided below.

Detailed training pertaining to electronic and behavioral ethics, and confidential reporting and investigation of improper practices, is provided to all DataChem/Paragon employees annually.

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Employees may report waste, abuse and fraud allegations to the Paragon Analytics representatives listed below, and/or to the Inspector General's Offices of the USDOE or USEPA, using the contact information given below. Employees reporting such allegations pertaining to DOE or EPA programs are afforded "Whistleblower Protection" per DEAR 952.203.70.

Contact Information:

Paragon Analytics: Ken Campbell, Lab Director	(970) 490-1511, ext.217
Paragon Analytics: Deb Scheib, QA Manager	(970) 490-1511, ext.227
USDOE OIG Hotline:	(800) 541-1625
USEPA OIG Hotline:	(888) 546-8740

Further information regarding the USDOE and USEPA policies discussed herein are provided in the following 7 attachments.

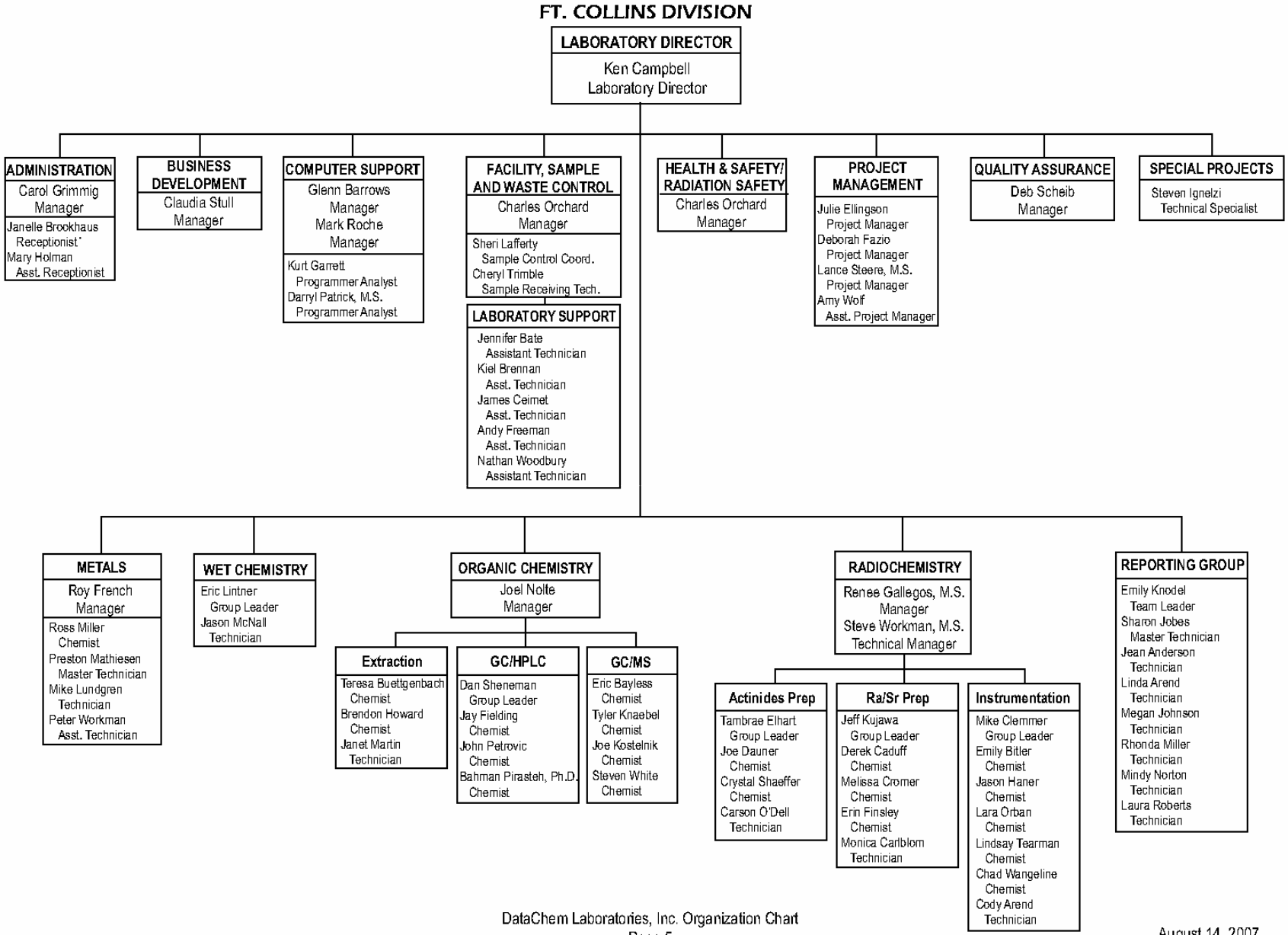
By my signature below, I acknowledge that I have read, understood and agree to abide by Paragon's Reporting of Improper Practices and Confidential Investigation (Waste, Abuse and Fraud Notification) Policies, while employed by Paragon:

_____
Printed Name

_____
Signature

_____
Date

Appendix B
Organization Chart


FT. COLLINS DIVISION
LABORATORY DIRECTOR
Ken Campbell
Laboratory Director
ADMINISTRATION
Carol Grimmig
Manager
Janelle Brookhaus
Receptionist*
Mary Holman
Asst. Receptionist
BUSINESS DEVELOPMENT
Claudia Stull
Manager
COMPUTER SUPPORT
Glenn Barrows
Manager
Mark Roche
Manager
Kurt Garrett
Programmer Analyst
Darryl Patrick, M.S.
Programmer Analyst
FACILITY, SAMPLE AND WASTE CONTROL
Charles Orchard
Manager
Sheri Lafferty
Sample Control Coord.
Cheryl Trimble
Sample Receiving Tech.
LABORATORY SUPPORT
Jennifer Bate
Assistant Technician
Kiel Brennan
Asst. Technician
James Ceimet
Asst. Technician
Andy Freeman
Asst. Technician
Nathan Woodbury
Assistant Technician
HEALTH & SAFETY/ RADIATION SAFETY
Charles Orchard
Manager
PROJECT MANAGEMENT
Julie Ellingson
Project Manager
Deborah Fazio
Project Manager
Lance Steere, M.S.
Project Manager
Amy Wolf
Asst. Project Manager
QUALITY ASSURANCE
Deb Scheib
Manager
SPECIAL PROJECTS
Steven Ignelzi
Technical Specialist
METALS
Roy French
Manager
Ross Miller
Chemist
Preston Mathiesen
Master Technician
Mike Lundgren
Technician
Peter Workman
Asst. Technician
WET CHEMISTRY
Eric Lintner
Group Leader
Jason McNall
Technician
ORGANIC CHEMISTRY
Joel Nolte
Manager
Extraction
Teresa Buettgenbach
Chemist
Brendon Howard
Chemist
Janet Martin
Technician
GC/HPLC
Dan Sheneman
Group Leader
Jay Fielding
Chemist
John Petrovic
Chemist
Bahman Pirasteh, Ph.D.
Chemist
GC/MS
Eric Bayless
Chemist
Tyler Knaebel
Chemist
Joe Kostelnik
Chemist
Steven White
Chemist
RADIOCHEMISTRY
Renee Gallegos, M.S.
Manager
Steve Workman, M.S.
Technical Manager
Actinides Prep
Tambrae Elhart
Group Leader
Joe Dauner
Chemist
Crystal Shaeffer
Chemist
Carson O'Dell
Technician
Ra/Sr Prep
Jeff Kujawa
Group Leader
Derek Caduff
Chemist
Melissa Cromer
Chemist
Erin Finsley
Chemist
Monica Carlblom
Technician
Instrumentation
Mike Clemmer
Group Leader
Emily Bitler
Chemist
Jason Haner
Chemist
Lara Orban
Chemist
Lindsay Tearman
Chemist
Chad Wangeline
Chemist
Cody Arend
Technician
REPORTING GROUP
Emily Knodel
Team Leader
Sharon Jobes
Master Technician
Jean Anderson
Technician
Linda Arend
Technician
Megan Johnson
Technician
Rhonda Miller
Technician
Mindy Norton
Technician
Laura Roberts
Technician

Appendix C

Capabilities, Preservation, Hold Times (Form 218)

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Note: Request 3X - 5X Minimum Quantities for Re-Runs & MS/ MSD

				Min. Quant.	Standard Quantity	Container Type	Preserv.	Req'd pH	Holding Time	Additional Sample Receiving Concerns
ORGANIC COMPOUNDS by GCMS (VOCs & SVOCs)										
VOCs w/ TICs	Water	24 Hrs	8260B	1x	3x	40 mL VOA	HCl / Cold	</= 2	14 Days	Must be headspace free
VOCs w/ TICs	Water	24 Hrs	8260B	1x	3x	40 mL VOA	Cold		7 Days	Must be headspace free
VOCs w/ TICs	Soil	24 Hrs	8260B	5 g	4 oz.	Glass	Cold		14 Days	
VOCs w/ TICs	Soil	24 Hrs	5035/8260B	1x	3x	Encore[tm]	Cold		48 hrs/14 Days frozen	Store frozen. Additional volume needed for % s
VOCs w/ TICs	Water	24 Hrs	524.2	1x	3x	40 mL VOA	$Na_2S_2O_3$ / Cold	</= 2	24 Hours	Must be headspace free
	Water	24 Hrs	524.2	1x	3x	40 mL VOA	HCl or $Na_2S_2O_3$ / Cold	</= 2	14 Days	Must be headspace free
VOCs w/ TICs	Water	24 Hrs	624M	1x	3x	40 mL VOA	$Na_2S_2O_3$ / Cold	</= 2	7 Days	Must be headspace free
	Water	24 Hrs	624M	1x	3x	40 mL VOA	HCl or $Na_2S_2O_3$ / Cold	</= 2	14 Days	Must be headspace free
SVOCs w/ TICs	Water	72 Hrs	8270C	1liter	2 liters	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
SVOCs w/ TICs	Soil	72 Hrs	8270C	30 g	4 oz.	Glass	Cold		14 Days	
FUELS										
BTEX only	Water	24 Hrs	8021B	1x	3x	40 mL VOA	HCl / Cold	</= 2	14 Days	Must be headspace free
BTEX only	Water	24 Hrs	8021B	1x	3x	40 mL VOA	Cold		7 Days	Must be headspace free
BTEX only	Soil	24 Hrs	8021B	5 g	4 oz.	Glass	Cold		14 Days	
TVPH as Gasoline	Water	24 Hrs	8015M	1x	3x	40 mL VOA	HCl / Cold	</= 2	14 Days	Must be headspace free
TVPH as Gasoline	Water	24 Hrs	8015M	1x	3x	40 mL VOA	Cold		7 Days	Must be headspace free
TVPH as Gasoline	Soil	24 Hrs	8015M	5g	4 oz.	Glass	Cold		14 Days	
TEPH as Diesel	Water	24 Hrs	8015M	100 ml	2 x 500	Amber Glass	HCl / Cold	</= 2	14 Days	Check for residual chlorine per PM direction
TEPH as Diesel	Water	24 Hrs	8015M	100 ml	2 x 500	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
TEPH as Diesel	Soil	24 Hrs	8015M	20 g	4 oz.	Glass	Cold		14 Days	
Oil and Grease	Water	24 Hrs	9070	1 Liter	2 Liter	Amber Glass	HCl / Cold	</= 2	28 Days	
Oil and Grease	Solid	24 Hrs	9071A	50 g	4 oz.	Amber Glass	Cold		28 Days	
TRPH - Hexane Extractable	Water	24 Hrs	1664	1 Liter	2x1 Liter	Amber Glass	HCl / Cold	</= 2	28 Days	
TRPH - Hexane Extractable	Solid	24 Hrs	1664	10 g	4 oz.	Amber Glass	Cold		28 Days	
PESTICIDES/HERBICIDES/PCBs/MISCELLANEOUS ORGANIC COMPOUNDS										
Organochlorine Pest/PCBs	Water	48 Hrs	8081A *	1 Liter	2 Liter	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
Organochlorine Pest/PCBs	Soil	48 Hrs	8081A *	30 g	8 oz.	Glass	Cold		14 Days	
PCBs Only	Water	48 Hrs	8082	1 Liter	2 Liter	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
PCBs Only	Soil	48 Hrs	8082	30 g	8 oz.	Glass	Cold		14 Days	
PCBs Only	Oil	48 Hrs	8082	1 g	2 oz.	Glass	Cold		14 Days	
Organophosphorus Pesticides	Water	48 Hrs	8141 *	1 Liter	2 Liter	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
Organophosphorus Pesticides	Soil	48 Hrs	8141 *	30 g	8 oz.	Glass	Cold		14 Days	
Chlorinated Herbicides	Water	72 Hrs	8151 *	1 Liter	2 Liter	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
Chlorinated Herbicides	Soil	96 Hrs	8151 *	30 g	8 oz.	Glass	Cold		14 Days	
PNAs (a.k.a. PAHs)	Water	48 Hrs	8310 *	1 Liter	1 liter	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
PNAs (a.k.a. PAHs)	Soil	96 Hrs	8310 *	30 g	4 oz.	Glass	Cold		14 Days	
EDB/DBCP	Water	48 Hrs	8011	1 x	3 x	40 ml VOA	HCl / Cold		14 Days	Must be headspace free
EDB/DBCP	Water	48 Hrs	504.1	1 x	3 x	40 ml VOA	HCl or $Na_2S_2O_3$ / Cold		14 Days	Must be headspace free

***SDWA (500 Series) and CWA (NPDES-600 Series) modified methods are available upon request (e.g. 515.1, 608, 610, & 614)**

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Note: Request 3X - 5X Minimum Quantities for Re-Runs & MS/ MSD

PARAMETER	MATRIX	Min TAT	METHOD	Min. Quant.	Standard Quantity	Container Type	Preserv.	Req'd pH	Holding Time	Additional Sample Receiving Concerns
EXPLOSIVES										
Nitroaromatics & Nitroamines	Water	24 Hrs	8330	350 ml	1 Liter	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
Nitroaromatics & Nitroamines	Soil	48 Hrs	8330	2 g	4 oz.	Glass	Cold		14 Days	
Nitroglycerin and PETN	Water	24 Hrs	8330M	350 ml	1 Liter	Amber Glass	Cold		7 Days	Check for residual chlorine per PM direction
Nitroglycerin and PETN	Soil	48 Hrs	8330M	2 g	4 oz.	Glass	Cold		14 Days	
Perchlorate	Water	24 Hrs	314.0	5 ml	125 ml	Plastic/Glass	Cold		28 Days	
Perchlorate	Soil	24 Hrs	314.0M	4 g	4 oz.	Plastic/Glass	Cold		28 Days	
Nitroguanidine	Water	24 Hrs	PAI SOP	1 x	3 x	40 ml VOA	Cold		7 Days	
Nitroguanidine	Soil	24 Hrs	PAI SOP	2 g	4 oz.	Glass	Cold		14 Days	
Nitrocellulose	Water	48 Hrs	PAI SOP	350 ml	1 Liter	Amber Glass	Cold		7 Days	
Nitrocellulose	Soil	48 Hrs	PAI SOP	2 g	4 oz.	Glass	Cold		14 Days	
RCRA CHARACTERIZATION										
Ignitability	Liquid	24 Hrs	1010	100 ml	500 mL	Amber Glass	Cold		28 Days	
Ignitability	Solid	24 Hrs	1010	100 g	4 oz.	Glass	Cold		28 Days	
Corrosivity/pH	Liquid	24 Hrs	150.1 / 9040	20 ml	250 mL	Plastic/Glass	Cold		ASAP	4 days after receipt
Corrosivity/pH	Solid	24 Hrs	9045	20 g	4 oz.	Plastic/Glass	Cold		ASAP	4 days after receipt
Reactivity-Cyanide & Sulfide	Liquid	24 Hrs	SW 846 7.3.3.2	10 g	250 mL	Amber Glass	Cold		ASAP	4 days after receipt. Must be headspace free. Preservation with NaOH to pH ≥ 12 not recomn
Reactivity-Cyanide & Sulfide	Solid	24 Hrs	SW 846 7.3.3.2	10 g	4 oz.	Amber Glass	Cold		ASAP	4 days after receipt. Must be headspace free.
Paint Filter Liquids	Misc.	24 Hrs	9095		4 oz.	Glass	Cold		14 Days	
TCLP										
Percent Solids Determination	Liquid	24 Hrs	1311	Variable	1Liter	Amber Glass	N/A		7 Days	Consult with PM for volume requirement
Extraction - Volatiles, ZHE	Solid	24 Hrs	1311	5 g	VOC	Glass	Cold		14 Days	Must be headspace free
Extraction - SVOCs & Metals	Solid	24 Hrs	1311	100 g	SV/Metal	Glass	Cold		14 Days	If metals only, 28 Days - Hg / 180 Days
SPLP	Solid	24 Hrs	1312	100 g	SV/Metal	Glass	Cold		14 Days	
VOCs	Leachate	48 Hrs	8260B		100 mL	Glass	Cold		7 Days	
SVOCs	Leachate	4 Days	8270C		100 mL	Glass	Cold		7 Days	
Organochlorine Pesticides	Leachate	72 Hrs	8081A		100 mL	Glass	Cold		7 Days	
Chlorinated Herbicides	Leachate	4 Days	8151A		100 mL	Glass	Cold		7 Days	
8 RCRA Metals	Leachate	48 Hrs	6010B & 7470A		100 mL	Glass	Cold		28-Hg / 180 Days	
METALS										
23 TAL Metals wo/CN (ICP/CVAA)	Water	24 Hrs	CLP SOW	50 ml	1 L	Plastic	$HN0_3$ / Cold	</= 2	180 Days	
23 TAL Metals wo/CN (ICP/CVAA)	Soil	24 Hrs	CLP SOW	50 ml	1 L	Plastic	Cold		180 Days	
ICP	Water	24 Hrs	6010	50 ml	500 ml	Plastic	$HN0_3$ / Cold	</= 2	180 Days	
ICP	Soil	24 Hrs	6010	1 g	4 oz.	Plastic	Cold		180 Days	
Mercury	Water	24 Hrs	7470	20 ml	1 L	Plastic	$HN0_3$ / Cold	</= 2	28 Days	RCRA and TAL metals include ICP and Hg
Mercury	Soil	24 Hrs	7471	0.6 g	4 oz.	Plastic	Cold		28 Days	RCRA and TAL metals include ICP and Hg
Chromium VI	Water	24 Hrs	7196	20 ml	500 ml	Plastic/Glass	Cold		24 Hrs	
Chromium VI	Soil	24 Hrs	7196	4 g	4 oz.	Plastic/Glass	Cold		28 Days	Clients sometimes specify shorter holding time
Chromium VI	Soil	24 Hrs	3060/7196	2.5 g	4 oz.	Plastic/Glass	Cold		30 Days	3060 = Alkaline Digestion. Clients sometimes specify shorter holding time
California Title 22 Metals		24 Hrs	Title 22	N/A	N/A	N/A	N/A			
Citric Acid or DI Water Extraction		24 Hrs	CAL-WET	N/A	N/A	N/A	N/A			
ICP-MS	Either		6020							

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Note: Request 3X - 5X Minimum Quantities for Re-Runs & MS/ MSD

PARAMETER	MATRIX	Min TAT	METHOD	Min. Quant.	Standard Quantity	Container Type	Preserv.	Req'd pH	Holding Time	Additional Sample Receiving Concerns
METALS DIGESTIONS										
Acid Digestion for total Dissolved or Recoverable Metals by ICP	Aqueous	24 Hrs	3005A / 200.2	N/A	N/A	N/A	$HN0_3$ / Cold	</= 2	180 Days	
Acid Digest. for Total Metals (ICP)	Aqueous	24 Hrs	3010A	N/A	N/A	N/A	$HN0_3$ / Cold	</= 2	180 Days	
Acid Digest. For Soils, Sludges, & Sed.	Solids	24 Hrs	3050B	N/A	N/A	N/A	N/A		180 Days	
Acid Digest. For Total Dissolution	Solids	24 Hrs	3050M	N/A	N/A	N/A	N/A		180 Days	
Digest Oil, Grease, or Waxes	Organics	24 Hrs	3050M	N/A	N/A	N/A	N/A		180 Days	
MISCELLANEOUS PARAMETERS/COMPOUNDS										
Alkalinity - Carbonate/Bicarb./Hydroxide	Water	24 Hrs	310.1M	100 ml	500 mL	Plastic/Glass	Cold		14 Days	
Acidity	Water	24 Hrs	305.10	100 ml	500 mL	Plastic/Glass	Cold		14 Days	
Ammonia	Water	24 Hrs	350.1	5 ml	125 mL	Plastic/Glass	H_2SO_4 / Cold	</= 2	28 Days	
Cyanide, Total	Water	24 Hrs	9014 or 335.2	50 ml	500 mL	Plastic/Glass	NaOH / Cold	>/=12	14 Days	
Cyanide, Total	Soil	24 Hrs	9010	1 g	4 oz.	Plastic/Glass	Cold		14 Days	
Cyanide (amenable)	Water	24 Hrs	9010	50 ml	500 mL	Plastic/Glass	NaOH / Cold	>/=12	14 Days	
Cyanide (amenable)	Soil	24 Hrs	9013.00	1 g	4 oz.	Plastic/Glass	Cold		14 Days	
Chloride	Water	24 Hrs	325.3	50 ml	250 mL	Plastic/Glass	Cold		28 Days	
Chloride	Soil	24 Hrs	325.3M	4 g	8 oz.	Plastic/Glass	Cold		28 Days	
Fluoride	Water	24 Hrs	340.2	10 ml	125 mL	Plastic/Glass	Cold		28 Days	
Fluoride	Soil	24 Hrs	340.2M	4 g	4 oz.	Plastic/Glass	Cold		28 Days	
Hardness by Calculation	Water	24 Hrs	6010 / 200.7	50 ml	125 mL	Plastic	Cold		180 Days	
Hydrogen Ion (pH)	Water	24 Hrs	150.1 / 9040	20 ml	125 mL	Plastic/Glass	Cold		ASAP	within 4 days after receipt
Hydrogen Ion (pH)	Soil	24 Hrs	9045	20 g	4 oz.	Plastic/Glass	Cold		ASAP	within 4 days after receipt
IC Anions: Br, Cl, F,SO_4	Water	24 Hrs	300.0/9056	5 ml	500 mL	Plastic/Glass	Cold		28 Days	
IC Anions: NO_2, NO_3, PO_4	Water	24 Hrs	300.0/9056	5 ml	500 mL	Plastic/Glass	Cold		48 Hrs	
Nitrate/Nitrite as N	Water	24 Hrs	353.2	5 ml	125 mL	Plastic/Glass	H_2SO_4 / Cold	</= 2	28 Days	
Nitrate as N	Water	24 Hrs	353.2	5 ml	125 mL	Plastic/Glass	Cold		48 Hrs	A sample must come preserved with H_2SO_4 for NO_2/NO_3
Nitrite as N	Water	24 Hrs	354.1	20 ml	250 mL	Plastic/Glass	Cold		48 Hrs	
Organic Carbon Total - (TOC)	Water	24 Hrs	415.1	1 ml	2 x 125	Amber Glass	acid ** / Cold	</= 2	28 Days	** phosphoric (H_3PO_4) preferred, sulfuric (H_2SO
Organic Carbon Total - (TOC)	Water	24 Hrs	9060	1 ml	2 x 125	Amber Glass	acid ** / Cold	</= 2	28 Days	
Organic Carbon Total - (TOC)	Soil	24 Hrs	Walkley-Black	10 g	4 oz.	Amber Glass	Cold		28 Days	
Percent Moisture	Soil	24 Hrs	PAI SOP	10g	4 oz.	Amber Glass	Cold		14 Days	
Phosphate - Ortho as P	Water	24 Hrs	365.2	25 ml	125 mL	Plastic	Cold		48 Hrs	
Phosphate - Ortho as P	Soil	24 Hrs	365.2M	4 g	4 oz.	Glass	Cold		28 Days	
Phosphorus - Total as P	Water	24 Hrs	365.2	50 ml	250 mL	Plastic	H_2SO_4 / Cold	</= 2	28 Days	
Phosphorus - Total as P	Soil	24 Hrs	365.2M	4 g	4 oz.	Glass	Cold		28 Days	
Sulfide	Water	24 Hrs	376.1	200 ml	500mL	Plastic/Glass	NaOH and ZnOAc / Cold	>/=9	7 Days	
Specific Conductance	Water	24 Hrs	120.1 or 9050	50 ml	250mL	Plastic/Glass	Cold		28 Days	
Total Dissolved Solids (TDS)	Water	24 Hrs	160.1	100 ml	500 mL	Plastic/Glass	Cold		7 Days	
Total Suspended Solids (TSS)	Water	24 Hrs	160.2	100 ml	500 mL	Plastic/Glass	Cold		7 Days	
Total Solids	Water	24 Hrs	160.3	100 ml	500 mL	Plastic/Glass	Cold		7 Days	
Total Volatile Solids	Water	24 Hrs	160.4	100 ml	500 mL	Plastic/Glass	Cold		7 Days	
Total Settleable Solids	Water	24 Hrs	160.5	100 ml	500 mL	Plastic/Glass	Cold		7 Days	
Soil Prep. - (Water Extraction)	Soil	24 Hrs	SW 846 7.3.4.1	10 g	N/A	N/A	Cold		N/A	

ALS - Fort Collins

Note: Request 3X - 5X Minimum Quantities for Re-Runs & MS/ MSD

PARAMETER	MATRIX	Min TAT	METHOD	Min. Quant.	Standard Quantity	Container Type	Preserv.	Req'd pH	Holding Time	Additional Sample Receiving Concerns
RADIOLOGICAL ANALYSES										
Alpha Spectrometry (AS)										
Americium - Isotopic (241)	Water	5 Days	Alpha Isotopic	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Americium - Isotopic (241)	Solid	5 Days	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Curium - Isotopic (242, 243, 244)	Water	5 Days	Alpha Isotopic	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Curium - Isotopic (242, 243, 244)	Solid	5 Days	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Neptunium - Isotopic (237)	Water	5 Days	Alpha Isotopic	2 Liter	2 Liters	Plastic	$HN0_3$	</= 2	N/A	
Neptunium - Isotopic (237)	Solid	5 Days	Alpha Isotopic	4 g	4 oz.	Plastic/Glass	N/A		N/A	
Plutonium - Isotopic (238, 239/240)	Water	3 Days	Alpha Isotopic	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Plutonium - Isotopic (238, 239/240)	Solid	72 Hrs	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Polonium - Isotopic (210)	Water	5 Days	Alpha Isotopic	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Polonium - Isotopic (210)	Solid	5 Days	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Thorium - Isotopic (228, 230, 232)	Water	72 Hrs	Alpha Isotopic	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Thorium - Isotopic (228, 230, 232)	Solid	72 Hrs	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Thorium - Isotopic (224, 228, 230, 232)	Water	5 Days	Alpha Isotopic	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Thorium - Isotopic (224, 228, 230, 232)	Solid	5 Days	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Uranium - Isotopic (233/234, 235, 238)	Water	72 Hrs	Alpha Isotopic	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Uranium - Isotopic (233/234, 235, 238)	Solid	72 Hrs	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Uranium - Total	Water	5 Days	Alpha Isotopic	1 Liter	100 ml	Plastic	$HN0_3$	</= 2	N/A	
Uranium - Total	Solid	5 Days	Alpha Isotopic	2 g	4 oz.	Plastic/Glass	N/A		N/A	
Gamma Spectrometry (GS)										
Gamma Emitters- Stock Library*,**	Water	24 Hrs	901.1	1 Liter	2 Liters	Plastic	$HN0_3$	</= 2	N/A	
Gamma Emitters- Stock Library*,**	Solid	24 Hrs	901.1M	150 g	500 g	Glass	N/A		N/A	
Gross Gamma	Water	24 Hrs	901.1	1 Liter	2 Liters	Plastic	$HN0_3$	</= 2	N/A	
Gross Gamma	Solid	24 Hrs	901.1M	300 g	500 g	Glass	N/A		N/A	
Iron - (55)	Water	5 Days	RESL Fe-01M	1 Liter	2 Liters	Plastic	$HN0_3$	</= 2	N/A	
Iron - (55)	Solid	5 Days	RESL Fe-01M	1 g	5 g	Glass	N/A		N/A	
Nickel - (59)	Water	5 Days	RESL Ni-01M	1 Liter	2 Liters	Plastic	$HN0_3$	</= 2	N/A	
Nickel - (59)	Solid	5 Days	RESL Ni-01M	1 g	5 g	Glass	N/A		N/A	
Ra -226/228(Bi/Pb-214 ingrowth)	Solid	27 Days	901.1M	150 g	500 g	Glass	N/A		N/A	
Ra-226/228 - (Screening)	Solid	48 Hrs	901.1M	150 g	500 g	Glass	N/A		N/A	
Liquid Scintillation Counting (LSC)										
Carbon - (14)	Water	5 Days	PAI SOP	50 ml	1 Liter	Amber	None		N/A	
Carbon - (14)	Solid	5 Days	PAI SOP	1 g	4 oz.	Glass	N/A		N/A	
Tritium	Water	72 Hours	906.0	30 ml	100 ml	Amber	None		N/A	
Tritium - (Water Exchangeable)	Solid	72 Hours	PAI SOP	20 g	4 oz.	Glass	N/A		N/A	
Nickel - (63)	Water	5 Days	PAI SOP	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
Nickel - (63)	Solid	5 Days	PAI SOP	1 g	4 oz.	Either	N/A		N/A	
Plutonium - (241)	Water	5 Days	PAI SOP	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
Plutonium - (241)	Solid	5 Days	PAI SOP	2 g	4 oz.	Either	N/A		N/A	
Radon - (222)	Water	5 Days	PAI SOP	40 ml	3 x	40 ml VOA	None		72 Hrs	Requires approval prior to receipt
Technetium - (99)	Water	72 Hrs	PAI SOP	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	

*** Client specifies Gamma Library: Natural Products (NP), Activation & Fission Products (FA), Combined FANP, or other stock libraries.**
**** Gamma Spec Custom List prices depend on isotopes requested. Isotopes and DQO's will be addressed on a case by case basis.**

ALS - Fort Collins

Note: Request 3X - 5X Minimum Quantities for Re-Runs & MS/ MSD

PARAMETER	MATRIX	Min TAT	METHOD	Min. Quant.	Standard Quantity	Container Type	Preserv.	Req'd pH	Holding Time	Additional Sample Receiving Concerns
Technetium - (99)	Solid	72 Hrs	PAI SOP	1 g	4 oz.	Either	N/A		N/A	
Gas Flow Proportional Counting (GFP)										
Gross Alpha/Beta	Water	24 Hrs	900.0 / 9310	150 ml	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Gross Alpha/Beta (Leach)	Solid	24 Hrs	900.0M / 9310M	3 g	4 oz.	Either	N/A		N/A	
Radium Total Alpha Emitting Isotopes	Water	72 Hrs	903.0 / 9315	500 ml	1 Liter	Plastic	$HN0_3$	</= 2	N/A	Some clients will request as Ra-226
Radium Total Alpha Emitting Isotopes	Solid	5 Days	903.0M / 9315M	1 g	4 oz.	Either	N/A		N/A	Preferred method for solids is Gamma Spec
Radium - (228)	Water	5 Days	904.0 / 9320	1.5 Liter	1.5 Liter	Plastic	$HN0_3$	</= 2	N/A	
Radium - (228)	Solid	5 Days	904.0M / 9320M	1 g	4 oz.	Either	N/A		N/A	Preferred method for solids is Gamma Spec
Iodine - (129)	Water	10 Days	902.0M	2 Liter	1 Liter	Plastic	None		N/A	
Iodine - (129)	Solid	10 Days	902.0M	2 g	4 oz.	Either	N/A		N/A	
Lead - (210)	Water	10 Days	PAI SOP	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Lead - (210)	Solid	10 Days	PAI SOP	1 g	4 oz.	Either	N/A		N/A	
Sr - (90) Total Radiostrontium	Water	72 Hrs	PAI SOP	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Sr - (90) Total Radiostrontium	Solid	72 Hrs	PAI SOP	1 g	4 oz.	Either	N/A		N/A	
Sr - (89/90) (See note below)	Water	15 Days	PAI SOP	1 Liter	1 Liter	Plastic	$HN0_3$	</= 2	N/A	
Sr - (89/90) (See note below)	Solid	15 Days	PAI SOP	1 g	4 oz.	Either	N/A		N/A	
Technetium - (99)	Water	72 Hrs	PAI SOP	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
Technetium - (99)	Solid	72 Hrs	PAI SOP	1 g	4 oz.	Either	N/A		N/A	
EPA Drinking Water Compliance Methodologies										
Gross Alpha and Beta (GFP)	Water	24 Hrs	900.0/9310	150 ml	1 Liter	Either	$HN0_3$	</= 2	N/A	
Gross Alpha Coprecipitation (GFP)	Water	5 Days	901.1	150 ml	1 Liter	Either	$HN0_3$	</= 2	N/A	
Radioiodine (GFP)	Water	5 Days	902.0	2 Liter	1 Liter	Amber	N/A		N/A	
Rn -222 by Alpha-Scintillation (Rn-Emanati	Water	5 Days	913.0	80 ml	3 x VOA	40 ml VOA	N/A		72 Hrs	Requires approval prior to receipt
Ra -226 by Alpha-Scintillation (Rn-Emanati	Water	30 Days	903.1	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
Ra -228 (GFP)	Water	15 Days	904.0	1.5 Liter	1.5 Liter	Either	$HN0_3$	</= 2	N/A	
Tritium by LSC	Water	24 Hrs	906.0	30 ml	1 Liter	Glass	N/A		N/A	
Total Uranium by Alpha Spec.	Water	72 Hrs	STM D3972-90	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
Isotopic Uranium by Alpha Spec.	Water	72 Hrs	STM D3972-90	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
Isotopic Thorium by Alpha Spec.	Water	72 Hrs	STM D3972-90	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
Gamma Spectroscopy	Water	24 Hrs	901.10	1 Liter	1 Liter	Either	$HN0_3$	</= 2	N/A	
SW 846 Compliance Methodologies										
Gross Alpha and Beta	Water	24 Hrs	9310	1 Liter	1 Liter	Either	$HN0_3$	</= 2	180 Days	
Ra-226 by GFP (Total Radium Alph	Water	72 Hrs	9315	1 Liter	1 Liter	Either	$HN0_3$	</= 2	180 Days	
Ra-228 by GFP	Water	10 Days	9320	1 Liter	1 Liter	Either	$HN0_3$	</= 2	180 Days	
Ra-228 by GFP	Soil	10 Days	9320	10g	4 oz.	Either	N/A		180 Days	
ORGANICS SAMPLE CLEAN-UPS & SPECIAL PREPARATIONS										
Alumina Column Clean-up		24 Hrs	3610	N/A	N/A	N/A	N/A		N/A	
Florisil Column Clean-up		24 Hrs	3620	N/A	N/A	N/A	N/A		N/A	
Silica Gel Clean-up		24 Hrs	3630	N/A	N/A	N/A	N/A		N/A	
Gel-Permeation Clean-up		24 Hrs	3640	N/A	N/A	N/A	N/A		N/A	
Sulfur Clean-up		24 Hrs	3660	N/A	N/A	N/A	N/A		N/A	
Sulfuric Acid Clean-up		24 Hrs	3665	N/A	N/A	N/A	N/A		N/A	
Waste Dilution	Both	24 Hrs	3580	N/A	N/A	N/A	N/A		N/A	

ALS - Fort Collins

Note: Request 3X - 5X Minimum Quantities for Re-Runs & MS/ MSD

PARAMETER	MATRIX	Min TAT	METHOD	Min. Quant.	Standard Quantity	Container Type	Preserv.	Req'd pH	Holding Time	Additional Sample Receiving Concerns
*** Sample clean-up may be included in the full analysis cost. Inquire for specifics.**										
Ex. Gel Permeation clean-ups are not universally/routinely performed for SW846 8270.										
ORGANICS SAMPLE EXTRACTIONS										
Separatory Funnel Liquid-Liquid Ext	Water	24 Hrs	3510	N/A	N/A	N/A	N/A		N/A	
Continuous Liquid-Liquid Ext.	Water	24 Hrs	3520	N/A	N/A	N/A	N/A		N/A	
Soxhlet Extraction	Solid	24 Hrs	3540	N/A	N/A	N/A	N/A		N/A	
Sonication Extraction	Solid	24 Hrs	3550	N/A	N/A	N/A	N/A		N/A	
Purge and Trap	Both	24 Hrs	5030	N/A	N/A	N/A	N/A		N/A	
Purge and Trap	Both	24 Hrs	5035	N/A	N/A	N/A	N/A		N/A	

*** Sample extraction costs are included in the full analysis cost. Items listed here are for preparation only requests.**

ADDITIONAL SERVICES

Rush Turn-Around Times
Typical Sample Kits are included at no additional charges: Bottles, coolers, preservatives, labels, and coolant.
Electronic Data Deliverables
Analysis of Hazardous and Mixed Waste Samples
Analysis of Sediments and Tissues
Analysis of Air Filters
On-Site Laboratory Services
Subcontracting of Specialty Analyses: Dioxins, Asbestos, Microscopy, & tests not listed above
Special Methods or Detection Limits
Specialty Method Development
Sample and Waste Disposal
Open for Saturday Sample Receipt

GENERAL NOTES

Typical Rush Turnaround Time (TAT) Surcharges **:
2.5X for Minimum TAT.
2X for Minimum TAT + 1 Business Day
1.75X for Minimum TAT + 2-3 Business Days
1.5X for Minimum TAT + 5 Business Days
1.25X for Minimum TAT + 10 Business Days

**** TATs are based on faxed sample results-within times determined as business days from sample receipt. (Sat. Delivery = Mon Rcpt.)**
Rush TATs should be requested at least 1 week before sample delivery and need Laboratory approval before sample receipt.

Volume Discounts are available upon request. Typical Discounts are: 20% for >10 sample SDGs or more for large projects
Payments are due within 30 days of invoice receipt, with 1.5% per month charges on late balances. Prompt payment discounts are 2%10 Net 30.
Samples received with short sample hold times, (3 business days or less), will accrue a 50% rush surcharge. Short hold time tests (<3 d) are exempt.
Subcontract analysis surcharges: "Invoicing Only" for 10% surcharge; Shipping & handling to sub-lab for 20%; PAI Reports for 30%-50%.
Typical Sample Kits must be requested at least 3 bus. days before Delivery Date, or rush shipping charges will apply. Un-returned supplies are available & billable at: materials cost + shipping costs + 20% handling.

ALS - Fort Collins

Note: Request 3X - 5X Minimum Quantities for Re-Runs & MS/ MSD

PARAMETER	MATRIX	Min TAT	METHOD	Min. Quant.	Standard Quantity	Container Type	Preserv.	Req'd pH	Holding Time	Additional Sample Receiving Concerns

Small Batches, < 5 samples, incur the greater of a $250 minimum or 5 sample charge, due to Method QC Reqmts. (Blanks, MS/MSDs, & LCS/LCSDs).
(Small Batch surcharges may be waived for large projects.)
Special Reporting Limits are available for additional costs.
Special Requirements raised after project initiation will typically incur additional surcharges of 5% - 30%:
Ex: TICs, special Detection Limits, extra report copies, EDDs, special reporting forms, multiple re-runs for dilutions, etc.

Radioactive Samples will typically incur a 25% Health and Safety Surcharge for:
Alpha > 1 nCi/L or 0.5 nCi/g;
Beta > 2 nCi/L or 1 nCi/g;
H-3 > 100 nCi/L or 1 nCi/g;
Gamma > 2 nCi/L or 1 nCi/g;

Note: *Radioactive samples require lab approval before receipt.*
Note: *Mixed waste or hazardous samples require special disposal costs or return costs and prior lab approval.*

Appendix D

Condition of Sample Upon Receipt (Form 201)

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

1. Does this project require any **special handling** in addition to standard Paragon procedures?		YES	**NO**
2. Are custody **seals** on **shipping containers** intact?	NONE	**YES**	NO
3. Are Custody seals on **sample containers** intact?	**NONE**	YES	NO
4. Is there a **COC (Chain-of-Custody) present** or other representative documents?		**YES**	NO
5. Are the **COC and bottle labels complete and legible**?		**YES**	NO
6. Is the **COC in agreement** with samples received? (IDs, dates, times, no. of samples, no. of containers, matrix, requested analyses, etc.)		**YES**	NO
7. Were **airbills / shipping documents** present and/or removable?	DROP OFF	**YES**	NO
8. Are all aqueous **samples requiring preservation preserved correctly?** (excluding volatiles)	N/A	**YES**	NO
9. Are all aqueous **non-preserved samples pH 4-9**?	N/A	**YES**	NO
10. Is there **sufficient sample** for the requested analyses?		**YES**	NO
11. Were all samples placed in the **proper containers** for the requested analyses?		**YES**	NO
12. Are all samples within **holding times** for the requested analyses?		**YES**	NO
13. Were all sample containers received **intact**? (not broken or leaking, etc.)		**YES**	NO
14. Are all samples requiring no headspace (VOC, GRO, Rx CN/S, radon), headspace free? **Size of bubble**: ____ < green pea ____> green pea	N/A	**YES**	NO
15. Were samples checked for and free from the presence of **residual chlorine?** (Applicable when PM has indicated samples are from a chlorinated water source; note if field preservation with sodium thiosulfate was not observed.)	**N/A**	YES	NO
16. Were the samples **shipped on ice**?		**YES**	NO
17. Were cooler temperatures measured at 0.1-6.0°C? **IR gun used*: #2 #4**	RAD ONLY	YES	NO

Cooler #:								
Temperature (°C):								
No. of custody seals on cooler:								
DOT Survey/ Acceptance Information — External µR/hr reading:								
Background µR/hr reading:								

Were external µR/hr readings ≤ two times background and within DOT acceptance criteria? **YES / NO / NA** (If no, see Form 008.)

Additional Information: PROVIDE DETAILS BELOW FOR A NO RESPONSE TO ANY QUESTION ABOVE, EXCEPT #1 AND #16

If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

*IR Gun #2: Oakton, SN 29922500201-0066 *IR Gun #4: Oakton, SN 2372220101-0002

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

Additional Information:

Was the laboratory directed to proceed with the analysis of any samples yielding the presence of residual chlorine? **YES / NO / NA**

NOTE:

No pH adjustments shall be made without prior consent of Project Manager. After pH adjustments, hold metals and radchem samples ≥ 24 hrs. before analysis.

Was the pH of any sample adjusted by the laboratory? **YES** (See Table below) / **NO**

pH Excursion:

Paragon Sample ID	Client Sample ID	Initial pH	Final pH	Reagent Used	Volume Added (mL)	Lot No. of Reagent	Requested Analysis	Initials / Date / Time

If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

Additional Information:

If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

NOTE:

No pH adjustments shall be made without prior consent of Project Manager. After pH adjustments, hold metals and radchem samples ≥ 24 hrs. before analysis.

Was the pH of any sample adjusted by the laboratory? **YES** (See Table below) / **NO**

pH Excursion:

Paragon Sample ID	Client Sample ID	Initial pH	Final pH	Reagent Used	Volume Added (mL)	Lot No. of Reagent	Requested Analysis	Initials / Date / Time

If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

Additional Information:

Sample ID Discrepancy:

	COC Information				Bottle Information			
Paragon Sample ID	Client Sample ID	Date	Time	Analysis	Bottle ID	Date	Time	Analysis

If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

Additional Information:

Headspace:

Paragon Sample ID	Client Sample ID	Requested Analyses	Temperature °C	Cooler Number

If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

Additional Information:

Temperature Excursion:

Paragon Sample ID	Client Sample ID	Requested Analyses	Temperature °C	Cooler Number

If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

CONDITION OF SAMPLE UPON RECEIPT FORM **ALS - Fort Collins**

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

Additional Information:

_____

Sample Weight:

Paragon Sample ID	Client Sample ID	Requested Analyses	Approximate Volume	Units

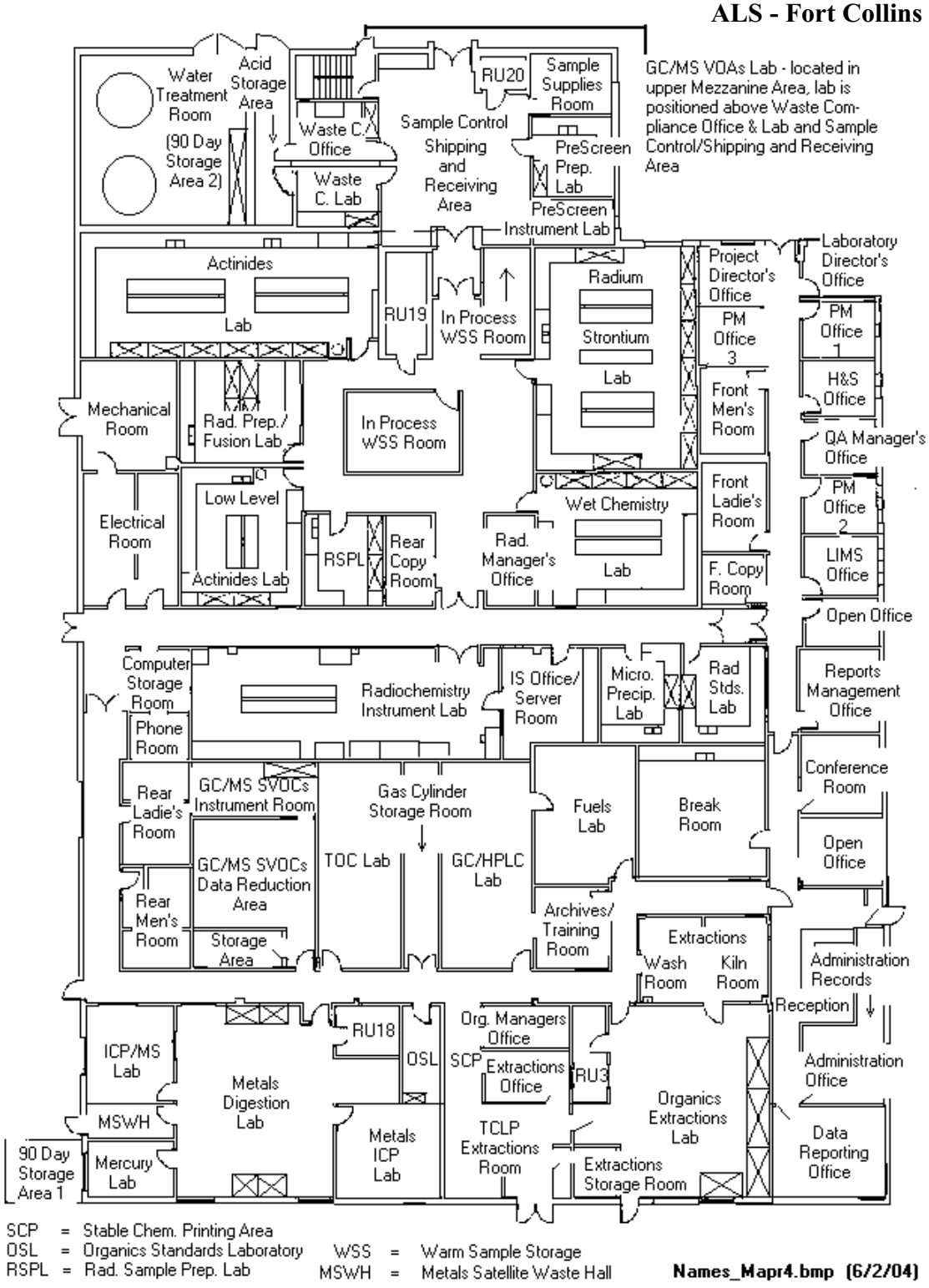
If applicable, was the client contacted? **YES / NO / NA** Contact: _____ Date/Time: _____

Project Manager Signature / Date: _____

Appendix E

Facility Diagram

ALS - Fort Collins



SCP = Stable Chem. Printing Area
OSL = Organics Standards Laboratory
RSPL = Rad. Sample Prep. Lab
WSS = Warm Sample Storage
MSWH = Metals Satellite Waste Hall

Names_Mapr4.bmp (6/2/04)

Appendix F

Nonconformance Report
(Example)

ALS Laboratory Group
ANALYTICAL CHEMISTRY & TESTING SERVICES

NCR #: 10463

PARAGON ANALYTICS
225 Commerce Drive ◆ Fort Collins, CO 80524 ◆ (800) 443-1511 ◆ (970) 490-1511 ◆ FAX (970) 490-1522

CONTROLLED
NON-CONFORMANCE REPORT

Non-Conformance

Initiated By: Lance R. Steere on 2/28/2008

Event Type: Method Requirements Not Met -- HTV

Event Explanation: Samples in these 5 WO's generally received with only 1-2 hours of hold time remaining. By the time they are delivered to the Wetchem lab, most of the hold times have expired. The lab was notified in all cases that samples were expected, and analysis commenced very soon after samples deleivered to the analysts. Morning sampling certainly challenges our ability to meet 24 hr hold times.

Action To Prevent Reccurence: N/A - see comments in explanation

Corrective Action

Corrective Action: Document in Narrative
Department Manager Approval: Deb Scheib
Approval Date: 2/29/2008
Corrective Action Comments:

Workorders Affected

Workorder -- Procedure		Approved By	Approval Date
0802004 -- SW7196	candy Friday was contacted on 2/28/2008	Lance R. Steere	2/28/2008
0802023 -- SW7196			
0802035 -- SW7196			
0802053 -- SW7196			
0802067 -- SW7196			

There Are No Associated Batches

NCR Approval

Project Manager Approval: LRS on 2/28/2008
Department Manager Approval: Deb Scheib on 2/29/2008
QA Manager Approval: Deb Scheib on 2/29/2008

Date Printed: Friday, February 29, 2008

Appendix G

Laboratory Equipment

Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (tower)	Ortec	Tower	N/A	RAD - Room 151	1996	Used	Service Contract
Alpha Spectrometer (tower)	Ortec	Tower	N/A	RAD - Room 151	1996	Used	Service Contract
Autosampler (Gas Chromatograph)	Hewlett Pac	18596B	3333A32917	GC - Room 132	1996	Used	Service Contract
Autosampler (Gas Chromatograph)	Hewlett Pac	18596B	3021A22050	GC - Room 132	1996	Used	Service Contract
Autosampler (Gas Chromatograph)	Hewlett Pac	18596A	2718A04983	GC - Room 132	1996	Used	Service Contract
Autosampler (Gas Chromatograph)	Hewlett Pac	18596B	3123A25278	GC - Room 132	1996	Used	Service Contract
Autosampler (Gas Chromatograph)	Hewlett Pac	18596B	3213A28142	Fuels - Room 135	1996	Used	Service Contract
Autosampler (Gas Chromatograph)	Hewlett Pac	18596A	2718A06165	GC - Room 132	1996	Used	Service Contract
Autosampler (Gas Chromatograph)	Hewlett Pac	18596A	2718A08628	SVOCs - Room 144	1996	Used	Service Contract
Autosampler (Gas Chromatograph), Purge and Trap	OI Corporati	MPM - 16 R - B	5017 - 9 - 027	Fuels - Room 131	1996	Reconditioned	Service Contract
Autosampler (Gas Chromatograph), Purge and Trap	Tekmar	14 - 2962 - 000	92051006	Fuels - Room 131	1996	Used	Service Contract
Autosampler (Gas Chromatograph), Purge and Trap	Tekmar	14 - 2963 - 000	92048014	Fuels - Room 131	1996	Used	Service Contract
Autosampler (Gas Chromatograph), Purge and Trap	Tekmar	ALS 2016	90052027	VOAs - Room 201	1996	Used	Service Contract
Autosampler (Gas Chromatograph), Purge and Trap (Archon)	Varian	Archon	12986	VOAs - Room 201	1999	New	Service Contract
Autosampler (Gas Chromatograph), Purge and Trap (Archon)	OI Corporati	4552	13833	VOAs - Room 201	2003	Reconditioned	Service Contract
Autosampler (IC anions analysis)	Dionex	AS40 - 1	99100054	Wet Chem	2004	Used	Outside Vendor
Autosampler (IC perchlorate analysis)	Dionex	AS40 - 1	99080031	Wet Chem	2004	Used	Outside Vendor
Autosampler (ICP axial trace)	Thermo Jarr	AS300	0780	Metals - Room 138	2004	Reconditioned	Service Contract
Autosampler (ICP radial conventional)	Thermo Jarr	AS300	C2392	Metals - Room 138	2004	Reconditioned	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	18594A	2835A12486	GC - Room 132	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	18594B	3214A28233	Fuels - Room 135	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	18594A	2929A15028	GC - Room 132	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	18594B	3334A33050	GC - Room 132	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	18594B	3018A22087	GC - Room 132	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	G1512A	CN00001367	SVOCs - Room 144	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	18594A	2835A12252	SVOCs - Room 144	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Hewlett Pac	18594B	3113A25745	GC - Room 132	1996	Used	Service Contract
Autosampler Controller (Gas Chromatograph)	Tekmar	LSC 2000	90080005	VOAs - Room 201	1996	New	Service Contract

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Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Autosampler Gas Chromatograph (MS)	Hewlett Pac	18596C	3512A41637	SVOCs - Room 144	1996	Used	Service Contract
Autosampler Gas Chromatograph (MS)	Hewlett Pac	7683	US91304815	SVOCs - Room 144	1996	Used	Service Contract
Autosampler Gas Chromatograph (MS)	Hewlett Pac	7683	US92805616	SVOCs - Room 144	1996	Used	Service Contract
Balance, Analytical	Mettler	AE200	N23692	Room 154	1996	Used	Outside Vendor
Balance, Analytical	Scientech	ZSA210	18901	RAD - Room 161	2006	New	Outside Vendor
Balance, Analytical	Mettler	AE100	NO1256	Wet Chem	1996	Used	Outside Vendor
Balance, Analytical	Mettler	AE50	N19696	Room 172	1996	Used	Outside Vendor
Balance, Analytical	Sartorious	AC211S	70605621	RAD - Room 163	1996	Used	Outside Vendor
Balance, Analytical	Mettler	AE200	N42207	RAD - Room 158	1996	Used	Outside Vendor
Balance, Analytical	Mettler	AB204	1117030900	RAD - Room 161	2004	Used	Outside Vendor
Balance, Laboratory	Sartorious	BA110S	20404145	Metals	1996	Used	Outside Vendor
Balance, Laboratory	Sartorious	PT150	70204290	VOAs - Room 201	1996	Used	Outside Vendor
Balance, Laboratory	Sartorious	PT120	20420557	RAD - Room 131	1996	Used	Outside Vendor
Balance, Laboratory	Sartorious	PT120	10720694	RAD - Room 161	1996	Used	Outside Vendor
Balance, Laboratory	A&D Weighi	GX-200	146529073	Metals	2005	New	Outside Vendor
Balance, Laboratory	Sartorious	A200S	38040253	EXT - Room 134	1996	Used	Outside Vendor
Balance, Laboratory	Sartorious	B410	38060012	EXT - Room 134	1996	Used	Outside Vendor
Balance, Laboratory	Sartorious	B410	10204728	EXT - Room 134	1996	Used	Outside Vendor
Balance, Laboratory	A&D Weighi	GX-300	146520485	Metals	2005	New	Outside Vendor
Balance, Laboratory	A&D Weighi	GX-300	146520486	Metals	2005	New	Outside Vendor
Balance, Toploading	Mettler	BB600	N50359	RAD - Room 162	1996	Used	Outside Vendor
Balance, Toploading	Mettler	B3002	1117472815	Room 154	1996	Used	Outside Vendor
Balance, Toploading	Sartorious	BA4100	30504754	Room 172	1996	Used	Outside Vendor
Balance, Toploading	Mettler	BB - 3000	N43426	RAD - Room 161	1996	Used	Outside Vendor
Balance, Toploading	Mettler	BB1200	M93676	Wet Chem	1996	Used	Outside Vendor
Balance, Toploading	Mettler	BD601	60183	RAD - Room 163	1996	Used	Outside Vendor
Balance, Toploading	Mettler	PB3002	P00572	RAD - Room 158	1996	Used	Outside Vendor
Balance, Toploading	Mettler	BB600	N50358	RAD - Room 164	1996	Used	Outside Vendor
Balance, Toploading	Mettler	BB300	N08587	Wet Chem	1996	Used	Outside Vendor
Centrifuge	Sorvall	Legend T	40534517	RAD - Room 161	2005	Used	Outside Vendor
Centrifuge	Sorvall	Legend T	40461622	RAD - Room 161	2005	Used	Outside Vendor
Centrifuge	Sorvall	Legend T	40513965	RAD - Room 158	2005	Used	Outside Vendor
Centrifuge	Sorvall	Legend T	40534516	RAD - Room 161	2005	Used	Outside Vendor
Centrifuge	Beckman	GP	9D064	RAD - Room 158	1996	Used	Outside Vendor
Centrifuge	Sorvall	Legend T	40461621	RAD - Room 161	2005	Used	Outside Vendor
Centrifuge	Sorvall	Legend T	40534518	RAD - Room 161	2005	Used	Outside Vendor

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Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Centrifuge	Beckman	GS - 6	GA92M22	RAD - Room 161	1996	Used	Outside Vendor
Centrifuge	Fisher Scie	Z510 (D-7209)	17910073	EXT - Room 134	1996	Used	Outside Vendor
Centrifuge	Beckman	GP	(not readily available)	RAD - Room 161	1996	Used	Outside Vendor
Chiller, Recirculating	Neslab Instr	CFT 75	293223132	EXT - Room 134	1996	Used	Outside Vendor
Chiller, Recirculating	Neslab Instr	CFT 75	89EMI-99780-9	EXT - Room 134	1996	Used	Outside Vendor
Computer	Compaq	Deskpro	6907 CL92B141	EXT - Room 134			
Computer	Dell	0932RV	00045-488-495-656	VOAs - Room 201			
Computer, Data System w/instrument card	Compaq	Deskpro	(See IS Records)	RAD - Room 151			
Computer, Data System w/instrument card	Hewlett Pac	Vectra VI	US71264309	HPLC - Room 135			
Computer, Data System w/instrument card	Compaq	Deskpro	6733BK62T966	Fuels - Room 135			
Computer, Data System w/instrument card	Hewlett Pac	Vectra	(See IS Records)	Metals			
Computer, Data System w/instrument card	Compaq	Deskpro	(See IS Records)	RAD - Room 151			
Computer, Data System w/instrument card	Dell	09D224	00019-098-720-657	VOAs - Room 201			
Computer, Data System w/instrument card	Hewlett Pac	5/200 MMX Series 4	US82306675	VOAs - Room 201			
Computer, Data System w/instrument card	Gateway	P5 - 120	(See IS Records)	RAD - Room 151			
Computer, Data System w/instrument card	Dell	Optiplex GX150	(See IS Records)	SVOCs - Room 144			
Computer, Data System w/instrument card	Hewlett Pac	Kayak XA	US92581734	SVOCs - Room 144			
Computer, Data System w/instrument card	Hewlett Pac	Kayak XA	US94359455	SVOCs - Room 144			
Computer, Data System w/instrument card	Compaq	Deskpro	(See IS Records)	RAD - Room 151			
Computer, Data System w/instrument card	Compaq	DP2000 5200MMX	6733BK62V012	VOAs - Room 201			
Computer, Data System w/instrument card	Compaq	Deskpro	(See IS Records)	HPLC - Room 135			
Computer, Data System w/instrument card	PERiCom	(not readily available)	027297	Metals			
Computer, Data System w/instrument card	Hewlett Pac	Vectra	US14607342	Metals			
Computer, Data System w/instrument card	Compaq	Deskpro	6686HVR5S060	Fuels - Room 131			
Computer, Data System w/instrument card	Compaq	Prolinea 5100	(See IS Records)	GC - Room 132			
Computer, Data System w/instrument card	Dell	Optiplex G1	(See IS Records)	Wet Chem			
Computer, Data System w/instrument card	Hewlett Pac	Vectra VI	US80101974	HPLC - Room 135			
Computer, Data System w/instrument card	Compaq	Prolinea 5100	6608HXQ2P583	GC - Room 132			
Computer, Data System w/instrument card	Compaq	Prolinea 5100	(See IS Records)	Wet Chem			
Concentrator (Gas Chromatograph), Purge & Trap	OI Analytica	OI - 4560	J609460598	Fuels - Room 131	1999	New	Service Contract
Concentrator (Gas Chromatograph), Purge & Trap	Tekmar	LSC 3000	3548A10477	Fuels - Room 131	2005	Reconditioned	Service Contract
Concentrator (Gas Chromatograph), Purge & Trap	OI Corporati	4560	J426460287	VOAs - Room 201	1996	Used	Service Contract
Concentrator (Gas Chromatograph), Purge & Trap	Tekmar	3000	95132004	VOAs - Room 201	2003	Reconditioned	Service Contract
Concentrator, RapidVap	Labconco	79100-00	246646	EXT - Room 134	1996	Used	Outside Vendor
Concentrator, RapidVap	Labconco	79100-00	246530	EXT - Room 134	1996	Used	Outside Vendor
Concentrator, RapidVap	Labconco	79100-00	246529	EXT - Room 134	1996	Used	Outside Vendor

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Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Cyanide Distillation Apparatus	BSL Co.	Midi-10	MCVA 129726	Wet Chem	1996	Used	In House
Cyanide Distillation Apparatus	Andrew Gla	11-10-R	A4R0609	Wet Chem	1996	Used	In House
Dessicators	Various	Various	Various	Labwide	1996	Used	In-House
Detector, Gas Chromatograph (MS)	Hewlett Pac	5973	US10451306	VOAs - Room 201	2003	Reconditioned	Service Contract
Detector, Gas Chromatograph (MS)	Hewlett Pac	5973	US80210987	SVOCs - Room 144	1996	Used	Service Contract
Detector, Gas Chromatograph (MS)	Hewlett Pac	5973	US91911895	SVOCs - Room 144	1996	Used	Service Contract
Detector, Gas Chromatograph (MS)	Hewlett Pac	5971A	3188A03493	VOAs - Room 201	1996	Used	Service Contract
Detector, Gas Chromatograph (MS)	Hewlett Pac	5971A	2749A00096	VOAs - Room 201	1996	New	Service Contract
Detector, Gas Chromatograph (MS)	Hewlett Pac	5973	US93112105	SVOCs - Room 144	1996	Used	Service Contract
Evaporator, Nitrogen	Organomati	120	6031	EXT - Room 134	1996	Used	Outside Vendor
Evaporator, Steam	Organomati	115	9250	EXT - Room 134	1996	Used	Outside Vendor
Extractor, Zero Headspace (10)	Assoc. Desi	3745 ZHE	varies	EXT - Room 134	1996	Used	In-House
Flow Injection Analyzer (Automated NO2/NO3, NH3)	Lachat	QuickChem 8000	A83000 - 642	Wet Chem	2000	Reconditioned	Outside Vendor
Freezer	Frigidaire	UFD - 14 - 64	39UB7828	Fuels - Room 135	2004	Used	Outside Vendor
Freezer	Residential	(not readily available)	(not readily available)	Sample Control	1996	Used	Outside Vendor
Freezer	Kenmore	253.9289112	WB94413689	VOAs - Room 201	2004	Used	Outside Vendor
Freezer	Frigidaire	FRU17B2JW9	WA43200842	VOAs - Room 201	2004	Used	Outside Vendor
Freezer	Frigidaire	FRU17B2JW8	WA42601180	VOAs - Room 201	2004	Used	Outside Vendor
Freezer	Frigidaire	FFU09K0AW2	WB22434917	VOAs - Room 201	2002	Used	Outside Vendor
Freezer	Montgomer	49258	(not readily available)	EXT - Room 134	2004	Used	Outside Vendor
Freezer	Residential	(not readily available)	(not readily available)	EXT - Room 134	1996	Used	Outside Vendor
Gamma Spectrometer	EG&G Orte	LS - 1116	892 - 106	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	1092 - 111	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	1092 - 113	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	892 - 105	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	892 - 107	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	992 - 108	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	1092 - 112	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	992 - 110	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	792 - 104	RAD - Room 151	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	694 - 123	RAD - Room 173	1996	Used	Service Contract
Gamma Spectrometer	EG&G Orte	LS - 1116	992 - 108	RAD - Room 151	1996	Used	Service Contract
Gas Chromatograph (Dual ECD)	Hewlett Pac	5890 Series II	2750A18841	GC - Room 132	1996	Used	Service Contract
Gas Chromatograph (Dual ECD)	Hewlett Pac	5890 Series II	3310A49739	GC - Room 132	1996	Used	Service Contract
Gas Chromatograph (Dual ECD)	Hewlett Pac	5890 Series II	3310A47805	GC - Room 132	1996	Used	Service Contract
Gas Chromatograph (Dual ECD)	Hewlett Pac	5890 Series II	3029A30072	GC - Room 132	1996	Used	Service Contract

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Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Gas Chromatograph (Dual FPD)	Hewlett Pac	5890A	2750A19027	GC - Room 132	1996	Used	Service Contract
Gas Chromatograph (FID)	Hewlett Pac	5890A	3121A35609	Fuels - Room 135	1996	Used	Service Contract
Gas Chromatograph (MS)	Hewlett Pac	5890 Series II	3336A51352	VOAs - Room 201	1996	Used	Service Contract
Gas Chromatograph (MS)	Hewlett Pac	6890	US10226006	VOAs - Room 201	2003	Reconditioned	Service Contract
Gas Chromatograph (MS)	Hewlett Pac	6890	US00029580	SVOCs - Room 144	1996	New	Service Contract
Gas Chromatograph (MS)	Hewlett Pac	6890	US00040094	SVOCs - Room 144	2001	New	Service Contract
Gas Chromatograph (MS)	Hewlett Pac	5890 Series II	3019A28661	VOAs - Room 201	1996	New	Service Contract
Gas Chromatograph (MS)	Hewlett Pac	6890	US00031554	SVOCs - Room 144	1996	Used	Service Contract
Gas Chromatograph (PID/FID)	Hewlett Pac	5890	2750A18840	Fuels - Room 131	1996	Used	Service Contract
Gas Chromatograph (PID/FID)	Hewlett Pac	5890	2443A03716	Fuels - Room 131	1996	Reconditioned	Service Contract
Gas Flow Proportional Counter	Tennelec	LB - 4110	43727	RAD - Room 151	1996	Reconditioned	Service Contract
Gas Flow Proportional Counter	Tennelec	LB - 5100	13923 (A)	RAD - Room 173	1996	Used	Service Contract
Gas Flow Proportional Counter	Tennelec	LB - 5100	13923 (B)	RAD - Room 173	1998	Reconditioned	Service Contract
Gas Flow Proportional Counter	Tennelec	LB - 4110	CR (13923)	RAD - Room 151	1996	Reconditioned	Service Contract
GPC (Gel Permeation Cleanup) Apparatus	OI Corporati	Autoprep 1000	9459SI	EXT - Room 134	2000	Reconditioned	Service Contract
Health Physics Equipment - Electra (alpha/beta meter)	NE Technol	12	134 - 1998	Room 168	1999	New	Outside Vendor
Health Physics Equipment - Electra (alpha/beta meter)	NE Technol	123	919 - 634	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - Electra (alpha/beta meter)	NE Technol	12	456 - 631	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - Electra (alpha/beta meter)	NE Technol	12	918 - 628	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - Electra (alpha/beta meter)	NE Technol	123	914 - 604	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - gamma dose rate meter	Ludlum	3	96160	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - gamma dose rate meter	Ludlum	192	136517	Sample Control	2002	New	Outside Vendor
Health Physics Equipment - gamma dose rate meter	Ludlum	19	89429	Sample Control	1996	Used	Outside Vendor
Health Physics Equipment - gamma dose rate meter	Ludlum	3	93958	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - Hand & Foot Monitor	Berthold	LB - 1043AS	80117	North Hall	1996	Used	Outside Vendor
Health Physics Equipment - Hand & Foot Monitor	Berthold	LB - 1043AS	111115 - 1310	South Hall	1996	Used	Outside Vendor
Health Physics Equipment - Pancake G-M (detector)	Ludlum	177	100213	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - Pancake G-M (detector)	Ludlum	177	94708	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - Pancake G-M (detector)	Ludlum	177	100195	Room 168	1996	Used	Outside Vendor
Health Physics Equipment - Shielded G-M (detector)	Ludlum	177	69733	Room 168	1996	Used	Outside Vendor
Heating Block	Enviro - Exp	Hot Block SZ154	3703CEC1779	RAD - Room 162	1996	Used	Outside Vendor
Heating Block	Enviro - Exp	Hot Block SZ100-	145CEC0366	RAD - Room 162	1996	Used	Outside Vendor
Heating Mantles (30 total)	Glas - Col	TM106	varies	EXT - Room 134	1996	Used	In House
Heating Mantles (6 total)	Electromant	MX	varies	RAD - Room 158	1996	Used	In House
Heating Mantles, 6 place (4 total)	Glas - Col	not readily available)	varies	RAD - Room 163	1996	Used	In House
Heating Mantles, 6 place (7 banks)	Glas - Col	not readily available)	varies	EXT - Room 134	1996	Used	In House

Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
High Performance Liquid Chromatograph, Autosampler	Hewlett Pac	Series 1050	3123A25526	HPLC - Room 135	1998	Reconditioned	Service Contract
High Performance Liquid Chromatograph, Autosampler	Waters	712 Wisp	71S - 001504	HPLC - Room 135	1996	Used	Service Contract
High Performance Liquid Chromatograph, Autosampler Brack	Hewlett Pac	29855A	3141A01648	HPLC - Room 135	1998	Reconditioned	Service Contract
High Performance Liquid Chromatograph, Controller	Waters	600E	6PLEPF380	HPLC - Room 135	1996	Used	Service Contract
High Performance Liquid Chromatograph, Fluorescence Dete	Waters	M470	470 - 002748	HPLC - Room 135	1996	Used	Service Contract
High Performance Liquid Chromatograph, Fluorescence Dete	Waters	420 - C	420 - 014858	HPLC - Room 142	1996	Used	Service Contract
High Performance Liquid Chromatograph, Fluorescence Dete	Waters	M420 - E	420 - 014858	HPLC - Room 142	1996	Used	Service Contract
High Performance Liquid Chromatograph, Fluorescence Dete	Waters	M490	490 - 005479	HPLC - Room 135	1996	Used	Service Contract
High Performance Liquid Chromatograph, Photodiode Array	Hewlett Pac	HP 1090	2427A00184	HPLC - Room 135	1997	Reconditioned	Service Contract
High Performance Liquid Chromatograph, Pump	Hewlett Pac	79852A	3405A02747	HPLC - Room 135	1998	Reconditioned	Service Contract
High Performance Liquid Chromatograph, Pump	Waters	Waters 600	600PF4091	HPLC - Room 135	1996	Used	Service Contract
High Performance Liquid Chromatograph, System Controller	Hewlett Pac	79856A	3114A00835	HPLC - Room 135	1998	Reconditioned	Service Contract
High Performance Liquid Chromatograph, UV Detector	Hewlett Pac	(not readily available)	3225J00991	HPLC - Room 135	1998	Reconditioned	Service Contract
Hood, Fume	Labconco	70700	33178	SVOCs - Room 144	2004	Used	In House
Hood, Fume	Labconco	(not readily available)	(not readily available)	HPLC - Room 135	2004	Used	In House
Hot Plate/Stir Plate (approx 60 total)	Thermolyne	varies	varies	Labwide	various	New	In House
Ignitability Apparatus	Pensky - M	89571	n/a	EXT - Room 134	1996	Used	In House
Inductively Coupled Plasma (ICP) - axial (trace)	Thermo Jarr	1342900	336490	Metals - Room 138	1996	Used	Service Contract
Inductively Coupled Plasma (ICP) - axial (trace)	Thermo Jarr	1342900	338590	Metals - Room 138	2006	Used	Service Contract
Inductively Coupled Plasma (ICP)/MS	Micromass	Platform ICP	WA057	Metals - Room 141	2004	Reconditioned	Service Contract
Infrared (IR) Temperature Gun	Raytek	Raynger ST	2992250201 - 0066	Sample Control	2004	New	Outside Vendor
Infrared (IR) Temperature Gun	Oakton	InfraPro	2372220101 - 0002	Sample Control	2000	New	Outside Vendor
Infrared (IR) Temperature Gun	Raytek	Raynger ST	2672490101 - 0045	RAD - Room 163	2000	New	Outside Vendor
Injector, (Gas Chromatograph)	Hewlett Pac	18593B	3120A26649	GC - Room 132	1996	Used	Service Contract
Injector, (Gas Chromatograph)	Hewlett Pac	18593B	3013A22331	GC - Room 132	1996	Used	Service Contract
Injector, (Gas Chromatograph)	Hewlett Pac	18593B	3013A22314	Fuels - Room 135	1996	Used	Service Contract
Injector, (Gas Chromatograph)	Hewlett Pac	18593A	2837A10891	GC - Room 132	1996	Used	Service Contract
Injector, (Gas Chromatograph)	Hewlett Pac	18593B	3120A26648	GC - Room 132	1996	Used	Service Contract
Injector, (Gas Chromatograph)	Hewlett Pac	18593B	3120A26692	SVOCs - Room 144	1996	Used	Service Contract
Injector, (Gas Chromatograph)	Hewlett Pac	18593A	2923A13890	GC - Room 132	1996	Used	Service Contract
Injector, Gas Chromatograph (MS)	Hewlett Pac	7683	US92908296	SVOCs - Room 144	1996	Used	Service Contract
Injector, Gas Chromatograph (MS)	Hewlett Pac	7683	US83902505	SVOCs - Room 144	1996	Used	Service Contract
Injector, Gas Chromatograph (MS)	Hewlett Pac	G1513A	US00000603	SVOCs - Room 144	1996	Used	Service Contract
Ion Chromatograph (IC) - Anions Analysis	Dionex	DX - 120	99060762	Wet Chem	1999	Reconditioned	Service Contract
Ion Chromatograph (IC) - Perchlorate Analysis	Dionex	DX - 120	98070245	Wet Chem	2000	Reconditioned	Service Contract
Ion Gauge Controller	Hewlett Pac	01	5568	VOAs - Room 201	1996	Used	Service Contract

Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Ion Gauge Controller	Hewlett Pac	59822B	4215	VOAs - Room 201	1996	New	Service Contract
Ion Gauge Controller	Hewlett Pac	59864B	not readily available)	VOAs - Room 201	2003	Reconditioned	Service Contract
Kiln	Cress	X - 31 - 910	8811	EXT - Room 134	1996	Used	Outside Vendor
Kiln	Cress	A - 31 - 945	9008	EXT - Room 134	1996	Used	Outside Vendor
Leak Detector	Gow Mac	21 - 250	F647002	HPLC - Room 135	1996	Used	Service Contract
Leak Detector	GL Science	LD - 228	LD AOB 0988	HPLC - Room 135	1996	Used	Service Contract
Liquid Scintillation Counter	Beckman	LS 6500	7068426	RAD - Room 131	1997	Reconditioned	Service Contract
Liquid Scintillation Counter	Packard	2700TR	406415	RAD - Room 132	2004	Used	Service Contract
Liquid Scintillation Counter	Beckman	LS 6000TA	598860	RAD - Room 131	1996	Used	Service Contract
Liquid Scintillation Counter	Wallac	1220	2200205	RAD - Room 151	2003	Reconditioned	Service Contract
Lunar Lander Pressure Filter	Millipore	(not readily available)	23-85041	EXT - Room 134	1996	Used	In House
Lunar Lander Pressure Filter	Millipore	(not readily available)	316.24-880464	EXT - Room 134	1996	Used	In House
Mercury Analyzer (Cold Vapor Atomic Absorption)	CETAC Tec	M-6000A	079730AST	Metals - Room 139	2002	Reconditioned	Outside Vendor
Meter, Conductivity	VWR Scient	23226 - 523	A22036	Wet Chem	1997	Used	In House
Meter, pH	Accumet	550	C0000643	Wet Chem	1996	Used	In House
Meter, pH	Corning	320	C5955	Metals	1996	Used	In House
Meter, pH	Corning	320	C5961	Wet Chem	1996	Used	In House
Mill, Ball	US Stonew	3 - Tier	BP - 93006	RAD - Room 164	1996	Used	In House
Millipore Water System	Millipore	Synergy 185	F6AN24973D	Metals	2006	New	Service Contract
Mixer, Homogenizer	Omni Intern	(not readily available)	90454	EXT - Room 134	1996	Used	In House
Mixer, Vortex	Barnstead I	M37615	1254040482941	Metals	1996	Used	In House
Mixer, Vortex	Thermolyne	M37615	(not readily available)	RAD - Room 158	1996	Used	In House
Mixer, Vortex	Thermolyne	M37615	376940783176	Wet Chem	1996	Used	In House
Mixer, Vortex	Thermolyne	M37615	871010543111	RAD - Room 158	1996	Used	In House
Mixer, Vortex	Thermolyne	M37615	871010332908	RAD - Room 158	1996	Used	In House
Mixer, Vortex	Thermolyne	M37615	871960809058	RAD - Room 158	1996	Used	In House
Mixer, Vortex	American S	S8223 - 1	24839	EXT - Room 134	1996	Used	In House
Muffle Furnace	Blue M	CW-7780F	CS-834	RAD - Room 162			Outside Vendor
Muffle Furnace	Thermolyne	30400	(not readily available)	RAD - Room 163	1996	Used	Outside Vendor
Muffle Furnace	Blue M	CW-7780-E-ST350	CS-1301	RAD - Room 162			Outside Vendor
Muffle Furnace	Thermolyne	30400	(not readily available)	RAD - Room 162	1996	Used	Outside Vendor
Muffle Furnace	Thermolyne	30400	(not readily available)	RAD - Room 162	1996	Used	Outside Vendor
Oven (Glassware)	VWR Scient	1130 GD	0401691	Fuels - Room 131	1996	Used	Outside Vendor
Oven, Drying	VWR Scient	1370 GD	(not readily available)	RAD - Room 164	1996	Used	Outside Vendor
Oven, Drying	VWR Scient	1327H	11020406	RAD - Room 158	2007	New	Outside Vendor
Oven, Drying	VWR Scient	1330 GD	(not readily available)	RAD - Room 164	1996	Used	Outside Vendor

Updated Equipment List

Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Oven, Drying	VWR Scient	1327H	1000103	RAD - Room 158	2003	New	Outside Vendor
Oven, Drying	VWR (Shel-	1305 U	1005291	EXT - Room 134	1996	Used	Outside Vendor
Oven, Drying (% Moist)	VWR Scient	1350 F	n/a	EXT - Room 134	1996	Used	Outside Vendor
Oven, Drying (Glassware)	VWR Scient	1320	0805088	VOAs - Room 201	1996	Used	Outside Vendor
Oven, Drying (Glassware)	VWR Scient	1370GD	(not readily available)	RAD - Room 158	1996	Used	Outside Vendor
Oven, Drying (Glassware)	VWR Scient	1350FM	(not readily available)	Wet Chem	1996	Used	Outside Vendor
Oven, Drying (Glassware)	VWR Scient	1330GD	(not readily available)	RAD - Room 163	1996	Used	Outside Vendor
Oven, Drying (TDS Analysis)	VWR Scient	1350G	0801788	Wet Chem	1996	Used	Outside Vendor
Oven, Drying (TS & TSS analysis)	Baxter Scie	N8620 - 5A	0292 - 0815	Wet Chem	1996	Used	Outside Vendor
Power Supply	OI Analytica	4430 REV 8	3661 - 8 - 129	Fuels - Room 131	1996	Reconditioned	Service Contract
Printer	Hewlett Pac	LaserJet 4 Plus	(See IS Records)	VOAs - Room 201			
Printer	Hewlett Pac	LaserJet 2100	USGH051602	HPLC - Room 135			
Printer	Hewlett Pac	Laserjet 2200D	(See IS Records)	Metals			
Printer	Hewlett Pac	Laserjet 4000	(See IS Records)	SVOCs - Room 144			
Printer	Hewlett Pac	LaserJet 4 Plus	(See IS Records)	RAD - Room 151			
Printer	Hewlett Pac	Laserjet 4050	(See IS Records)	SVOCs - Room 144			
Printer	Hewlett Pac	LaserJet 4 Plus	(See IS Records)	SVOCs - Room 144			
Printer	Hewlett Pac	Laserjet 2100	USGH051620	Fuels - Room 135			
Printer	Hewlett Pac	Laserjet 2200D	US8RB09307	Wet Chem			
Pump, ICP/MS	Gilson	Minipuls 3	610G1667	Metals - Room 141	2004	Reconditioned	Service Contract
Pump, Vacuum	Edwards	E2M2	61522	SVOCs - Room 144	1996	Used	Service Contract
Pump, Vacuum	Edwards	1.5	996256881	SVOCs - Room 144	1996	Used	Service Contract
Pump, Vacuum	Edwards	AVS - 28A	5520	Room 168	1996	Used	Outside Vendor
Pump, Vacuum	Edwards	E2M2	95 - 2003851	SVOCs - Room 144	1996	Used	Service Contract
Pump, Vacuum	Millipore	DOA - V152 -AA	1008	EXT - Room 134	1996	Used	Outside Vendor
Pump, Vacuum	Edwards	AVS - 28A	5521	Room 168	1996	Used	Outside Vendor
Pump, Vacuum, Direct Drive	Edwards	E2M2	(not readily available)	VOAs - Room 201	2003	Reconditioned	Service Contract
Pump, Vacuum, Direct Drive	Edwards	E2M2	(not readily available)	VOAs - Room 201	1996	Used	Service Contract
Pump, Vacuum, Direct Drive	Edwards	E2M2	(not readily available)	VOAs - Room 201	1996	Used	Service Contract
Refractometer, Differential	Waters	M410	410 - 004776	HPLC - Room 142	1996	Used	Service Contract
Refrigerator	GE	TAX4DNYAWH	GS 138749	VOAs - Room 201	2004	New	Outside Vendor
Refrigerator	GE	TAX4DNYAKH	GS 139521	Wet Chem	2004	Used	Outside Vendor
Refrigerator	GE	TAX4DNCAWH	LA312372	HPLC - Room 135	2004	Used	Outside Vendor
Refrigerator	TRUE	GDM41	359861	EXT - Room 134	2004	Used	Outside Vendor
Refrigerator (walk-in)	Custom Buil	N/A	N/A	EXT - Room 134	1996	Used	Outside Vendor
Refrigerator (walk-in)	Custom Buil	N/A	N/A	Metals	1996	Used	Outside Vendor

Updated Equipment List

Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Refrigerator (walk-in)	Custom Buil	N/A	N/A	Room	1996	Used	Outside Vendor
Refrigerator (walk-in)	Custom Buil	N/A	N/A	Sample Control	1996	Used	Outside Vendor
Refrigerator/Freezer	Residential	(not readily available)	(not readily available)	HPLC - Room 135	1996	Used	Outside Vendor
Refrigerator/Freezer	Maytag	PTB1953GRW	12038349ZQ	SVOCs - Room 144	2001	New	Outside Vendor
Refrigerator/Freezer	Estate	TT18CKXWN00	EA1228011	HPLC - Room 135	2004	Used	Outside Vendor
Refrigerator/Freezer	Sanyo	SR1290W	901101794	EXT - Room 134	2004	Used	Outside Vendor
Refrigerator/Freezer	Estate	TT18CKXWN00	EA1228020	HPLC - Room 135	2004	Used	Outside Vendor
Riffle Splitter	Gibson	SP - 3	(Not readily available)	RAD - Room 164	1996	Used	In House
Sample Heater (Gas Chromatograph), Purge & Trap	Tekmar	14 - 3310 - 000	88180007	Fuels - Room 131	1996	Used	Service Contract
Sample Heater (Gas Chromatograph), Purge & Trap	OI Corporati	4430	3525 - 8 - 104	Fuels - Room 131	1996	Used	Service Contract
Sample Heater (Gas Chromatograph), Purge & Trap	OI Corporati	4430 R - C	90 - 632	Fuels - Room 131	1996	Used	Service Contract
Sample Heater (Gas Chromatograph), Purge & Trap	Tekmar	14 - 3310 - 000	90288001	Fuels - Room 131	1996	New	Service Contract
Sample Heater (Gas Chromatograph), Purge & Trap	OI Corporati	MHC	D424464032	Fuels - Room 131	1996	Reconditioned	Service Contract
Sampler, Air Quality	GAST Mfg.	1023 - V303Q - G583	0792	RAD - Room 173	1996	Used	Outside Vendor
Scaler w/ Lucas Cell Counter	Ludlum	1000	148035	RAD - Room 158	1996	Reconditioned	In House
Scaler w/ Lucas Cell Counter	Ludlum	1000	128303	RAD - Room 158	1996	Reconditioned	In House
Scaler w/ Lucas Cell Counter	Ludlum	2000	10082	RAD - Room 158	1996	Reconditioned	In House
Scaler w/ Lucas Cell Counter	Ludlum	1000	95539	RAD - Room 158	1996	Reconditioned	In House
Server (data server for all GCs)	Dell	PowerEdge 1900	Gcserver	Server Room 152	2007	New	In House
Server (data server for all images)	Custom	Custom Built	2ksvr2	Server Room 152	1996	Used	In House
Server (domain controller and backup server)	Dell	PowerEdge 2600	2000server	Server Room 152	2004	Used	In House
Server (Landesk server)	Dell	PowerEdge 2600	Landesk ld_srvr	Server Room 152	2004	Used	In House
Server (LIMS SQL server)	Dell	PowerEdge 2950	SQLserver2005	Server Room 152	2005	New	In House
Server (main Novell server and legacy server	Compaq	Proliant 800	Paragon (Novell)	Server Room 152	1996	Used	In House
Server (nas for disk backup prior to tape)	Dell	Powervault NF500	(yet to be named)	Server Room 152	2007	New	In House
Server (nas for future image storage)	Dell	Powervault 745n	2ksvr2 nas	Server Room 152	2006	New	In House
Server (NT domain controller)	Compaq	Proliant 3000	NTserver2	Server Room 152	2004	Used	In House
Shaker	Red Devil E	5400	99DD0234	RAD - Room 164	1996	Used	In House
Shaker, Platform	New Bruns	C2	200434430	RAD - Room 162	2005	Used	In-House
Sonic Bath	Branson	8210R - MT	97075070	EXT - Room 134	1996	Used	In House
Sonicator	Branson	450	B180341	EXT - Room 134	1996	Used	In House
Sonicator	Branson	450	B100255	EXT - Room 134	1996	Used	In House
Sonicator, Double	Ultrasonics	VC600-2	15282E	EXT - Room 134	1996	Used	In House
Sonicator, Ultrasonic Cleaner	Branson	3210	b3200R-1	Metals	1996	Used	In House
Steam Generator	Chromalox	CMB-9. 0A0031 -243	22241-13893	EXT - Room 134	1996	Used	Outside Vendor
Total Hydrocarbon Analyzer	Buck Scient	404	626	Metals	1996	Used	Outside Vendor

Updated Equipment List

Instrument	Manufacture	Model	Serial Number	Location	Purchas	Condition	Servicing
Total Organic Carbon (TOC) Analyzer & Autosampler	Tekmar - D	14 - 7045 - 000	01011007	TOC - Room 135	2002	Reconditioned	Outside Vendor
Tumbler, Rotary (12 position)	Assoc. Desi	3740 - 12 - BRE	1900	EXT - Room 134	1996	Used	In House
Tumbler, Rotary (12 position)	Assoc. Desi	3740 - 12 - BRE	1878	EXT - Room 134	1996	Used	In House
Tumbler, Rotary (6 position)	Assoc. Desi	3740 - 12 - BRE	(not readily available)	EXT - Room 134	1996	Used	In House
Tumbler, Rotary (6 position)	Assoc. Desi	3740 - 12 - BRE	(not readily available)	EXT - Room 134	1996	Used	In House
Tumbler, Rotary (6 position)	Assoc. Desi	3740 - 12 - BRE	1379	EXT - Room 134	1996	Used	In House
Tumbler, Rotary (6 position)	Assoc. Desi	3740 - 12 - BRE	1637	EXT - Room 134	1996	Used	In House
UV Spectrophotometer	Sequoia - T	Model 340	905970923742	Wet Chem	1997	Reconditioned	Outside Vendor
Water Bath	Precision	185	10AZ-9	Wet Chem	1996	Used	In House

Appendix H

List of Standard Operating Procedures (SOPs)

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SOP Table of Contents

SOP	Scheduled Date for Review	Title	Notes	Author
001-049 SAFETY/WASTE				
001 R7	11/15/2008	Treatment of Quarantined Soils, Aqueous Extracts, and Solid Residues and Cleaning Containers Used To Store Quarantined Sample Materials		CRO
002 R7	8/15/2009	Laboratory Fume Hood Velocity Monitoring	re-released w/o revision 10/2/07	CRO
003 R5	9/15/2009	Management of Nonradioactive Hazardous Waste		CRO
008 R8	1/15/2009	Initial Receipt of Radioactive Samples and External Radiation Exposure Rate and Removeable Radioactive Material Contamination Survey of Incoming Radioactive Material Packages		CRO
009 R7	1/15/2009	Incoming Radioactive Material Packages That Exceed Removable Radioactive Material Contamination Limits	upon next rev., combine with 008?	CRO
010 R4	7/20/2010	Survey of Laboratory Areas for Radioactive Contamination	re-released w/o revision 7/20/08	CRO
012 R6	7/20/2010	Contamination Surveys using Portable Survey Meters (Electra, Micro Roentgen)	CONTAINS OPERATOR AID! re-released w/o revision 7/20/08	CRO
015 R6	9/15/2009	Disposal of Radioactive Waste		CRO
016 R6	8/15/2009	Electron Capture Detector Leak Tests		JFN
017 R5	12/15/2008	Effluent Monitoring and Release		CRO
024 R3	8/15/2008	Disposal of Short Lived Radionuclides by Decay in Storage		CRO
026 R2	8/15/2008	Radioactive Materials Inventory Control Using LIMS		CRO
027 R1	11/15/2008	Packaging Samples for Return to Client		CRO
029 R2	7/15/2009	Calibration and Use of the Berthold LB 1043 AS Hand and Foot Monitors		CRO
030 R1	11/15/2010	Operation of the Rampactor Compactor	re-released w/o revision 2/29/08	CRO
050-099 DATA REPORTING				
052 R8	9/15/2008	Data Package Review Procedures for Stable Chemistry Methods		EXK
069 R8	9/15/2008	Managing and Archiving Client Workorders and Records, and Retrieving Archived Information		DAS
100-199 ADMINISTRATION				
103 R7	8/15/2009	Qualification and Use of Subcontract Laboratories		DAS
127 R9	2/15/2009	Procurement of Supplies and Materials, Including Radioactive Materials, and Evaluation of Purchased Items Received		DAS

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SOP	Scheduled Date for Review	Title	Notes	Author
132 R6	12/15/2008	Building Security		CRO
143 R4	10/15/2009	New Employee Quality Assurance Orientation and Training	Add HS overview next revision	DAS
200-299	**SAMPLE CONTROL**			
202 R10	12/15/2008	Login and Distribution of Samples and Workorders		CRO
205 R8	11/21/2008	Preparation of Bottle Orders, Shipping Sample Kits, and Maintaining Inventory of Bottles, Preservatives, and Labels	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed)	CRO
210 R6	11/21/2008	Use and Calibration Verification of Infrared Temperature Guns		CRO
300-399	**GENERAL CHEMISTRY**			
300 R13	3/15/2010	Standards, Solvents, Acids, Bases and Reagents Management in the Laboratory		DAS
303 R10	10/15/2008	Control, Format and Review of Laboratory Logbooks		DAS
305 R10	1/15/2009	Balance Calibration, Verification and Utilization		DAS
306 R4	8/15/2008	The Use of Significant Figures and Rules For Rounding Numbers	re-released w/o revision 7/26/06	DAS
317 R10	1/15/2009	Removing and Returning Equipment From Service		DAS
318 R6	8/15/2008	Chain-of-Custody		DAS
319 R8	1/15/2009	Generation and Monitoring of Deionized (DI) Water		DAS
320 R8	2/15/2009	Monitoring and Recording of Oven Temperatures		DAS
321 R5	9/15/2008	Calibration Verification of Pipettes and Pippettors		DAS
326 R7	2/15/2009	Monitoring and Recording Refrigerator and Freezer Temperatures		DAS
329 R6	1/15/2010	Method Demonstration Procedures: Instrument Detection Limit (IDL) and Method Detection Limit (MDL) Studies; Demonstration of Capability (DOC)	contol limits removed from SOP, title changed	DAS
334 R7	3/15/2010	Glassware Cleaning Procedures and Maintenance of Glassware Used in The Organics and Inorganics Departments	NOTE-SOP CONTAINS OPERATOR AID (REPLACE!)	DAS
336 R0	12/15/2009	Representative Laboratory Subsampling	Formerly SOP 721, now labwide. Inquire about additional Appendices w/each annual review.	DAS
400-499	**GC/HPLC and FUELS**			
402 R12	7/8/2008	Determination of Organochlorine Pesticides by Gas Chromatography - Methods SW8081A and EPA 608		JFN
404 R15	8/15/2009	Analysis of Nitroaromatics and Nitroamines (Explosives Residues) by HPLC -- Method SW8330		JFN
406 R13	7/18/2010	Total Extractable Petroleum Hydrocarbons (TEPH), Diesel Range Organics (DRO), by Gas Chromatography -- Method SW8015B and California LUFT		JFN

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407 R8	7/25/2008	Organophosphorus Compounds by Gas Chromatography - Methods SW8141A and EPA 614		JFN
408 R11	8/15/2009	Analysis of Nitroglycerin and/or PETN by HPLC -- Method SW8332		JFN
409 R5	8/11/2008	Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography -- Methods SW8082 and EPA 608		JFN
424 R12	5/11/2008	Determination of Aromatic Volatile Organics by Gas Chromatography - Method SW8021B		JFN
425 R12	5/28/2008	Analysis of Total Volatile Petroleum Hydrocarbon (TVPH) Gasoline Range Organics (GRO) by Gas Chromatography -- Methods SW8015B and CAL-LUFT		JFN
434 R8	8/28/2008	Analysis of Chlorinated Herbicides by Gas Chromatography - Methods SW 8151A, EPA 615 and EPA 515.1		JFN
438 R10	4/15/2009	Microextraction and Analysis of EDB and DBCP in Water by Gas Chromatography - Methods EPA 504.1 and SW8011		JFN
439 R5	10/18/2008	Analysis of Nitroguanidine by HPLC -- Methods CRREL 89-35 and SW8000B		JFN
444 R1	6/21/2008	Extraction and Determination of Glycols by Gas Chromatography -- Method SW8015B	re-released without revision 11/21/06	JFN
446 R1	11/4/2008	Analysis of Crystal Violet in Water by HPLC		JFN
447 R0	11/21/2008	Determination of Hexavalent Chromium in Air by Ion Chromatography		JFN
448 R0	3/15/2010	Determination of Perchlorate in Liquids and Solids using High Performance Liquid Chromatography, Electrospray Ionization Tandem Mass Spectrometry (LC/MS/MS)	Officially issued 3/20/08	SLI
500-599 GCMS				
506 R15	4/15/2009	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Capillary Column Technique - Methods SW8270D and EPA 625		JFN
511 R8	1/15/2009	Volatiles Reagent Water Preparation and Blank Analysis		JFN
512 R10	1/15/2009	Refrigerator Blank Preparation and Analysis		JFN
525 R12	4/15/2009	Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry -- Methods SW8260B and EPA 624		JFN
600-699 EXTRACTIONS				
603 R10	4/15/2009	Extraction of Hydrocarbons From Soil and Water Samples For Analysis by Method SW8015		JFN
604 R8	11/15/2009	Silica Gel Cleanup -- Method SW3630C		JFN
607 R9	8/15/2009	Extract Concentration Using Kuderna-Danish Apparatus	Contains Steam Generator Operator's Aid	JFN
608 R12	9/15/2009	Method for Toxicity Characteristic Leaching Procedure (TCLP) Extraction of Wastes for the Analysis of Volatile Organic Compounds by Zero Headspace Extraction (ZHE) - Method SW1311	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
609 R12	9/15/2009	Method for Toxicity Characteristic Leaching Procedure (TCLP) of Wastes and Soils For The Analysis of Metals and Semivolatile Organics - Method SW1311	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
617 R13	3/15/2010	Continuous Liquid/Liquid Extraction (CLE) -- Method SW3520C	SOP contains Timer Operator's Aid	JFN
622 R6	12/8/2008	Waste Dilution Extraction -- Method SW3580A		JFN

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625 R11	3/15/2010	Soxhlet Extraction -- Method SW3540C	SOP contains Timer Operator's Aid	JFN
626 R9	9/14/2008	Separatory Funnel Liquid-Liquid Extraction -- Method SW3510C		JFN
629 R10	8/15/2009	Determination of Ignitability by The Pensky-Martens Closed-Cup Tester -- Method SW1010A		JFN
634 R6	10/1/2008	Sulfur Cleanup -- Method SW3660B		JFN
637 R9	8/15/2009	Concentration and Solvent Exchange by The Nitrogen Blowdown Technique	Re-issued/amended 12/26/07 (Navy Findings), traininng conducted	JFN
640 R7	4/15/2009	Extraction and Gravimetric Determination of Hexane Extractable Material in Solids -- Method SW9071B		JFN
641 R8	12/25/2008	Gel Permeation Chromatography (GPC) Cleanup -- Method SW3640A		JFN
642 R8	6/15/2009	Gravimetric Determination of Percent Moisture For Solid Matrices		JFN
648 R7	11/15/2009	Florisil Cleanup -- Method SW3620B		JFN
651 R9	5/15/2009	Sulfuric Acid Cleanup -- Method SW3665A		JFN
658 R7	1/15/2009	Paint Filter Liquids Test -- Method SW9095A	re-released w/o revision 11/9/07	JFN
663 R7	2/15/2009	Monitoring TCLP Tumbler Revolutions and Room Temperature		DAS
664 R8	11/15/2009	Extraction and Derivatization of Samples For Herbicide Analysis by Gas Chromatography -- Methods SW8151A, EPA 615 and EPA 515.1	Contains Timer Operator's Aid	JFN
665 R7	11/15/2009	Extraction of Explosives from Water and Soil -- Methods SW8330 and SW8332		JFN
666 R6	9/15/2009	Waste Extraction Test (Cal-WET) For The Analysis of Metals and Semivolatile Organic Compounds		JFN
668 R4	9/15/2009	Synthetic Precipitation Leaching Procedure (SPLP) For The Analysis of Metals and Semivolatile Organics -- Method SW1312	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
669 R4	9/15/2009	Method for Synthetic Precipitation Leaching Procedure (SPLP) Extraction of Samples For The Analysis of Volatile Organic Compounds by Zero Headspace Extraction (ZHE) -- Method SW1312	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
670 R12	11/15/2009	Analysis of Total Organic Carbon By Methods EPA 415.1, SW9060, and SM5310 C		JFN
671 R6	4/15/2009	Determination of n-Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry For Aqueous Samples -- Methods EPA 1664 and SW9070A	Contains Steam Generator Operator's Aid	JFN
672 R3	4/15/2009	Extraction and Gravimetric Determination of Lipids in Tissues	Contains Steam Generator Operator's Aid	JFN
673 R2	6/15/2009	Extraction of Polychlorinated Biphenyl Wipes Using Ultrasonic Bath Agitation		JFN
700-799	**RADIOCHEMISTRY**			
700 R10	7/15/2008	Preparation of Environmental And Drinking Water Samples For Tritium Analysis -- Method EPA 906.0		RXG
701 R0	7/25/2009	DRAFT: Determination of Ra-226 by Alpha Spectrometry using Astatine 217 Tracer	New	RXG
702 R19	6/15/2009	Preparation of Gross Alpha and Gross Beta in Environmental Matrices -- EPA Method 900.0 and SW-846 Method 9310		RXG

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703 R8	7/17/2010	Sample Prescreening		RXG
704 R9	6/15/2009	Analysis of Tritium and Other Beta-Emitting Nuclides by Liquid Scintillation Counting -- Method EPA 906.0		RXG
707 R10	8/15/2009	Radiostrontium in Water, Soil, Filters, Vegetation and Hazardous Waste Samples		RXG
708 R8	7/18/2010	Determination of Minimum Detectable Concentrations for Radioanalytical Methods		RXG
709 R6	8/15/2008	Verification and Validation of Radioanalytical Software		RXG
711 R7	6/15/2008	Preparation of Water and Solid Samples for the Analysis of Polonium-210 -- EML Procedure Po-01		RXG
712 R14	8/15/2009	Determination of Total Alpha-Emitting Radium Isotopes in Drinking Water -- EPA Method 903.0 and SW9315		RXG
713 R10	7/21/2010	Analysis of Gamma Emitting Radionuclides by Gamma Spectrometry -- Method EPA 901.1		RXG
714 R11	8/15/2009	Analysis of Alpha Emitting Radionuclides by Alpha Spectrometry		RXG
715 R15	7/15/2008	Review of Radioanalytical Data		RXG
724 R10	6/15/2009	Analysis of Alpha and Beta Emitting Radionuclides by Gas Flow Proportional Counter -- EPA Method 900.0		RXG
726 R6	6/15/2009	Determination of Lead -210 in Soils, Sediments, and Waters		RXG
733 R7	4/15/2009	Checking the pH of Aqueous Samples in the Radiochemistry Department		RXG
739 R9	4/15/2009	Preparation of Samples for Analysis by Gamma Spectroscopy		RXG
746 R8	7/15/2008	Determination of Radium-228 According to EPA Method 904.0 or SW846 Method 9320, With Modifications		RXG
748 R4	4/15/2009	Preparation of Water and Solid Samples For The Analysis of Fe-55 by Eichrom Method FEW01		RXG
751 R2	4/15/2009	Actinides -- Americium/Curium Separation -- Purification by TRU and TEVA Spec Column		RXG
753 R3	7/15/2008	Determination of Radioactive Iodine in Environmental Samples -- EPA Method 902.0		RXG
754 R5	4/15/2009	Preparation of Solid Samples For Tritium Analysis by Microwave Oven		RXG
755 R9	7/17/2010	Determination of Technetium-99 in Solid and Water/Aqueous Samples	Editorial changes only; no technical revisions.	RXG
758 R2	5/15/2008	Determination of Promethium-147 in Water		RXG
760 R6	7/18/2010	Preparation of Solid Samples by Potassium Pyrosulfate Fusion		RXG
765 R4	6/15/2008	Separation and Analysis of Neptunium-237 in Environmental Matrices		RXG
766 R6	7/17/2010	Witnessing the Addition of Carriers, Tracers and Standards in Radiochemistry Samples	re-released w/o revision 7/17/08	RXG
767 R7	4/15/2009	Sample Preparation: Filter Leaching		RXG
772 R4	4/15/2009	Preparation of Water and Soil Samples for the Analysis of Carbon-14 Using Potassium Permanganate -- EPA EERF Method C-01		RXG
773 R10	4/15/2009	Total Dissolution of Solids for the Radiochemical Determination of Actinides and Other Non-Volatile Radionuclides		RXG
774 R1	7/18/2010	Nickel 59, 63 in Water and Soil Samples Using Eichrom Nickel Resin		RXG
776 R11	7/15/2009	Preparation of Water Samples for Actinides		RXG
777 R9	5/15/2009	Actinides - Thorium and Plutonium Sequential Separation by Anion Exchange		RXG
778 R12	8/15/2008	Actinides - Uranium, Plutonium, and Americium/Curium (Partial) Sequential Separation by Ion Exchange		RXG

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SOP	Scheduled Date for Review	Title	Notes	Author
780 R8	7/18/2010	Actinides - Americium/Curium Separation -- Purification by Methanolic Anion Exchange and TEVA Spec Column	Only clerical corrections/updates made, no technical revisions	RXG
783 R8	8/15/2009	Radium-226 in Aqueous and Soil Matrices -- Radon Emanation Technique--Method EPA 903.1		RXG
784 R0	8/15/2008	Radium-228 Determination for SDWA Compliance Analysis -- Method 904.0	was DRAFT, then published 10/5/06	RXG
785 R4	7/18/2010	Total Activity in Environmental Matrices		RXG
786 R5	8/15/2009	Gross Alpha in Water by Coprecipitation Method -- SM7110C		RXG
791 R3	5/15/2009	Preparation of Silica Gel Samples For Tritium Analysis		RXG
792 R0	5/15/2009	Preparation of Ra226 for Analysis by Alpha Spectrometry	was DRAFT, formally published 9/8/07	RXG
799 R3	6/15/2008	Determination of Radon-222 in Water Samples by Liquid Scintillation Counting - SM 7500-Rn B and ASTM D5072-92		RXG
800-899	**METALS**			
806 R13	7/15/2009	Digestion of Waters, Soils and Wastes for Metals Analysis -- Methods SW3005A, SW3010A, SW3050B, EPA 200.2 and CLP SOW ILMO3.0 and ILMO4.0		RTF
807 R11	7/15/2008	Determination of Metals by Inductively Coupled Plasma Emission Spectroscopy - Method EPA 200.7 (Trace ICAP)		RTF
812 R14	7/15/2009	Preparation and Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy -- Methods SW7470A, SW7471A, EPA 245.1, ILMO3.0, ILMO4.0		RTF
827 R6	7/15/2009	Determination of Elements by Inductively Coupled Plasma Mass Spectrometry -- Methods EPA 200.8 AND SW6020A		REM
834 R7	7/15/2009	Determination of Metals by Inductively Coupled Plasma Emission Spectroscopy -- Method SW6010B (Trace ICAP)		RTF
900-999	**QUALITY ASSURANCE**			
901 R7	1/15/2009	Verifying Weights		DAS
923 R8	2/15/2009	Verification of Thermometers		DAS
926 R8	6/15/2008	Review, Revision, Distribution and Archiving of Controlled Documents		DAS
928 R8	3/15/2010	Non-Conformances and Corrective Actions		DAS
937 R7	6/15/2008	Internal Audits		DAS
939 R3	8/15/2009	Manual Re-Integration Policy and Procedures		JFN
1100-1199	**WET CHEMISTRY**			
1100 R10	1/15/2009	Determination of Total Suspended Solids (TSS or Total Non-Filterable Residue) -- Methods EPA 160.2 and SM2540D		EAL
1101 R10	1/15/2009	Total Solids, Total Dissolved Solids (TDS or Total Filterable Residue), and Total Fixed and Volatile Solids -- Methods EPA 160.3, EPA 160.1, and EPA 160.4 and Methods SM2540B, SM2540C and SM2540E		EAL
1104 R6	7/20/2010	Potentiometric Determnation of (Simple) Fluoride in Water and Soil Using an Ion Selective Electrode -- Methods EPA 340.2, SW9214 and SM4500-F~C		EAL
1106 R7	7/20/2010	Bicarbonate, Carbonate, Hydroxide, and Total Alkalinity by Titration -- Methods EPA 310.1 and SM2320B		EAL

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SOP	Scheduled Date for Review	Title	Notes	Author
1110 R12	1/15/2009	Determination of Total and Amenable Cyanide (Distillation) - - Methods SW9010B, SW9013, SW9014, EPA 335.1, EPA 335.2 and CLP Inorganic SOW (ILMO4.0); Determination of Weak and Dissociable Cyanide -- Method SM4500-CN I		EAL
1112 R5	1/15/2009	Determination of Reactive Cyanide and Sulfide -- EPA Method SW-846, Chapter 7	re-released without revision 1/19/07	EAL
1113 R11	3/15/2010	Determination of Inorganic Anions by Ion Chromatography -- Methods EPA 300.0 and SW9056		EAL
1117 R3	4/15/2009	Total Organic Carbon in Soil by Rapid Dicromate Oxidation -- MSA Walkley-Black Method	re-released w/o revision 8/15/07	EAL
1119 R6	2/15/2010	Determination of Total Phosphorus and Ortho-Phosphate in Water -- Methods EPA 365.2 and SM4500-P B(5) and E		EAL
1120 R5	12/15/2008	Determination of Total Sulfides in Water -- Methods EPA 376.1 and SM4500-S2F		EAL
1121 R6	3/15/2010	Determination of Hexavalent Chromium in Solid Matrices Using Alkaline Digestion (Method SW3060A) and Analysis by Method SW7196A		EAL
1122 R6	7/20/2010	Determination of Hexavalent Chromium by Methods SW7196A and SM3500-Cr-B		EAL
1125 R4	7/20/2010	Determination of Perchlorate in Water Using Ion Chromatography -- Methods EPA 314.0 and SW9058	re-released w/o revision 7/20/08; (include maintenance next update)	EAL
1126 R16	12/15/2008	Determination of pH by Electrometric Meaurement -- Methods EPA 150.1, SW9040B, SW9045C and SM4500-H+ B		EAL
1127 R7	7/21/2010	Determination of Nitrogen as Nitrate Plus Nitrite, Nitrite, and Nitrate in Environmental Water and Soil Samples Using a Colorimetric, Automated, Cadmium Reduction Procedure -- Methods EPA 353.2, SM4500-NO3-I, and Quikchem Method 10-107-04-1-C		EAL
1128 R9	2/15/2010	Determination of Specific Conductance -- EPA Methods 120.1, SW9050A, and SM2510B		EAL
1129 R6	2/15/2010	Determination of Ammonia Using An Automated Phenolate Procedure -- Methods EPA 350.1, SM4500 NH3-NH, and Quikchem Method 10-107-06-1-C		EAL
1130 R5	7/21/2010	Determination of Nitrogen, Nitrite (as NO2-N) in Water And Soil by Colorimetric Spectrophotometric Determination -- EPA Method 354.1 and SM4500-NO2 -B		EAL
1132 R3	1/15/2009	Sediment Load		EAL
1133 R3	1/15/2009	Acidity by Titration - Methods EPA 350.1 and SM2310B		EAL
1400-1499		**INFORMATIONS SYSTEMS MANAGEMENT**		
1400 R6	1/15/2009	Process Software Validation		MSR
1401 R5	1/15/2009	Computer and LIMS Backup and Restoration Protocols	was actually re-released without revision 3/9/06; revisions were made and SOP was published 1/15/07	GRB
1402 R6	1/15/2010	Laboratory Information Management System (LIMS) Version Control	Review LIMS Change Management for update as well.	MSR
MISC-		**ANNUAL DOCUMENTS/REFRESHERS**		
CHP R12	9/16/2008	Chemical Hygiene Plan (CHP)		CRO
ECP R6	9/16/2008	Emergency and Contingency Plan (ECP)		CRO

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SOP	Scheduled Date for Review	Title	Notes	Author
FORM159	12/31/2008	Annual IS and LIMS Policy Training	Year 2008 (see G67), Effective 1/7/08	DAS
FORM162	12/31/2008	Annual Ethical Behavior Policy Training	Re-released w/o revision, see G67 for 08 annual sign-off	DAS
FORM166	12/31/2008	Annual Waste, Abuse and Fraud Reporting Notification	Re-released w/o revision, see G67 for 08 annual sign-off	DAS
LQAP R12	9/17/2009	Laboratory Quality Assurance Plan (LQAP)		DAS
RESPP R	6/20/2008	Respiratory Protection Plan (RESPP)		CRO
RPP R5	8/15/2008	Radiation Protection Plan (RPP)		CRO
WMP R7	10/24/2009	Waste Management Plan (WMP)		CRO

Appendix I

Certifications & Licenses

State of California—Health and Human Services Agency
California Department of Public Health

MARK B HORTON, MD, MSPH
Director

ARNOLD SCHWARZENEGGER
Governor

October 14, 2008

KENNETH D. CAMPBELL
PARAGON ANALYTICS, A division of DataChem Laboratories, Inc.
225 COMMERCE DRIVE
FORT COLLINS, CO 80524

Dear KENNETH D. CAMPBELL: Certificate No. 06251CA

This is to advise you that the laboratory named above has been accredited under National Environmental Laboratory Accreditation Program (NELAP) as an environmental testing laboratory pursuant to the provisions of the Health and Safety Code (HSC), Division 101, Part 1, Chapter 4, Section 100825, et seq.

The Fields of Accreditation for which this laboratory has been accredited are enclosed. Recognition of accreditation is subject to maintaining accreditation with the primary Accrediting Authority. In addition, the laboratory shall comply with the National Environmental Laboratory Accreditation Conference (NELAC) Standards and all associated California Environmental Laboratory Accreditation Program Branch (ELAP) regulations and statutes.

Please note that your laboratory is required to notify California ELAP of any major changes in key accreditation criteria within 30 calendar days of the change. This written notification includes, but is not limited to, changes in ownership, location, key personnel, and major instrumentation (HSC 100845(b) and (d), and NELAC Standard Section 4.3.2). The certificate must be returned to California ELAP upon loss of accredited status.

Your continued cooperation with the above requirements is essential for maintaining the high quality of the data produced by environmental laboratories accredited by the State of California.

If you have any questions, please contact Mandy Mok at (510) 620-3155.

Sincerely,

George C. Kulasingam, Ph.D., Chief
Environmental Laboratory Accreditation Program Branch

Enclosure

CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM - NELAP RECOGNIZED

NELAP Fields of Accreditation

PARAGON ANALYTICS, A division of DataChem Laboratories, Inc. **Lab Phone** (970) 490-1511
FORT COLLINS
225 COMMERCE DRIVE
FORT COLLINS, CO 80524

Certificate No: 06251CA Renew Date: 08/31/2009 Primary AA: UT ATL2

106 - Radiochemistry of Drinking Water			
106.010	001	EPA 900.0	Gross Alpha
106.010	002	EPA 900.0	Gross Beta
106.030	003	EPA 901.1	Gamma Emitters
106.050	001	EPA 903.0	Total Alpha Radium
106.050	002	EPA 903.0	Radium-226
106.051	001	EPA 903.1	Radium-226
106.060	001	EPA 904.0	Radium-228
106.080	001	EPA 906.0	Tritium
106.092	001	EPA 200.8	Uranium
106.210	001	DOE Sr-01	Strontium-89, 90
106.220	001	DOE Sr-02	Strontium-89, 90
106.230	001	DOE U-02	Uranium
106.250	003	DOE 4.5.2.3	Gamma Emitters
106.452	001	ASTM D3972-97	Uranium
108 - Inorganic Chemistry of Wastewater			
108.020	001	EPA 120.1	Conductivity
108.112	001	EPA 200.7	Boron
108.112	002	EPA 200.7	Calcium
108.112	003	EPA 200.7	Hardness (calc.)
108.112	004	EPA 200.7	Magnesium
108.112	005	EPA 200.7	Potassium
108.112	006	EPA 200.7	Silica
108.112	007	EPA 200.7	Sodium
108.120	001	EPA 300.0	Bromide
108.120	002	EPA 300.0	Chloride
108.120	003	EPA 300.0	Fluoride
108.120	004	EPA 300.0	Nitrate
108.120	005	EPA 300.0	Nitrite
108.120	007	EPA 300.0	Phosphate, Ortho
108.120	008	EPA 300.0	Sulfate
108.200	001	EPA 350.1	Ammonia
108.232	001	EPA 353.2	Nitrate-nitrite
108.381	001	EPA 1664A	Oil and Grease

108.410	001	SM2320B	Alkalinity
108.420	001	SM2340B	Hardness (calc.)
108.430	001	SM2510B	Conductivity
108.440	001	SM2540B	Residue, Total
108.441	001	SM2540C	Residue, Filterable
108.442	001	SM2540D	Residue, Non-filterable
108.470	001	SM4500-CN C	Cyanide, Manual Distillation
108.472	001	SM4500-CN E	Cyanide, Total
108.473	001	SM4500-CN G	Cyanide, amenable
108.480	001	SM4500-F C	Fluoride
108.490	001	SM4500-H+ B	pH
108.498	001	SM4500-NH3 H (18th)	Ammonia
108.510	001	SM4500-NO2 B	Nitrite
108.540	001	SM4500-P E	Phosphate, Ortho
108.541	001	SM4500-P E	Phosphorus, Total
108.582	001	SM4500-S= F (19th/20th)	Sulfide
108.611	001	SM5310C	Total Organic Carbon

109 - Toxic Chemical Elements of Wastewater

109.010	001	EPA 200.7	Aluminum
109.010	002	EPA 200.7	Antimony
109.010	003	EPA 200.7	Arsenic
109.010	004	EPA 200.7	Barium
109.010	005	EPA 200.7	Beryllium
109.010	007	EPA 200.7	Cadmium
109.010	009	EPA 200.7	Chromium
109.010	010	EPA 200.7	Cobalt
109.010	011	EPA 200.7	Copper
109.010	012	EPA 200.7	Iron
109.010	013	EPA 200.7	Lead
109.010	015	EPA 200.7	Manganese
109.010	016	EPA 200.7	Molybdenum
109.010	017	EPA 200.7	Nickel
109.010	019	EPA 200.7	Selenium
109.010	021	EPA 200.7	Silver
109.010	023	EPA 200.7	Thallium
109.010	024	EPA 200.7	Tin
109.010	026	EPA 200.7	Vanadium
109.010	027	EPA 200.7	Zinc
109.020	001	EPA 200.8	Aluminum
109.020	002	EPA 200.8	Antimony
109.020	003	EPA 200.8	Arsenic

109.020	006	EPA 200.8	Cadmium
109.020	009	EPA 200.8	Copper
109.020	010	EPA 200.8	Lead
109.020	012	EPA 200.8	Molybdenum
109.020	014	EPA 200.8	Selenium
109.020	015	EPA 200.8	Silver
109.020	016	EPA 200.8	Thallium
109.020	017	EPA 200.8	Vanadium
109.190	001	EPA 245.1	Mercury
109.809	002	SM3500-Cr B (20th)	Chromium (VI)
109.811	001	SM3500-Cr D (18th/19th)	Chromium (VI)

110 - Volatile Organic Chemistry of Wastewater

110.040	001	EPA 624	Benzene
110.040	002	EPA 624	Bromodichloromethane
110.040	003	EPA 624	Bromoform
110.040	004	EPA 624	Bromomethane
110.040	005	EPA 624	Carbon Tetrachloride
110.040	006	EPA 624	Chlorobenzene
110.040	007	EPA 624	Chloroethane
110.040	008	EPA 624	2-Chloroethyl Vinyl Ether
110.040	009	EPA 624	Chloroform
110.040	010	EPA 624	Chloromethane
110.040	011	EPA 624	Dibromochloromethane
110.040	012	EPA 624	1,2-Dichlorobenzene
110.040	013	EPA 624	1,3-Dichlorobenzene
110.040	014	EPA 624	1,4-Dichlorobenzene
110.040	015	EPA 624	1,1-Dichloroethane
110.040	016	EPA 624	1,2-Dichloroethane
110.040	017	EPA 624	1,1-Dichloroethene
110.040	018	EPA 624	trans-1,2-Dichloroethene
110.040	019	EPA 624	1,2-Dichloropropane
110.040	020	EPA 624	cis-1,3-Dichloropropene
110.040	021	EPA 624	trans-1,3-Dichloropropene
110.040	022	EPA 624	Ethylbenzene
110.040	023	EPA 624	Methylene Chloride
110.040	024	EPA 624	1,1,2,2-Tetrachloroethane
110.040	025	EPA 624	Tetrachloroethene
110.040	026	EPA 624	Toluene
110.040	027	EPA 624	1,1,1-Trichloroethane
110.040	028	EPA 624	1,1,2-Trichloroethane
110.040	029	EPA 624	Trichloroethene

110.040	030	EPA 624	Trichlorofluoromethane
110.040	031	EPA 624	Vinyl Chloride

111 - Semi-volatile Organic Chemistry of Wastewater

111.100	001	EPA 625	Acenaphthene
111.100	002	EPA 625	Acenaphthylene
111.100	003	EPA 625	Anthracene
111.100	004	EPA 625	Benzidine
111.100	005	EPA 625	Benz(a)anthracene
111.100	006	EPA 625	Benzo(b)fluoranthene
111.100	007	EPA 625	Benzo(k)fluoranthene
111.100	008	EPA 625	Benzo(g,h,i)perylene
111.100	009	EPA 625	Benzo(a)pyrene
111.100	010	EPA 625	Benzyl Butyl Phthalate
111.100	011	EPA 625	Bis(2-chloroethoxy)methane
111.100	012	EPA 625	Bis(2-chloroethyl) Ether
111.100	013	EPA 625	Bis(2-chloroisopropyl) Ether
111.100	014	EPA 625	Di(2-ethylhexyl) Phthalate
111.100	015	EPA 625	4-Bromophenyl Phenyl Ether
111.100	016	EPA 625	4-Chloro-3-methylphenol
111.100	017	EPA 625	2-Chloronaphthalene
111.100	018	EPA 625	2-Chlorophenol
111.100	019	EPA 625	4-Chlorophenyl Phenyl Ether
111.100	020	EPA 625	Chrysene
111.100	021	EPA 625	Dibenz(a,h)anthracene
111.100	022	EPA 625	1,2-Dichlorobenzene
111.100	023	EPA 625	1,3-Dichlorobenzene
111.100	024	EPA 625	1,4-Dichlorobenzene
111.100	025	EPA 625	3,3'-Dichlorobenzidine
111.100	026	EPA 625	2,4-Dichlorophenol
111.100	027	EPA 625	Diethyl Phthalate
111.100	028	EPA 625	2,4-Dimethylphenol
111.100	029	EPA 625	Dimethyl Phthalate
111.100	030	EPA 625	Di-n-butyl phthalate
111.100	031	EPA 625	Di-n-octyl phthalate
111.100	032	EPA 625	2,4-Dinitrophenol
111.100	033	EPA 625	2,4-Dinitrotoluene
111.100	034	EPA 625	2,6-Dinitrotoluene
111.100	035	EPA 625	Fluoranthene
111.100	036	EPA 625	Fluorene
111.100	037	EPA 625	Hexachlorobenzene
111.100	038	EPA 625	Hexachlorobutadiene

111.100	039	EPA 625	Hexachlorocyclopentadiene
111.100	040	EPA 625	Hexachloroethane
111.100	041	EPA 625	Indeno(1,2,3-c,d)pyrene
111.100	042	EPA 625	Isophorone
111.100	043	EPA 625	2-Methyl-4,6-dinitrophenol
111.100	044	EPA 625	Naphthalene
111.100	045	EPA 625	Nitrobenzene
111.100	046	EPA 625	2-Nitrophenol
111.100	047	EPA 625	4-Nitrophenol
111.100	048	EPA 625	N-nitrosodimethylamine
111.100	049	EPA 625	N-nitrosodi-n-propylamine
111.100	050	EPA 625	N-nitrosodiphenylamine
111.100	051	EPA 625	Pentachlorophenol
111.100	052	EPA 625	Phenanthrene
111.100	053	EPA 625	Phenol
111.100	054	EPA 625	Pyrene
111.100	055	EPA 625	1,2,4-Trichlorobenzene
111.100	056	EPA 625	2,4,6-Trichlorophenol
111.101	036	EPA 625	Other Extractables
111.170	001	EPA 608	Aldrin
111.170	002	EPA 608	a-BHC
111.170	003	EPA 608	b-BHC
111.170	004	EPA 608	d-BHC
111.170	005	EPA 608	g-BHC (Lindane)
111.170	006	EPA 608	Chlordane
111.170	007	EPA 608	4,4'-DDD
111.170	008	EPA 608	4,4'-DDE
111.170	009	EPA 608	4,4'-DDT
111.170	010	EPA 608	Dieldrin
111.170	011	EPA 608	Endosulfan I
111.170	012	EPA 608	Endosulfan II
111.170	013	EPA 608	Endosulfan Sulfate
111.170	014	EPA 608	Endrin
111.170	015	EPA 608	Endrin Aldehyde
111.170	016	EPA 608	Heptachlor
111.170	017	EPA 608	Heptachlor Epoxide
111.170	018	EPA 608	Toxaphene
111.170	019	EPA 608	PCB-1016
111.170	020	EPA 608	PCB-1221
111.170	021	EPA 608	PCB-1232
111.170	022	EPA 608	PCB-1242

111.170	023	EPA 608	PCB-1248
111.170	024	EPA 608	PCB-1254
111.170	025	EPA 608	PCB-1260
111.170	030	EPA 608	Organochlorine Pesticides
111.170	031	EPA 608	PCBs
111.273	001	EPA 1664A	Oil and Grease

112 - Radiochemistry of Wastewater

112.010	001	EPA 900.0	Gross Alpha
112.010	002	EPA 900.0	Gross Beta
112.020	001	EPA 903.0	Total Alpha Radium
112.021	001	EPA 903.1	Radium-226
112.050	001	SM7500-Ra C	Radium-226
112.140	002	EPA 901.1	Gamma
112.160	001	EPA 904.0	Radium-228
112.180	001	EPA 906.0	Tritium
112.510	001	DOE Sr-02	Strontium
112.520	001	DOE U-02	Uranium

114 - Inorganic Chemistry of Hazardous Waste

114.010	001	EPA 6010B	Antimony
114.010	002	EPA 6010B	Arsenic
114.010	003	EPA 6010B	Barium
114.010	004	EPA 6010B	Beryllium
114.010	005	EPA 6010B	Cadmium
114.010	006	EPA 6010B	Chromium
114.010	007	EPA 6010B	Cobalt
114.010	008	EPA 6010B	Copper
114.010	009	EPA 6010B	Lead
114.010	010	EPA 6010B	Molybdenum
114.010	011	EPA 6010B	Nickel
114.010	012	EPA 6010B	Selenium
114.010	013	EPA 6010B	Silver
114.010	014	EPA 6010B	Thallium
114.010	015	EPA 6010B	Vanadium
114.010	016	EPA 6010B	Zinc
114.020	001	EPA 6020	Antimony
114.020	002	EPA 6020	Arsenic
114.020	005	EPA 6020	Cadmium
114.020	008	EPA 6020	Copper
114.020	009	EPA 6020	Lead
114.020	010	EPA 6020	Molybdenum
114.020	012	EPA 6020	Selenium

114.020	013	EPA 6020	Silver	
114.020	014	EPA 6020	Thallium	
114.020	015	EPA 6020	Vanadium	
114.103	001	EPA 7196A	Chromium (VI)	
114.140	001	EPA 7470A	Mercury	
114.141	001	EPA 7471A	Mercury	
114.222	001	EPA 9014	Cyanide	
114.240	001	EPA 9040B	Corrosivity - pH Determination	
114.241	001	EPA 9045C	Corrosivity - pH Determination	
114.250	001	EPA 9056	Fluoride	
114.270	001	EPA 9214	Fluoride	
115 - Extraction Test of Hazardous Waste				
115.020	001	EPA 1311	Toxicity Characteristic Leaching Procedure (TCLP)	
115.021	001	EPA 1311	TCLP Inorganics	
115.022	001	EPA 1311	TCLP Extractables	
115.023	001	EPA 1311	TCLP Volatiles	
115.030	001	CCR Chapter11, Article 5, Appendix II	Waste Extraction Test (WET)	CA Primary AA
115.040	001	EPA 1312	Synthetic Precipitation Leaching Procedure (SPLP)	
116 - Volatile Organic Chemistry of Hazardous Waste				
116.010	000	EPA 8011	EDB and DBCP	
116.010	001	EPA 8011	1,2-Dibromoethane	
116.010	002	EPA 8011	Dibromochloropropane	
116.030	001	EPA 8015B	Gasoline-range Organics	
116.040	002	EPA 8021B	Benzene	
116.040	011	EPA 8021B	Chlorobenzene	
116.040	023	EPA 8021B	1,2-Dichlorobenzene	
116.040	024	EPA 8021B	1,3-Dichlorobenzene	
116.040	025	EPA 8021B	1,4-Dichlorobenzene	
116.040	039	EPA 8021B	Ethylbenzene	
116.040	041	EPA 8021B	Methyl tert-butyl Ether (MTBE)	
116.040	047	EPA 8021B	Toluene	
116.040	056	EPA 8021B	Xylenes, Total	
116.040	061	EPA 8021B	Aromatic Volatiles	
116.040	062	EPA 8021B	BTEX	
116.080	000	EPA 8260B	Volatile Organic Compounds	
116.080	001	EPA 8260B	Acetone	
116.080	002	EPA 8260B	Acetonitrile	
116.080	003	EPA 8260B	Acrolein	
116.080	004	EPA 8260B	Acrylonitrile	
116.080	007	EPA 8260B	Benzene	
116.080	010	EPA 8260B	Bromochloromethane	

116.080	011	EPA 8260B	Bromodichloromethane
116.080	012	EPA 8260B	Bromoform
116.080	013	EPA 8260B	Bromomethane
116.080	015	EPA 8260B	Carbon Disulfide
116.080	016	EPA 8260B	Carbon Tetrachloride
116.080	018	EPA 8260B	Chlorobenzene
116.080	019	EPA 8260B	Chloroethane
116.080	020	EPA 8260B	2-Chloroethyl Vinyl Ether
116.080	021	EPA 8260B	Chloroform
116.080	022	EPA 8260B	Chloromethane
116.080	026	EPA 8260B	Dibromochloromethane
116.080	027	EPA 8260B	Dibromochloropropane
116.080	028	EPA 8260B	1,2-Dibromoethane
116.080	030	EPA 8260B	Dibromomethane
116.080	031	EPA 8260B	1,2-Dichlorobenzene
116.080	032	EPA 8260B	1,3-Dichlorobenzene
116.080	033	EPA 8260B	1,4-Dichlorobenzene
116.080	036	EPA 8260B	Dichlorodifluoromethane
116.080	037	EPA 8260B	1,1-Dichloroethane
116.080	038	EPA 8260B	1,2-Dichloroethane
116.080	039	EPA 8260B	1,1-Dichloroethene
116.080	040	EPA 8260B	trans-1,2-Dichloroethene
116.080	041	EPA 8260B	cis-1,2-Dichloroethene
116.080	042	EPA 8260B	1,2-Dichloropropane
116.080	043	EPA 8260B	1,3-Dichloropropane
116.080	044	EPA 8260B	2,2-Dichloropropane
116.080	045	EPA 8260B	1,1-Dichloropropene
116.080	046	EPA 8260B	cis-1,3-Dichloropropene
116.080	047	EPA 8260B	trans-1,3-Dichloropropene
116.080	050	EPA 8260B	1,4-Dioxane
116.080	053	EPA 8260B	Ethylbenzene
116.080	056	EPA 8260B	Hexachlorobutadiene
116.080	057	EPA 8260B	Hexachloroethane
116.080	058	EPA 8260B	2-Hexanone (MBK)
116.080	059	EPA 8260B	Iodomethane
116.080	064	EPA 8260B	Methyl tert-butyl Ether (MTBE)
116.080	065	EPA 8260B	Methylene Chloride
116.080	066	EPA 8260B	Methyl Ethyl Ketone
116.080	068	EPA 8260B	4-Methyl-2-pentanone (MIBK)
116.080	069	EPA 8260B	Naphthalene
116.080	081	EPA 8260B	1,1,1,2-Tetrachloroethane

116.080	082	EPA 8260B	1,1,2,2-Tetrachloroethane
116.080	083	EPA 8260B	Tetrachloroethene
116.080	084	EPA 8260B	Toluene
116.080	086	EPA 8260B	1,2,3-Trichlorobenzene
116.080	087	EPA 8260B	1,2,4-Trichlorobenzene
116.080	088	EPA 8260B	1,1,1-Trichloroethane
116.080	089	EPA 8260B	1,1,2-Trichloroethane
116.080	090	EPA 8260B	Trichloroethene
116.080	091	EPA 8260B	Trichlorofluoromethane
116.080	092	EPA 8260B	1,2,3-Trichloropropane
116.080	093	EPA 8260B	Vinyl Acetate
116.080	094	EPA 8260B	Vinyl Chloride
116.080	095	EPA 8260B	Xylenes, Total
116.080	099	EPA 8260B	Bromobenzene
116.080	100	EPA 8260B	n-Butylbenzene
116.080	101	EPA 8260B	sec-Butylbenzene
116.080	102	EPA 8260B	tert-Butylbenzene
116.080	103	EPA 8260B	2-Chlorotoluene
116.080	104	EPA 8260B	4-Chlorotoluene
116.080	105	EPA 8260B	Isopropylbenzene
116.080	106	EPA 8260B	N-propylbenzene
116.080	107	EPA 8260B	Styrene
116.080	108	EPA 8260B	1,2,4-Trimethylbenzene
116.080	109	EPA 8260B	1,3,5-Trimethylbenzene

117 - Semi-volatile Organic Chemistry of Hazardous Waste

117.010	001	EPA 8015B	Diesel-range Total Petroleum Hydrocarbons
117.110	000	EPA 8270C	Extractable Organics
117.110	001	EPA 8270C	Acenaphthene
117.110	002	EPA 8270C	Acenaphthylene
117.110	007	EPA 8270C	Aniline
117.110	008	EPA 8270C	Anthracene
117.110	011	EPA 8270C	Benz(a)anthracene
117.110	012	EPA 8270C	Benzo(b)fluoranthene
117.110	013	EPA 8270C	Benzo(k)fluoranthene
117.110	014	EPA 8270C	Benzo(g,h,i)perylene
117.110	015	EPA 8270C	Benzo(a)pyrene
117.110	016	EPA 8270C	Benzoic Acid
117.110	018	EPA 8270C	Benzyl Alcohol
117.110	019	EPA 8270C	Benzyl Butyl Phthalate
117.110	020	EPA 8270C	Bis(2-chloroethoxy)methane
117.110	021	EPA 8270C	Bis(2-chloroethyl) Ether

117.110	022	EPA 8270C	Bis(2-chloroisopropyl) Ether
117.110	023	EPA 8270C	Di(2-ethylhexyl) Phthalate
117.110	024	EPA 8270C	4-Bromophenyl Phenyl Ether
117.110	026	EPA 8270C	4-Chloroaniline
117.110	027	EPA 8270C	4-Chloro-3-methylphenol
117.110	029	EPA 8270C	2-Chloronaphthalene
117.110	031	EPA 8270C	4-Chlorophenyl Phenyl Ether
117.110	032	EPA 8270C	Chrysene
117.110	036	EPA 8270C	Dibenz(a,h)anthracene
117.110	037	EPA 8270C	Dibenzofuran
117.110	039	EPA 8270C	1,2-Dichlorobenzene
117.110	040	EPA 8270C	1,3-Dichlorobenzene
117.110	041	EPA 8270C	1,4-Dichlorobenzene
117.110	042	EPA 8270C	3,3'-Dichlorobenzidine
117.110	043	EPA 8270C	2,4-Dichlorophenol
117.110	045	EPA 8270C	Diethyl Phthalate
117.110	053	EPA 8270C	2,4-Dimethylphenol
117.110	054	EPA 8270C	Dimethyl Phthalate
117.110	055	EPA 8270C	Di-n-butyl phthalate
117.110	056	EPA 8270C	Di-n-octyl phthalate
117.110	060	EPA 8270C	2,4-Dinitrophenol
117.110	061	EPA 8270C	2,4-Dinitrotoluene
117.110	062	EPA 8270C	2,6-Dinitrotoluene
117.110	067	EPA 8270C	Fluoranthene
117.110	068	EPA 8270C	Fluorene
117.110	069	EPA 8270C	Hexachlorobenzene
117.110	070	EPA 8270C	Hexachlorobutadiene
117.110	071	EPA 8270C	Hexachlorocyclopentadiene
117.110	072	EPA 8270C	Hexachloroethane
117.110	075	EPA 8270C	Indeno(1,2,3-c,d)pyrene
117.110	076	EPA 8270C	Isophorone
117.110	080	EPA 8270C	2-Methyl-4,6-dinitrophenol
117.110	083	EPA 8270C	2-Methylnaphthalene
117.110	084	EPA 8270C	2-Methylphenol
117.110	085	EPA 8270C	3-Methylphenol
117.110	087	EPA 8270C	Naphthalene
117.110	092	EPA 8270C	2-Nitroaniline
117.110	093	EPA 8270C	3-Nitroaniline
117.110	094	EPA 8270C	4-Nitroaniline
117.110	095	EPA 8270C	Nitrobenzene
117.110	096	EPA 8270C	2-Nitrophenol

117.110	097	EPA 8270C	4-Nitrophenol
117.110	100	EPA 8270C	N-nitrosodimethylamine
117.110	101	EPA 8270C	N-nitrosodi-n-propylamine
117.110	102	EPA 8270C	N-nitrosodiphenylamine
117.110	110	EPA 8270C	Pentachlorophenol
117.110	112	EPA 8270C	Phenanthrene
117.110	113	EPA 8270C	Phenol
117.110	119	EPA 8270C	Pyrene
117.110	125	EPA 8270C	2,3,4,6-Tetrachlorophenol
117.110	129	EPA 8270C	1,2,4-Trichlorobenzene
117.110	130	EPA 8270C	2,4,5-Trichlorophenol
117.110	131	EPA 8270C	2,4,6-Trichlorophenol
117.170	000	EPA 8330	Nitroaromatics and Nitramines
117.170	001	EPA 8330	4-Amino-2,6-dinitrotoluene
117.170	002	EPA 8330	2-Amino-4,6-dinitrotoluene
117.170	003	EPA 8330	1,3-Dinitrobenzene
117.170	004	EPA 8330	2,4-Dinitrotoluene
117.170	005	EPA 8330	2,6-Dinitrotoluene
117.170	006	EPA 8330	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
117.170	007	EPA 8330	Methyl-2,4,6-trinitrophenylnitramine
117.170	008	EPA 8330	Nitrobenzene
117.170	009	EPA 8330	2-Nitrotoluene
117.170	010	EPA 8330	3-Nitrotoluene
117.170	011	EPA 8330	4-Nitrotoluene
117.170	012	EPA 8330	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
117.170	013	EPA 8330	1,3,5-Trinitrobenzene
117.170	014	EPA 8330	2,4,6-Trinitrotoluene
117.190	001	EPA 8332	Nitroglycerine
117.210	000	EPA 8081A	Organochlorine Pesticides
117.210	001	EPA 8081A	Aldrin
117.210	002	EPA 8081A	a-BHC
117.210	003	EPA 8081A	b-BHC
117.210	004	EPA 8081A	d-BHC
117.210	005	EPA 8081A	g-BHC (Lindane)
117.210	007	EPA 8081A	a-Chlordane
117.210	008	EPA 8081A	g-Chlordane
117.210	009	EPA 8081A	Chlordane (tech.)
117.210	013	EPA 8081A	4,4'-DDD
117.210	014	EPA 8081A	4,4'-DDE
117.210	015	EPA 8081A	4,4'-DDT
117.210	020	EPA 8081A	Dieldrin

117.210	021	EPA 8081A	Endosulfan I
117.210	022	EPA 8081A	Endosulfan II
117.210	023	EPA 8081A	Endosulfan Sulfate
117.210	024	EPA 8081A	Endrin
117.210	025	EPA 8081A	Endrin Aldehyde
117.210	026	EPA 8081A	Endrin Ketone
117.210	027	EPA 8081A	Heptachlor
117.210	028	EPA 8081A	Heptachlor Epoxide
117.210	033	EPA 8081A	Methoxychlor
117.210	039	EPA 8081A	Toxaphene
117.220	000	EPA 8082	PCBs
117.220	001	EPA 8082	PCB-1016
117.220	002	EPA 8082	PCB-1221
117.220	003	EPA 8082	PCB-1232
117.220	004	EPA 8082	PCB-1242
117.220	005	EPA 8082	PCB-1248
117.220	006	EPA 8082	PCB-1254
117.220	007	EPA 8082	PCB-1260
117.240	002	EPA 8141A	Azinphos Methyl
117.240	005	EPA 8141A	Chlorpyrifos
117.240	007	EPA 8141A	Demeton-O
117.240	008	EPA 8141A	Demeton-S
117.240	009	EPA 8141A	Diazinon
117.240	011	EPA 8141A	Disulfoton
117.240	015	EPA 8141A	Malathion
117.240	016	EPA 8141A	Mevinphos
117.240	017	EPA 8141A	Naled
117.240	019	EPA 8141A	Parathion Methyl
117.240	020	EPA 8141A	Phorate
117.240	022	EPA 8141A	Ronnel
117.250	000	EPA 8151A	Chlorinated Herbicides
117.250	001	EPA 8151A	2,4-D
117.250	002	EPA 8151A	2,4-DB
117.250	003	EPA 8151A	2,4,5-T
117.250	004	EPA 8151A	2,4,5-TP
117.250	005	EPA 8151A	5-Hydroxydicamba
117.250	006	EPA 8151A	Dalapon
117.250	007	EPA 8151A	Dichlorprop
117.250	008	EPA 8151A	Dinoseb
117.250	009	EPA 8151A	MCPA
117.250	010	EPA 8151A	MCPP

118 - Radiochemistry of Hazardous Waste			
118.010	001	EPA 9310	Gross Alpha
118.010	002	EPA 9310	Gross Beta
118.020	001	EPA 9315	Radium, Total
118.030	001	EPA 9320	Radium-228
118.271	001	DOE Sr-02	Strontium
118.290	001	DOE U-02	Uranium
120 - Physical Properties of Hazardous Waste			
120.010	001	EPA 1010	Ignitability
120.040	001	Section 7.3 SW-846	Reactive Cyanide
120.050	001	Section 7.3 SW-846	Reactive Sulfide
120.070	001	EPA 9040B	Corrosivity - pH Determination
120.080	001	EPA 9045C	Corrosivity - pH Determination

NELAP - RECOGNIZED

CALIFORNIA STATE

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM BRANCH

CERTIFICATE OF NELAP ACCREDITATION

Is hereby granted to

PARAGON ANALYTICS, A division of DataChem Laboratories, Inc.

FORT COLLINS

225 COMMERCE DRIVE

FORT COLLINS, CO 80524

Scope of the Certificate is limited to the
"NELAP Fields of Accreditation"
which accompany this Certificate.

Continued accredited status depends on successful
ongoing participation in the program.

This Certificate is granted in accordance with provisions of
Section 100825, et seq. of the Health and Safety Code.

Certificate No.: **06251CA**

Expiration Date: **08/31/2009**

Effective Date: **08/31/2008**

Richmond, California
subject to forfeiture or revocation

George C. Kulasingam, Ph.D., Chief
Environmental Laboratory Accreditation Program Branch

STATE OF COLORADO

Bill Ritter, Jr., Governor
James B. Martin, Executive Director

Dedicated to protecting and improving the health and environment of the people of Colorado

Laboratory Services Division
8100 Lowry Blvd.
Denver, Colorado 80230-6928
(303) 692-3090

www.cdphe.state.co.us/lr

Colorado Department
of Public Health
and Environment

November 13, 2008

Ms. Deb Scheib
ALS Laboratory Group
formerly, Paragon Analytics (a Division of Data-Chem Laboratories, Inc.)
225 Commerce Drive
Fort Collins, CO 80524

RE: Radiochemistry Certification

Dear Ms. Scheib:

On October 22 & November 6, 2008 an on-site assessment was performed at ALS Laboratory Group (formerly, Paragon Analytics) in Fort Collins to evaluate the laboratory's adherence to certification protocol outlined in the EPA Manual for the Certification of Laboratories Analyzing Drinking Water (5th Edition, 2005), and to quality control and procedural requirements in the individual methods under review. During the visit, I interviewed key personnel in the Radiochemistry department, including Renee Gallegos (Manager) and Steve Workman (Technical Manager), along with other personnel involved with sample receiving, sample prep, instrumentation, etc. I found all items in compliance with method requirements. My overall impression was that the Radiochemistry staff is technically competent and well managed.

Enclosed is your new Colorado Department of Public Health and Environment Safe Drinking Water (SDW) Radiochemistry Certificate and status report dated November1, 2008, which is effective through October 31, 2009, unless suspended or revoked prior to that date, and is based on your laboratory's successful completion of the on-site assessment and successful participation in recent PT Studies (ERA RAD-72/74 & MRAD-8).

This certification must be renewed by October 2009. Routine on-site inspections are conducted every two years (biennial), unless the certification is modified. In all probability there will not be an assessment at the time of renewal, but it is the laboratory's responsibility to submit a renewal application and annual certification fee. If you have any questions, or if there are changes that may affect your certification status, you can reach me at (303) 692-3045.

Sincerely,

Ken Johnson, Certification Officer
Laboratory Services Division

Enclosures: As Stated

H:\ALSparagon-radcertltr11132008.doc

STATE OF COLORADO
SAFE DRINKING WATER ACT
RADIOCHEMISTRY CERTIFICATION

Name: **Paragon Analytics**
Division of Data-Chem Laboratories, Inc.
225 Commerce Drive
Fort Collins, Colorado 80524

Date: **November 1, 2008**

RADIONUCLIDES

STATUS	NATURALLY OCCURRING	METHOD	DESCRIPTION
(A)	Gross Alpha	EPA-900.0	Evaporation
(A)	Gross Beta	EPA-900.0	Evaporation
(A)	Radium-226	EPA-903.0	Radiochemical
(A)	Radium-226	EPA-903.1	Radon Emanation
(A)	Radium-228	EPA-904.0	Radiochemical
(A)	Uranium	DOE-U-02	Alpha Spectrometry
	MAN-MADE		
(N)	Iodine-131	----------	----------
(N)	Strontium-89 / 90	----------	----------
(A)	Tritium	EPA-906.0	Liquid Scintillation
	GAMMA EMITTERS		
(A)	Barium-133	EPA-901.1	Gamma-Ray Spectrometry
(A)	Cesium-134	EPA-901.1	Gamma-Ray Spectrometry
(A)	Cesium-137	EPA-901.1	Gamma-Ray Spectrometry
(A)	Cobalt-60	EPA-901.1	Gamma-Ray Spectrometry
(A)	Zinc-65	EPA-901.1	Gamma-Ray Spectrometry

(A) = Approved / Certified
(N) = Not Certified
(P) = Provisionally Certified
(I) = Interim

STATE OF COLORADO

Department of Public Health and Environment

under Primacy Agreement with the
United States Environmental Protection Agency
Pursuant to the Safe Drinking Water Regulations, 40CFR, Part 141

Certifies

ALS LABORATORY GROUP

Environmental Division
225 Commerce Drive
Fort Collins, CO 80524

is in compliance with the criteria and procedures of the EPA Manual for the Certification of Laboratories Analyzing Drinking Water. The laboratory may perform Radiochemical Analysis on public drinking water for the following analytes:

Gross α/β, Radium 226/228, Uranium, Tritium, Gamma Emitters.

Approved for the methods on attached list dated November 1, 2008.

EFFECTIVE: November 1, 2008 through October 31, 2009.

STATE OF COLORADO
NIL SINE NUMINE
1876

David A. Butcher, Director
Laboratory Services Division

Laboratory Services Division
Colorado Department of Public Health and Environment

LITHO. IN U.S.A.

STATE OF CONNECTICUT

DEPARTMENT OF PUBLIC HEALTH

REGULATORY SERVICES BRANCH
ENVIRONMENTAL HEALTH SECTION
ENVIRONMENTAL LABORATORY CERTIFICATION PROGRAM

Ms. Debra Scheib
Paragon Analytics – Division of DataChem Laboratories
225 Commerce Drive
Fort Collins, CO 80524

July 18, 2008

Dear Ms. Scheib:

Enclosed are Paragon Analytics' new Connecticut Certificate of Approval and Approved Analytes List. Please review the documents carefully and notify the program of any errors or omissions. Note that Connecticut certifies out of state laboratories by reciprocity. Certification could only be granted for those analytes for which documentation of certification was provided.

Sincerely yours,

Jeffrey C. Curran
Public Health Services Manager

Phone: (860) 509- 7389
Telephone Device for the Deaf: (860) 509-7191
410 Capitol Avenue - MS #51LAB
P.O. Box 340308 Hartford, CT 06134

STATE OF CONNECTICUT

DEPARTMENT OF PUBLIC HEALTH
ENVIRONMENTAL HEALTH SECTION

ENVIRONMENTAL LABORATORY CERTIFICATION PROGRAM

APPROVED ANALYTES REPORT
FOR ALL MATRICES

Paragon Analytics - Div. of DataChem Labs

CT-APP-NUM PH-0232

LOCATION

225 COMMERCE DRIVE

Fort Collins **CO** **80524-**

PHONE **(970)-490-1511**

REGISTERED OWNER/ AUTHORIZED AGENT **Ken Campbell**

DIRECTOR **Ken Campbell**

CO DIRECTOR(S)

APPROVED BY _____ DATE 07/16/2008 9:08:00 AM

JEFFREY C. CURRAN

LABORATORY APPROVAL EXPIRATION DATE 06/30/2010

LABORATORY STATUS **APPROVED**

ANY QUESTIONS CONCERNING THIS DOCUMENT SHOULD BE ADDRESSED TO
THE ENVIRONMENTAL LABORATORY CERTIFICATION PROGRAM AT (860) 509-7389

DRINKING WATER (SDWA)

STATUS REPORTED ON 07/16/2008

SOC: REGULATED SYNTHETIC ORGANIC CHEMICAL
WITH MINIMUM MDL REQUIREMENTS

ANALYTE NAME

RADIOCHEMICALS

GROSS ALPHA

GROSS BETA

GAMMA (PHOTON) EMITTERS

RADIUM - 226

RADIUM - 228

STRONTIUM - 89

STRONTIUM - 90

TRITIUM

URANIUM

NON-POTABLE WATER/ WASTEWATER

STATUS REPORTED ON 07/16/2008

ANALYTE NAME

PHYSICALS

PH

CONDUCTIVITY

MINERALS

ALKALINITY

CHLORIDE

FLUORIDE

HARDNESS, TOTAL

HARDNESS, CALCIUM

SILICA

SULFATE

SULFIDE

NUTRIENTS

AMMONIA

NITRATE

NITRITE

O-PHOSPHATE

TOTAL PHOSPHOROUS

METALS

ALUMINUM

ANTIMONY

ARSENIC

BARIUM

BERYLLIUM

BORON

CADMIUM

CALCIUM

CHROMIUM

CHROMIUM - Hexavalent

COBALT

COPPER

IRON

LEAD

MAGNESIUM

MANGANESE

MERCURY

MOLYBDENUM

NICKEL

POTASSIUM

SELENIUM

SILVER

SODIUM

STRONTIUM

THALLIUM

TIN

TITANIUM

VANADIUM

ZINC

RESIDUE

TOTAL RESIDUE (SOLIDS)

TOTAL VOLATILE RESIDUE

TOTAL DISSOLVED SOLIDS

DEMANDS

TOTAL ORGANIC CARBON

MISCELLANEOUS

CYANIDE (TOTAL)

INORGANIC DISINFECTION BY-PRODUCTS

BROMIDE

PERCHLORATE

PESTICIDES/ PCB's

POLYCHLORINATED BIPHENYLS

ORGANOCHLORINE PESTICIDES (Single Response)

CHLORDANE (TECHNICAL)

TOXAPHENE

SOLVENTS

OIL AND GREASE

HERBICIDES

DALAPON

DICAMBA

DINOSEB

2,4-D

2,4-DB

2,4,5-T

2,4,5- TP (SILVEX)

DICHLOROPROP

MCPA

MCPP

ORGANICS

ACID EXTRACTABLES (PHENOLS)

BENZIDINES

PHTHALATE ESTERS

NITROSAMINES

NITROAROMATICS & ISOPHORONE

POLYNUCLEAR AROMATIC HYDROCARBONS

HALOETHERS

CHLORINATED HYDROCARBONS

VOLATILE ORGANICS

RADIOCHEMICALS

GROSS ALPHA

GROSS BETA

GAMMA (PHOTON) EMITTERS

RADIUM - 226

RADIUM - 228

STRONTIUM - 90

TRITIUM

URANIUM

SOLID WASTE/SOIL

STATUS REPORTED ON 07/16/2008

ANALYTE NAME

PHYSICALS

PH

METALS

ALUMINUM
ANTIMONY
ARSENIC
BARIUM
BERYLLIUM
BORON
CADMIUM
CALCIUM
CHROMIUM
CHROMIUM - Hexavalent
COBALT
COPPER
IRON
LEAD
MAGNESIUM
MANGANESE
MERCURY
MOLYBDENUM
NICKEL
POTASSIUM
SELENIUM
SILVER
SODIUM
STRONTIUM
THALLIUM
TIN
TITANIUM
VANADIUM
ZINC

DEMANDS

TOTAL ORGANIC CARBON

MISCELLANEOUS

CYANIDE (TOTAL)
IGNITABILITY
CORROSIVITY
TCLP LEACH (1311)
SPLP LEACH (1312)
REACTIVITY

PESTICIDES/ PCB's

POLYCHLORINATED BIPHENYLS
ORGANOCHLORINE PESTICIDES (Single Response)
CHLORDANE (TECHNICAL)
TOXAPHENE

SOLVENTS

OIL AND GREASE

HERBICIDES

DALAPON
DICAMBA
DINOSEB
2,4-D
2,4-DB
2,4,5-T
2,4,5- TP (SILVEX)
DICHLOROPROP
MCPA
MCPP

SOLID WASTE ORGANICS

VOLATILE ORGANICS (SW)
ACID EXTRACTABLES (PHENOLS) (SW)
3,3'-DICHLOROBENZIDINE (SW)
PHTHALATES (SW)
NITROSOAMINES (SW)
NITROAROMATICS & CYCLIC KETONES (SW)
PAH's (SW)
HALOETHERS (SW)
CHLORINATED HYDROCARBONS (SW)

RADIOCHEMICALS

GROSS ALPHA
GROSS BETA
RADIUM - 226
RADIUM - 228

END OF SECTION FOR Paragon Analytics - Div. of DataChem Labs

REPORT PROFILE

Report Printed on: 07/16/2008 9:08:01 AM
Report Name: APPROVED TESTS_ALT_NEW
Printed by: jeff
Report published from: CERTIFICATION REPORTS screen #3

lab code = ID1242P
test code = *
matrix code = *
matrix selection = ALL OR SOME MATRICES SELECTED
certifications approved or provisional on 07/16/2008

THIS IS THE LAST PAGE OF THE REPORT

State of Connecticut, Department of Public Health

Approved Environmental Laboratory

THIS IS TO CERTIFY THAT THE LABORATORY DESCRIBED BELOW HAS BEEN APPROVED BY THE STATE DEPARTMENT OF PUBLIC HEALTH PURSUANT TO APPLICABLE PROVISIONS OF THE PUBLIC HEALTH CODE AND GENERAL STATUTES OF CONNECTICUT, FOR MAKING THE EXAMINATIONS, DETERMINATIONS OR TESTS SPECIFIED BELOW WHICH HAVE BEEN AUTHORIZED IN WRITING BY THAT DEPARTMENT.

PARAGON ANALYTICS – DIVISION OF DATACHEM LABORATORIES

LOCATED AT 225 Commerce Drive IN Fort Collins, Colorado 80524

AND REGISTERED IN THE NAME OF Ken Campbell

THIS CERTIFICATE IS ISSUED IN THE NAME OF Ken Campbell WHO HAS BEEN DESIGNATED BY THE REGISTERED OWNER\AUTHORIZED AGENT TO BE IN CHARGE OF THE LABORATORY WORK COVERED BY THIS CERTIFICATE OF APPROVAL AS FOLLOWS:

DRINKING WATER, NON-POTABLE WATER/WASTEWATER, SOLID WASTE/SOIL

Examination For:

INORGANIC CHEMICALS

ORGANIC CHEMICALS

RADIOCHEMICALS

SEE COMPUTER PRINT-OUT FOR SPECIFIC TESTS APPROVED

THIS CERTIFICATE EXPIRES June 30, 2010 AND IS REVOCABLE FOR CAUSE BY THE STATE DEPARTMENT OF PUBLIC HEALTH

DATED AT HARTFORD, CONNECTICUT, THIS 16th DAY OF July 2008

Registration No.

PH - 0232

SUZANNE BLANCAFLOR, MS
CHIEF, ENVIRONMENTAL HEALTH SECTION

Laboratory Scope of Accreditation

Attachment to Certificate #: E87914-06, expiration date June 30, 2009. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E87914 **EPA Lab Code: CO00078** **(970) 490-1511**

E87914
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
1,1,1,2-Tetrachloroethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,1,1-Trichloroethane	EPA 624	Volatile Organics	NELAP	8/8/2005
1,1,1-Trichloroethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,1,2,2-Tetrachloroethane	EPA 624	Volatile Organics	NELAP	8/8/2005
1,1,2,2-Tetrachloroethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,1,2-Trichloroethane	EPA 624	Volatile Organics	NELAP	8/8/2005
1,1,2-Trichloroethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,1-Dichloroethane	EPA 624	Volatile Organics	NELAP	8/8/2005
1,1-Dichloroethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,1-Dichloroethylene	EPA 624	Volatile Organics	NELAP	8/8/2005
1,1-Dichloropropene	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2,3-Trichlorobenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2,3-Trichloropropane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2,4-Trichlorobenzene	EPA 625	Extractable Organics	NELAP	8/8/2005
1,2,4-Trichlorobenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2,4-Trichlorobenzene	EPA 8270	Extractable Organics	NELAP	8/8/2005
1,2,4-Trimethylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2-Dibromo-3-chloropropane (DBCP)	EPA 8011	Volatile Organics	NELAP	8/8/2005
1,2-Dibromo-3-chloropropane (DBCP)	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 8011	Volatile Organics	NELAP	8/8/2005
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2-Dichlorobenzene	EPA 624	Volatile Organics	NELAP	8/8/2005
1,2-Dichlorobenzene	EPA 625	Extractable Organics	NELAP	8/8/2005
1,2-Dichlorobenzene	EPA 8021	Volatile Organics	NELAP	8/8/2005
1,2-Dichlorobenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2-Dichlorobenzene	EPA 8270	Extractable Organics	NELAP	8/8/2005
1,2-Dichloroethane	EPA 624	Volatile Organics	NELAP	8/8/2005
1,2-Dichloroethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,2-Dichloropropane	EPA 624	Volatile Organics	NELAP	8/8/2005
1,2-Dichloropropane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,3,5-Trimethylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,3,5-Trinitrobenzene (1,3,5-TNB)	EPA 8330	Extractable Organics	NELAP	8/8/2005
1,3-Dichlorobenzene	EPA 624	Volatile Organics	NELAP	8/8/2005
1,3-Dichlorobenzene	EPA 625	Extractable Organics	NELAP	8/8/2005
1,3-Dichlorobenzene	EPA 8021	Volatile Organics	NELAP	8/8/2005
1,3-Dichlorobenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005

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Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
1,3-Dichlorobenzene	EPA 8270	Extractable Organics	NELAP	8/8/2005
1,3-Dichloropropane	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,3-Dinitrobenzene (1,3-DNB)	EPA 8330	Extractable Organics	NELAP	8/8/2005
1,4-Dichlorobenzene	EPA 624	Volatile Organics	NELAP	8/8/2005
1,4-Dichlorobenzene	EPA 625	Extractable Organics	NELAP	8/8/2005
1,4-Dichlorobenzene	EPA 8021	Volatile Organics	NELAP	8/8/2005
1,4-Dichlorobenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
1,4-Dichlorobenzene	EPA 8270	Extractable Organics	NELAP	8/8/2005
1-Chlorohexane	EPA 8260	Volatile Organics	NELAP	8/8/2005
2,2-Dichloropropane	EPA 8260	Volatile Organics	NELAP	8/8/2005
2,3,4,6-Tetrachlorophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,4,5-T	EPA 615	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
2,4,5-T	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
2,4,5-Trichlorophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,4,6-Trichlorophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
2,4,6-Trichlorophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,4,6-Trinitrotoluene (2,4,6-TNT)	EPA 8330	Extractable Organics	NELAP	8/8/2005
2,4-D	EPA 615	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
2,4-D	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
2,4-DB	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
2,4-Dichlorophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
2,4-Dichlorophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,4-Dimethylphenol	EPA 625	Extractable Organics	NELAP	8/8/2005
2,4-Dimethylphenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,4-Dinitrophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
2,4-Dinitrophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,4-Dinitrotoluene (2,4-DNT)	EPA 625	Extractable Organics	NELAP	8/8/2005
2,4-Dinitrotoluene (2,4-DNT)	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,4-Dinitrotoluene (2,4-DNT)	EPA 8330	Extractable Organics	NELAP	8/8/2005
2,6-Dinitrotoluene (2,6-DNT)	EPA 625	Extractable Organics	NELAP	8/8/2005
2,6-Dinitrotoluene (2,6-DNT)	EPA 8270	Extractable Organics	NELAP	8/8/2005
2,6-Dinitrotoluene (2,6-DNT)	EPA 8330	Extractable Organics	NELAP	8/8/2005
2-Amino-4,6-dinitrotoluene (2-am-dnt)	EPA 8330	Extractable Organics	NELAP	8/8/2005
2-Butanone (Methyl ethyl ketone, MEK)	EPA 8260	Volatile Organics	NELAP	8/8/2005
2-Chloroethyl vinyl ether	EPA 624	Volatile Organics	NELAP	8/8/2005
2-Chloroethyl vinyl ether	EPA 8260	Volatile Organics	NELAP	8/8/2005

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Paragon Analytics
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Analyte	Method/Tech	Category	Certification Type	Effective Date
2-Chloronaphthalene	EPA 625	Extractable Organics	NELAP	8/8/2005
2-Chloronaphthalene	EPA 8270	Extractable Organics	NELAP	8/8/2005
2-Chlorophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
2-Chlorophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2-Chlorotoluene	EPA 8260	Volatile Organics	NELAP	8/8/2005
2-Hexanone	EPA 8260	Volatile Organics	NELAP	8/8/2005
2-Methyl-4,6-dinitrophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
2-Methyl-4,6-dinitrophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2-Methylnaphthalene	EPA 8270	Extractable Organics	NELAP	8/8/2005
2-Methylphenol (o-Cresol)	EPA 625	Extractable Organics	NELAP	8/8/2005
2-Methylphenol (o-Cresol)	EPA 8270	Extractable Organics	NELAP	8/8/2005
2-Nitroaniline	EPA 8270	Extractable Organics	NELAP	8/8/2005
2-Nitrophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
2-Nitrophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
2-Nitrotoluene	EPA 8330	Extractable Organics	NELAP	8/8/2005
3,3'-Dichlorobenzidine	EPA 625	Extractable Organics	NELAP	8/8/2005
3,3'-Dichlorobenzidine	EPA 8270	Extractable Organics	NELAP	8/8/2005
3-Methylphenol (m-Cresol)	EPA 8270	Extractable Organics	NELAP	8/8/2005
3-Nitroaniline	EPA 8270	Extractable Organics	NELAP	8/8/2005
3-Nitrotoluene	EPA 8330	Extractable Organics	NELAP	8/8/2005
4,4'-DDD	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
4,4'-DDD	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
4,4'-DDE	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
4,4'-DDE	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
4,4'-DDT	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
4,4'-DDT	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
4-Amino-2,6-dinitrotoluene (4-am-dnt)	EPA 8330	Extractable Organics	NELAP	8/8/2005
4-Bromophenyl phenyl ether	EPA 625	Extractable Organics	NELAP	8/8/2005
4-Bromophenyl phenyl ether	EPA 8270	Extractable Organics	NELAP	8/8/2005
4-Chloro-3-methylphenol	EPA 625	Extractable Organics	NELAP	8/8/2005
4-Chloro-3-methylphenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
4-Chloroaniline	EPA 8270	Extractable Organics	NELAP	8/8/2005
4-Chlorophenyl phenylether	EPA 625	Extractable Organics	NELAP	8/8/2005
4-Chlorophenyl phenylether	EPA 8270	Extractable Organics	NELAP	8/8/2005
4-Chlorotoluene	EPA 8260	Volatile Organics	NELAP	8/8/2005
4-Methyl-2-pentanone (MIBK)	EPA 8260	Volatile Organics	NELAP	8/8/2005

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Analyte	Method/Tech	Category	Certification Type	Effective Date
4-Methylphenol (p-Cresol)	EPA 625	Extractable Organics	NELAP	8/8/2005
4-Methylphenol (p-Cresol)	EPA 8270	Extractable Organics	NELAP	8/8/2005
4-Nitroaniline	EPA 8270	Extractable Organics	NELAP	8/8/2005
4-Nitrophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
4-Nitrophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
4-Nitrotoluene	EPA 8330	Extractable Organics	NELAP	8/8/2005
Acenaphthene	EPA 625	Extractable Organics	NELAP	8/8/2005
Acenaphthene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Acenaphthylene	EPA 625	Extractable Organics	NELAP	8/8/2005
Acenaphthylene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Acetone	EPA 8260	Volatile Organics	NELAP	8/8/2005
Acrolein (Propenal)	EPA 624	Volatile Organics	NELAP	8/8/2005
Acrolein (Propenal)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Acrylonitrile	EPA 624	Volatile Organics	NELAP	8/8/2005
Acrylonitrile	EPA 8260	Volatile Organics	NELAP	8/8/2005
Aldrin	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aldrin	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Alkalinity as CaCO3	EPA 310.1	General Chemistry	NELAP	8/8/2005
alpha-BHC (alpha-Hexachlorocyclohexane)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
alpha-BHC (alpha-Hexachlorocyclohexane)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
alpha-Chlordane	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aluminum	EPA 200.7	Metals	NELAP	8/8/2005
Aluminum	EPA 6010	Metals	NELAP	8/8/2005
Amenable cyanide	EPA 335.1	General Chemistry	NELAP	8/8/2005
Amenable cyanide	EPA 9010/9014	General Chemistry	NELAP	8/8/2005
Ammonia as N	EPA 350.1	General Chemistry	NELAP	8/8/2005
Aniline	EPA 625	Extractable Organics	NELAP	8/8/2005
Aniline	EPA 8270	Extractable Organics	NELAP	8/8/2005
Anthracene	EPA 625	Extractable Organics	NELAP	8/8/2005
Anthracene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Antimony	EPA 200.7	Metals	NELAP	8/8/2005
Antimony	EPA 6010	Metals	NELAP	8/8/2005
Aroclor-1016 (PCB-1016)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1016 (PCB-1016)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1221 (PCB-1221)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1221 (PCB-1221)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	8/8/2005

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Analyte	Method/Tech	Category	Certification Type	Effective Date
Aroclor-1232 (PCB-1232)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1232 (PCB-1232)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1242 (PCB-1242)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1242 (PCB-1242)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1248 (PCB-1248)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1248 (PCB-1248)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1254 (PCB-1254)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1254 (PCB-1254)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1260 (PCB-1260)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Aroclor-1260 (PCB-1260)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Arsenic	EPA 200.7	Metals	NELAP	8/8/2005
Arsenic	EPA 6010	Metals	NELAP	8/8/2005
Azinphos-methyl (Guthion)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Barium	EPA 200.7	Metals	NELAP	8/8/2005
Barium	EPA 6010	Metals	NELAP	8/8/2005
Benzene	EPA 624	Volatile Organics	NELAP	8/8/2005
Benzene	EPA 8021	Volatile Organics	NELAP	8/8/2005
Benzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Benzidine	EPA 625	Extractable Organics	NELAP	8/8/2005
Benzidine	EPA 8270	Extractable Organics	NELAP	8/8/2005
Benzo(a)anthracene	EPA 625	Extractable Organics	NELAP	8/8/2005
Benzo(a)anthracene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Benzo(a)pyrene	EPA 625	Extractable Organics	NELAP	8/8/2005
Benzo(a)pyrene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Benzo(b)fluoranthene	EPA 625	Extractable Organics	NELAP	8/8/2005
Benzo(b)fluoranthene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Benzo(g,h,i)perylene	EPA 625	Extractable Organics	NELAP	8/8/2005
Benzo(g,h,i)perylene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Benzo(k)fluoranthene	EPA 625	Extractable Organics	NELAP	8/8/2005
Benzo(k)fluoranthene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Benzoic acid	EPA 8270	Extractable Organics	NELAP	8/8/2005
Benzyl alcohol	EPA 8270	Extractable Organics	NELAP	8/8/2005
Beryllium	EPA 200.7	Metals	NELAP	8/8/2005
Beryllium	EPA 6010	Metals	NELAP	8/8/2005
beta-BHC (beta-Hexachlorocyclohexane)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
beta-BHC (beta-Hexachlorocyclohexane)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005

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Analyte	Method/Tech	Category	Certification Type	Effective Date
bis(2-Chloroethoxy)methane	EPA 625	Extractable Organics	NELAP	8/8/2005
bis(2-Chloroethoxy)methane	EPA 8270	Extractable Organics	NELAP	8/8/2005
bis(2-Chloroethyl) ether	EPA 625	Extractable Organics	NELAP	8/8/2005
bis(2-Chloroethyl) ether	EPA 8270	Extractable Organics	NELAP	8/8/2005
bis(2-Chloroisopropyl) ether (2,2'-Oxybis(1-chloropropane))	EPA 625	Extractable Organics	NELAP	8/8/2005
bis(2-Chloroisopropyl) ether (2,2'-Oxybis(1-chloropropane))	EPA 8270	Extractable Organics	NELAP	8/8/2005
bis(2-Ethylhexyl) phthalate (DEHP)	EPA 625	Extractable Organics	NELAP	8/8/2005
bis(2-Ethylhexyl) phthalate (DEHP)	EPA 8270	Extractable Organics	NELAP	8/8/2005
Bolstar (Sulprofos)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Boron	EPA 200.7	Metals	NELAP	8/8/2005
Boron	EPA 6010	Metals	NELAP	8/8/2005
Bromide	EPA 300.0	General Chemistry	NELAP	8/8/2005
Bromide	EPA 9056	General Chemistry	NELAP	8/8/2005
Bromobenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Bromochloromethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
Bromodichloromethane	EPA 624	Volatile Organics	NELAP	8/8/2005
Bromodichloromethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
Bromoform	EPA 624	Volatile Organics	NELAP	8/8/2005
Bromoform	EPA 8260	Volatile Organics	NELAP	8/8/2005
Butyl benzyl phthalate	EPA 625	Extractable Organics	NELAP	8/8/2005
Butyl benzyl phthalate	EPA 8270	Extractable Organics	NELAP	8/8/2005
Cadmium	EPA 200.7	Metals	NELAP	8/8/2005
Cadmium	EPA 6010	Metals	NELAP	8/8/2005
Calcium	EPA 200.7	Metals	NELAP	8/8/2005
Calcium	EPA 6010	Metals	NELAP	8/8/2005
Carbazole	EPA 8270	Extractable Organics	NELAP	8/8/2005
Carbon disulfide	EPA 8260	Volatile Organics	NELAP	8/8/2005
Carbon tetrachloride	EPA 624	Volatile Organics	NELAP	8/8/2005
Carbon tetrachloride	EPA 8260	Volatile Organics	NELAP	8/8/2005
Chlordane (tech.)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Chloride	EPA 300.0	General Chemistry	NELAP	8/8/2005
Chloride	EPA 325.3	General Chemistry	NELAP	8/8/2005
Chloride	EPA 9056	General Chemistry	NELAP	8/8/2005
Chlorobenzene	EPA 624	Volatile Organics	NELAP	8/8/2005
Chlorobenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005

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Analyte	Method/Tech	Category	Certification Type	Effective Date
Chloroethane	EPA 624	Volatile Organics	NELAP	8/8/2005
Chloroethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
Chloroform	EPA 624	Volatile Organics	NELAP	8/8/2005
Chloroform	EPA 8260	Volatile Organics	NELAP	8/8/2005
Chlorpyrifos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Chromium	EPA 200.7	Metals	NELAP	8/8/2005
Chromium	EPA 6010	Metals	NELAP	8/8/2005
Chromium VI	EPA 7196	Metals	NELAP	8/8/2005
Chrysene	EPA 625	Extractable Organics	NELAP	8/8/2005
Chrysene	EPA 8270	Extractable Organics	NELAP	8/8/2005
cis-1,2-Dichloroethylene	EPA 8260	Volatile Organics	NELAP	8/8/2005
cis-1,3-Dichloropropene	EPA 624	Volatile Organics	NELAP	8/8/2005
cis-1,3-Dichloropropene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Cobalt	EPA 200.7	Metals	NELAP	8/8/2005
Cobalt	EPA 6010	Metals	NELAP	8/8/2005
Conductivity	EPA 120.1	General Chemistry	NELAP	8/8/2005
Copper	EPA 200.7	Metals	NELAP	8/8/2005
Copper	EPA 6010	Metals	NELAP	8/8/2005
Coumaphos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Dalapon	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
delta-BHC	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
delta-BHC	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Demeton-o	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Demeton-s	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Diazinon	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Dibenz(a,h) anthracene	EPA 625	Extractable Organics	NELAP	8/8/2005
Dibenz(a,h) anthracene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Dibenzofuran	EPA 8270	Extractable Organics	NELAP	8/8/2005
Dibromochloromethane	EPA 624	Volatile Organics	NELAP	8/8/2005
Dibromochloromethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
Dibromomethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
Dicamba	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Dichlorodifluoromethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
Dichloroprop (Dichlorprop)	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Dichlorovos (DDVP, Dichlorvos)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Dieldrin	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005

Laboratory Scope of Accreditation

Attachment to Certificate #: E87914-06, expiration date June 30, 2009. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E87914 **EPA Lab Code: CO00078** **(970) 490-1511**

E87914
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Dieldrin	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Diesel range organics (DRO)	EPA 8015	Extractable Organics	NELAP	8/8/2005
Diethyl phthalate	EPA 625	Extractable Organics	NELAP	8/8/2005
Diethyl phthalate	EPA 8270	Extractable Organics	NELAP	8/8/2005
Dimethyl phthalate	EPA 625	Extractable Organics	NELAP	8/8/2005
Dimethyl phthalate	EPA 8270	Extractable Organics	NELAP	8/8/2005
Di-n-butyl phthalate	EPA 625	Extractable Organics	NELAP	8/8/2005
Di-n-butyl phthalate	EPA 8270	Extractable Organics	NELAP	8/8/2005
Di-n-octyl phthalate	EPA 625	Extractable Organics	NELAP	8/8/2005
Di-n-octyl phthalate	EPA 8270	Extractable Organics	NELAP	8/8/2005
Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Disulfoton	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endosulfan I	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endosulfan I	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endosulfan II	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endosulfan II	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endosulfan sulfate	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endosulfan sulfate	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endrin	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endrin	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endrin aldehyde	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Endrin aldehyde	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Ethoprop	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Ethylbenzene	EPA 624	Volatile Organics	NELAP	8/8/2005
Ethylbenzene	EPA 8021	Volatile Organics	NELAP	8/8/2005
Ethylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Fensulfothion	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Fenthion	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Fluoranthene	EPA 625	Extractable Organics	NELAP	8/8/2005
Fluoranthene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Fluorene	EPA 625	Extractable Organics	NELAP	8/8/2005
Fluorene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Fluoride	EPA 300.0	General Chemistry	NELAP	8/8/2005
Fluoride	EPA 340.2	General Chemistry	NELAP	8/8/2005
Fluoride	EPA 9056	General Chemistry	NELAP	8/8/2005
gamma-BHC (Lindane, gamma-Hexachlorocyclohexane)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005

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Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
gamma-BHC (Lindane, gamma-Hexachlorocyclohexane)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
gamma-Chlordane	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Gasoline range organics (GRO)	EPA 8015	Volatile Organics	NELAP	8/8/2005
Gross-alpha	EPA 900	Radiochemistry	NELAP	12/1/2005
Gross-alpha	EPA 9310	Radiochemistry	NELAP	12/1/2005
Gross-beta	EPA 900	Radiochemistry	NELAP	12/1/2005
Gross-beta	EPA 9310	Radiochemistry	NELAP	12/1/2005
Heptachlor	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Heptachlor	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Heptachlor epoxide	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Heptachlor epoxide	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Hexachlorobenzene	EPA 625	Extractable Organics	NELAP	8/8/2005
Hexachlorobenzene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Hexachlorobutadiene	EPA 625	Extractable Organics	NELAP	8/8/2005
Hexachlorobutadiene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Hexachlorobutadiene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Hexachlorocyclopentadiene	EPA 625	Extractable Organics	NELAP	8/8/2005
Hexachlorocyclopentadiene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Hexachloroethane	EPA 625	Extractable Organics	NELAP	8/8/2005
Hexachloroethane	EPA 8270	Extractable Organics	NELAP	8/8/2005
Ignitability	EPA 1010	General Chemistry	NELAP	8/8/2005
Indeno(1,2,3-cd)pyrene	EPA 625	Extractable Organics	NELAP	8/8/2005
Indeno(1,2,3-cd)pyrene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Iodomethane (Methyl iodide)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Iron	EPA 200.7	Metals	NELAP	8/8/2005
Iron	EPA 6010	Metals	NELAP	8/8/2005
Isophorone	EPA 625	Extractable Organics	NELAP	8/8/2005
Isophorone	EPA 8270	Extractable Organics	NELAP	8/8/2005
Isopropylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Lead	EPA 200.7	Metals	NELAP	8/8/2005
Lead	EPA 6010	Metals	NELAP	8/8/2005
Lithium	EPA 200.7	Metals	NELAP	8/8/2005
Lithium	EPA 6010	Metals	NELAP	8/8/2005
Magnesium	EPA 200.7	Metals	NELAP	8/8/2005
Magnesium	EPA 6010	Metals	NELAP	8/8/2005
Manganese	EPA 200.7	Metals	NELAP	8/8/2005

Laboratory Scope of Accreditation

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Fort Collins, CO 80524

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Manganese	EPA 6010	Metals	NELAP	8/8/2005
MCPA	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
MCPP	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Mercury	EPA 245.1	Metals	NELAP	8/8/2005
Mercury	EPA 7470	Metals	NELAP	8/8/2005
Merphos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Methoxychlor	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Methyl bromide (Bromomethane)	EPA 624	Volatile Organics	NELAP	8/8/2005
Methyl bromide (Bromomethane)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Methyl chloride (Chloromethane)	EPA 624	Volatile Organics	NELAP	8/8/2005
Methyl chloride (Chloromethane)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Methyl parathion (Parathion, methyl)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Methyl tert-butyl ether (MTBE)	EPA 8021	Volatile Organics	NELAP	8/8/2005
Methyl tert-butyl ether (MTBE)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Methylene chloride	EPA 624	Volatile Organics	NELAP	8/8/2005
Methylene chloride	EPA 8260	Volatile Organics	NELAP	8/8/2005
Mevinphos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Molybdenum	EPA 200.7	Metals	NELAP	8/8/2005
Molybdenum	EPA 6010	Metals	NELAP	8/8/2005
m-Xylene	EPA 8021	Volatile Organics	NELAP	8/8/2005
m-Xylene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Naled	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Naphthalene	EPA 625	Extractable Organics	NELAP	8/8/2005
Naphthalene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Naphthalene	EPA 8270	Extractable Organics	NELAP	8/8/2005
n-Butylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Nickel	EPA 200.7	Metals	NELAP	8/8/2005
Nickel	EPA 6010	Metals	NELAP	8/8/2005
Nitrate	EPA 9056	General Chemistry	NELAP	8/8/2005
Nitrate as N	EPA 300.0	General Chemistry	NELAP	8/8/2005
Nitrite	EPA 9056	General Chemistry	NELAP	8/8/2005
Nitrite as N	EPA 300.0	General Chemistry	NELAP	8/8/2005
Nitrite as N	EPA 354.1	General Chemistry	NELAP	8/8/2005
Nitrobenzene	EPA 625	Extractable Organics	NELAP	8/8/2005
Nitrobenzene	EPA 8270	Extractable Organics	NELAP	8/8/2005
n-Nitrosodimethylamine	EPA 625	Extractable Organics	NELAP	8/8/2005

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E87914
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
n-Nitrosodimethylamine	EPA 8270	Extractable Organics	NELAP	8/8/2005
n-Nitrosodi-n-propylamine	EPA 625	Extractable Organics	NELAP	8/8/2005
n-Nitrosodi-n-propylamine	EPA 8270	Extractable Organics	NELAP	8/8/2005
n-Nitrosodiphenylamine	EPA 625	Extractable Organics	NELAP	8/8/2005
n-Nitrosodiphenylamine	EPA 8270	Extractable Organics	NELAP	8/8/2005
n-Propylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	EPA 8330	Extractable Organics	NELAP	8/8/2005
Oil & Grease	EPA 1664	General Chemistry	NELAP	8/8/2005
Orthophosphate as P	EPA 300.0	General Chemistry	NELAP	8/8/2005
Orthophosphate as P	EPA 365.2	General Chemistry	NELAP	8/8/2005
Orthophosphate as P	EPA 9056	General Chemistry	NELAP	8/8/2005
o-Xylene	EPA 8021	Volatile Organics	NELAP	8/8/2005
o-Xylene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Pentachlorophenol	EPA 625	Extractable Organics	NELAP	8/8/2005
Pentachlorophenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
pH	EPA 150.1	General Chemistry	NELAP	8/8/2005
Phenanthrene	EPA 625	Extractable Organics	NELAP	8/8/2005
Phenanthrene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Phenol	EPA 625	Extractable Organics	NELAP	8/8/2005
Phenol	EPA 8270	Extractable Organics	NELAP	8/8/2005
Phorate	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Phosphorus, total	EPA 365.2	General Chemistry	NELAP	8/8/2005
p-Isopropyltoluene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Potassium	EPA 200.7	Metals	NELAP	8/8/2005
Potassium	EPA 6010	Metals	NELAP	8/8/2005
p-Xylene	EPA 8021	Volatile Organics	NELAP	8/8/2005
p-Xylene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Pyrene	EPA 625	Extractable Organics	NELAP	8/8/2005
Pyrene	EPA 8270	Extractable Organics	NELAP	8/8/2005
Pyridine	EPA 8270	Extractable Organics	NELAP	8/8/2005
Radium-226	EPA 903.1	Radiochemistry	NELAP	12/1/2005
Radium-228	EPA 9320	Radiochemistry	NELAP	12/1/2005
RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)	EPA 8330	Extractable Organics	NELAP	8/8/2005
Residue-filterable (TDS)	EPA 160.1	General Chemistry	NELAP	8/8/2005
Residue-nonfilterable (TSS)	EPA 160.2	General Chemistry	NELAP	8/8/2005
Residue-total	EPA 160.3	General Chemistry	NELAP	8/8/2005

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E87914
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Ronnel	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
sec-Butylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Selenium	EPA 200.7	Metals	NELAP	8/8/2005
Selenium	EPA 6010	Metals	NELAP	8/8/2005
Silica as SiO2	EPA 200.7	Metals	NELAP	8/8/2005
Silver	EPA 200.7	Metals	NELAP	8/8/2005
Silver	EPA 6010	Metals	NELAP	8/8/2005
Silvex (2,4,5-TP)	EPA 615	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Silvex (2,4,5-TP)	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Sodium	EPA 200.7	Metals	NELAP	8/8/2005
Sodium	EPA 6010	Metals	NELAP	8/8/2005
Stirofos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Strontium	EPA 200.7	Metals	NELAP	8/8/2005
Styrene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Sulfate	EPA 300.0	General Chemistry	NELAP	8/8/2005
Sulfide	EPA 376.1	General Chemistry	NELAP	8/8/2005
tert-Butylbenzene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Tetrachloroethylene (Perchloroethylene)	EPA 624	Volatile Organics	NELAP	8/8/2005
Tetrachloroethylene (Perchloroethylene)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Tetryl (methyl-2,4,6-trinitrophenylnitramine)	EPA 8330	Extractable Organics	NELAP	8/8/2005
Thallium	EPA 200.7	Metals	NELAP	8/8/2005
Thallium	EPA 6010	Metals	NELAP	8/8/2005
Tin	EPA 200.7	Metals	NELAP	8/8/2005
Tin	EPA 6010	Metals	NELAP	8/8/2005
Titanium	EPA 200.7	Metals	NELAP	8/8/2005
Titanium	EPA 6010	Metals	NELAP	8/8/2005
Tokuthion (Prothiophos)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Toluene	EPA 624	Volatile Organics	NELAP	8/8/2005
Toluene	EPA 8021	Volatile Organics	NELAP	8/8/2005
Toluene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Total cyanide	EPA 335.2	General Chemistry	NELAP	8/8/2005
Total nitrate-nitrite	EPA 353.2	General Chemistry	NELAP	8/8/2005
Total organic carbon	EPA 415.1	General Chemistry	NELAP	8/8/2005
Total radium	EPA 903	Radiochemistry	NELAP	12/1/2005
Total radium	EPA 9315	Radiochemistry	NELAP	12/1/2005
Toxaphene (Chlorinated camphene)	EPA 608	Pesticides-Herbicides-PCB's	NELAP	8/8/2005

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E87914
Paragon Analytics
225 Commerce Drive
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Matrix: Non-Potable Water

Analyte	Method/Tech	Category	Certification Type	Effective Date
Toxaphene (Chlorinated camphene)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
trans-1,2-Dichloroethylene	EPA 624	Volatile Organics	NELAP	8/8/2005
trans-1,2-Dichloroethylene	EPA 8260	Volatile Organics	NELAP	8/8/2005
trans-1,3-Dichloropropylene	EPA 624	Volatile Organics	NELAP	8/8/2005
trans-1,3-Dichloropropylene	EPA 8260	Volatile Organics	NELAP	8/8/2005
Trichloroethene (Trichloroethylene)	EPA 624	Volatile Organics	NELAP	8/8/2005
Trichloroethene (Trichloroethylene)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Trichlorofluoromethane	EPA 624	Volatile Organics	NELAP	8/8/2005
Trichlorofluoromethane	EPA 8260	Volatile Organics	NELAP	8/8/2005
Trichloronate	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	8/8/2005
Vanadium	EPA 200.7	Metals	NELAP	8/8/2005
Vanadium	EPA 6010	Metals	NELAP	8/8/2005
Vinyl acetate	EPA 8260	Volatile Organics	NELAP	8/8/2005
Vinyl chloride	EPA 624	Volatile Organics	NELAP	8/8/2005
Vinyl chloride	EPA 8260	Volatile Organics	NELAP	8/8/2005
Xylene (total)	EPA 624	Volatile Organics	NELAP	8/8/2005
Xylene (total)	EPA 8021	Volatile Organics	NELAP	8/8/2005
Xylene (total)	EPA 8260	Volatile Organics	NELAP	8/8/2005
Zinc	EPA 200.7	Metals	NELAP	8/8/2005
Zinc	EPA 6010	Metals	NELAP	8/8/2005

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E87914
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
1,1,1,2-Tetrachloroethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,1,1-Trichloroethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,1,2,2-Tetrachloroethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,1,2-Trichloroethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,1-Dichloroethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,1-Dichloroethylene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,1-Dichloropropene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2,3-Trichlorobenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2,3-Trichloropropane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2,4-Trichlorobenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2,4-Trichlorobenzene	EPA 8270	Extractable Organics	NELAP	10/24/2003
1,2,4-Trimethylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2-Dibromo-3-chloropropane (DBCP)	EPA 8011	Volatile Organics	NELAP	10/24/2003
1,2-Dibromo-3-chloropropane (DBCP)	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 8011	Volatile Organics	NELAP	10/24/2003
1,2-Dibromoethane (EDB, Ethylene dibromide)	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2-Dichlorobenzene	EPA 8021	Volatile Organics	NELAP	10/24/2003
1,2-Dichlorobenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2-Dichlorobenzene	EPA 8270	Extractable Organics	NELAP	10/24/2003
1,2-Dichloroethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,2-Dichloropropane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,3,5-Trimethylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,3,5-Trinitrobenzene (1,3,5-TNB)	EPA 8330	Extractable Organics	NELAP	10/24/2003
1,3-Dichlorobenzene	EPA 8021	Volatile Organics	NELAP	10/24/2003
1,3-Dichlorobenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,3-Dichlorobenzene	EPA 8270	Extractable Organics	NELAP	10/24/2003
1,3-Dichloropropane	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,3-Dinitrobenzene (1,3-DNB)	EPA 8330	Extractable Organics	NELAP	10/24/2003
1,4-Dichlorobenzene	EPA 8021	Volatile Organics	NELAP	10/24/2003
1,4-Dichlorobenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
1,4-Dichlorobenzene	EPA 8270	Extractable Organics	NELAP	10/24/2003
1-Chlorohexane	EPA 8260	Volatile Organics	NELAP	10/24/2003
2,2-Dichloropropane	EPA 8260	Volatile Organics	NELAP	10/24/2003
2,3,4,6-Tetrachlorophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2,4,5-T	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
2,4,5-Trichlorophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003

Laboratory Scope of Accreditation

Attachment to Certificate #: E87914-06, expiration date June 30, 2009. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E87914 **EPA Lab Code: CO00078** **(970) 490-1511**

E87914
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
2,4,6-Trichlorophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2,4,6-Trinitrotoluene (2,4,6-TNT)	EPA 8330	Extractable Organics	NELAP	10/24/2003
2,4-D	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
2,4-DB	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
2,4-Dichlorophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2,4-Dimethylphenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2,4-Dinitrophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2,4-Dinitrotoluene (2,4-DNT)	EPA 8270	Extractable Organics	NELAP	10/24/2003
2,4-Dinitrotoluene (2,4-DNT)	EPA 8330	Extractable Organics	NELAP	10/24/2003
2,6-Dinitrotoluene (2,6-DNT)	EPA 8270	Extractable Organics	NELAP	10/24/2003
2,6-Dinitrotoluene (2,6-DNT)	EPA 8330	Extractable Organics	NELAP	10/24/2003
2-Amino-4,6-dinitrotoluene (2-am-dnt)	EPA 8330	Extractable Organics	NELAP	10/24/2003
2-Butanone (Methyl ethyl ketone, MEK)	EPA 8260	Volatile Organics	NELAP	10/24/2003
2-Chloroethyl vinyl ether	EPA 8260	Volatile Organics	NELAP	10/24/2003
2-Chloronaphthalene	EPA 8270	Extractable Organics	NELAP	10/24/2003
2-Chlorophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2-Chlorotoluene	EPA 8260	Volatile Organics	NELAP	10/24/2003
2-Hexanone	EPA 8260	Volatile Organics	NELAP	10/24/2003
2-Methyl-4,6-dinitrophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2-Methylnaphthalene	EPA 8270	Extractable Organics	NELAP	10/24/2003
2-Methylphenol (o-Cresol)	EPA 8270	Extractable Organics	NELAP	10/24/2003
2-Nitroaniline	EPA 8270	Extractable Organics	NELAP	10/24/2003
2-Nitrophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
2-Nitrotoluene	EPA 8330	Extractable Organics	NELAP	10/24/2003
3,3'-Dichlorobenzidine	EPA 8270	Extractable Organics	NELAP	10/24/2003
3-Methylphenol (m-Cresol)	EPA 8270	Extractable Organics	NELAP	10/24/2003
3-Nitroaniline	EPA 8270	Extractable Organics	NELAP	10/24/2003
3-Nitrotoluene	EPA 8330	Extractable Organics	NELAP	10/24/2003
4,4'-DDD	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
4,4'-DDE	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
4,4'-DDT	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
4-Amino-2,6-dinitrotoluene (4-am-dnt)	EPA 8330	Extractable Organics	NELAP	10/24/2003
4-Bromophenyl phenyl ether	EPA 8270	Extractable Organics	NELAP	10/24/2003
4-Chloro-3-methylphenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
4-Chloroaniline	EPA 8270	Extractable Organics	NELAP	10/24/2003
4-Chlorophenyl phenylether	EPA 8270	Extractable Organics	NELAP	10/24/2003

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Paragon Analytics
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Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
4-Chlorotoluene	EPA 8260	Volatile Organics	NELAP	10/24/2003
4-Methyl-2-pentanone (MIBK)	EPA 8260	Volatile Organics	NELAP	10/24/2003
4-Methylphenol (p-Cresol)	EPA 8270	Extractable Organics	NELAP	10/24/2003
4-Nitroaniline	EPA 8270	Extractable Organics	NELAP	10/24/2003
4-Nitrophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
4-Nitrotoluene	EPA 8330	Extractable Organics	NELAP	10/24/2003
Acenaphthene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Acenaphthene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Acenaphthylene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Acenaphthylene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Acetone	EPA 8260	Volatile Organics	NELAP	10/24/2003
Acrolein (Propenal)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Acrylonitrile	EPA 8260	Volatile Organics	NELAP	10/24/2003
Aldrin	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
alpha-BHC (alpha-Hexachlorocyclohexane)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Aluminum	EPA 6010	Metals	NELAP	10/24/2003
Amenable cyanide	EPA 9014	General Chemistry	NELAP	10/24/2003
Aniline	EPA 8270	Extractable Organics	NELAP	10/24/2003
Anthracene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Anthracene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Antimony	EPA 6010	Metals	NELAP	10/24/2003
Aroclor-1016 (PCB-1016)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Aroclor-1221 (PCB-1221)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Aroclor-1232 (PCB-1232)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Aroclor-1242 (PCB-1242)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Aroclor-1248 (PCB-1248)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Aroclor-1254 (PCB-1254)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Aroclor-1260 (PCB-1260)	EPA 8082	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Arsenic	EPA 6010	Metals	NELAP	10/24/2003
Azinphos-methyl (Guthion)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Barium	EPA 6010	Metals	NELAP	10/24/2003
Benzene	EPA 8021	Volatile Organics	NELAP	10/24/2003
Benzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Benzo(a)anthracene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Benzo(a)anthracene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Benzo(a)pyrene	EPA 8270	Extractable Organics	NELAP	10/24/2003

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Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
Benzo(a)pyrene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Benzo(b)fluoranthene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Benzo(b)fluoranthene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Benzo(g,h,i)perylene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Benzo(g,h,i)perylene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Benzo(k)fluoranthene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Benzo(k)fluoranthene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Benzoic acid	EPA 8270	Extractable Organics	NELAP	10/24/2003
Benzyl alcohol	EPA 8270	Extractable Organics	NELAP	10/24/2003
Beryllium	EPA 6010	Metals	NELAP	10/24/2003
beta-BHC (beta-Hexachlorocyclohexane)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
bis(2-Chloroethoxy)methane	EPA 8270	Extractable Organics	NELAP	10/24/2003
bis(2-Chloroethyl) ether	EPA 8270	Extractable Organics	NELAP	10/24/2003
bis(2-Chloroisopropyl) ether (2,2'-Oxybis(1-chloropropane))	EPA 8270	Extractable Organics	NELAP	10/24/2003
bis(2-Ethylhexyl) phthalate (DEHP)	EPA 8270	Extractable Organics	NELAP	10/24/2003
Bolstar (Sulprofos)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Boron	EPA 6010	Metals	NELAP	10/24/2003
Bromide	EPA 9056	General Chemistry	NELAP	10/24/2003
Bromobenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Bromochloromethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
Bromodichloromethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
Bromoform	EPA 8260	Volatile Organics	NELAP	10/24/2003
Butyl benzyl phthalate	EPA 8270	Extractable Organics	NELAP	10/24/2003
Cadmium	EPA 6010	Metals	NELAP	10/24/2003
Calcium	EPA 6010	Metals	NELAP	10/24/2003
Carbazole	EPA 8270	Extractable Organics	NELAP	10/24/2003
Carbon disulfide	EPA 8260	Volatile Organics	NELAP	10/24/2003
Carbon tetrachloride	EPA 8260	Volatile Organics	NELAP	10/24/2003
Chloride	EPA 9056	General Chemistry	NELAP	10/24/2003
Chlorobenzene	EPA 8021	Volatile Organics	NELAP	10/24/2003
Chlorobenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Chloroethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
Chloroform	EPA 8260	Volatile Organics	NELAP	10/24/2003
Chlorpyrifos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Chromium	EPA 6010	Metals	NELAP	10/24/2003
Chromium VI	EPA 7196	General Chemistry	NELAP	10/24/2003

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Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
Chrysene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Chrysene	EPA 8310	Extractable Organics	NELAP	10/24/2003
cis-1,2-Dichloroethylene	EPA 8260	Volatile Organics	NELAP	10/24/2003
cis-1,3-Dichloropropene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Cobalt	EPA 6010	Metals	NELAP	10/24/2003
Conductivity	EPA 9050	General Chemistry	NELAP	10/24/2003
Copper	EPA 6010	Metals	NELAP	10/24/2003
Dalapon	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
delta-BHC	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Demeton-o	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Demeton-s	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Diazinon	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Dibenz(a,h) anthracene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Dibenz(a,h) anthracene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Dibenzofuran	EPA 8270	Extractable Organics	NELAP	10/24/2003
Dibromochloromethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
Dibromomethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
Dicamba	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Dichlorodifluoromethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
Dichloroprop (Dichlorprop)	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Dichlorovos (DDVP, Dichlorvos)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Dieldrin	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Diesel range organics (DRO)	EPA 8015	Extractable Organics	NELAP	10/24/2003
Diethyl phthalate	EPA 8270	Extractable Organics	NELAP	10/24/2003
Dimethyl phthalate	EPA 8270	Extractable Organics	NELAP	10/24/2003
Di-n-butyl phthalate	EPA 8270	Extractable Organics	NELAP	10/24/2003
Di-n-octyl phthalate	EPA 8270	Extractable Organics	NELAP	10/24/2003
Dinoseb (2-sec-butyl-4,6-dinitrophenol, DNBP)	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Disulfoton	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Endosulfan I	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Endosulfan II	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Endosulfan sulfate	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Endrin	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Endrin aldehyde	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Endrin ketone	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Ethoprop	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003

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Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
Ethylbenzene	EPA 8021	Volatile Organics	NELAP	10/24/2003
Ethylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Extractable cyanide	EPA 9010/9013	General Chemistry	NELAP	10/24/2003
Fensulfothion	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Fenthion	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Fluoranthene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Fluoranthene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Fluorene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Fluorene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Fluoride	EPA 9056	General Chemistry	NELAP	10/24/2003
gamma-BHC (Lindane, gamma-Hexachlorocyclohexane)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Gasoline range organics (GRO)	EPA 8015	Extractable Organics	NELAP	10/24/2003
Gross-alpha	EPA 9310	Radiochemistry	NELAP	1/1/2004
Gross-beta	EPA 9310	Radiochemistry	NELAP	1/1/2004
Heptachlor	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Heptachlor epoxide	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Hexachlorobenzene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Hexachlorobutadiene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Hexachlorobutadiene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Hexachlorocyclopentadiene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Hexachloroethane	EPA 8270	Extractable Organics	NELAP	10/24/2003
Ignitability	EPA 1010	General Chemistry	NELAP	10/24/2003
Indeno(1,2,3-cd)pyrene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Indeno(1,2,3-cd)pyrene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Iodomethane (Methyl iodide)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Iron	EPA 6010	Metals	NELAP	10/24/2003
Isophorone	EPA 8270	Extractable Organics	NELAP	10/24/2003
Isopropylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Lead	EPA 6010	Metals	NELAP	10/24/2003
Lithium	EPA 6010	Metals	NELAP	10/24/2003
Magnesium	EPA 6010	Metals	NELAP	10/24/2003
Manganese	EPA 6010	Metals	NELAP	10/24/2003
MCPA	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
MCPP	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Mercury	EPA 7470	Metals	NELAP	10/24/2003
Mercury	EPA 7471	Metals	NELAP	10/24/2003

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Analyte	Method/Tech	Category	Certification Type	Effective Date
Merphos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Methoxychlor	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Methyl bromide (Bromomethane)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Methyl chloride (Chloromethane)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Methyl parathion (Parathion, methyl)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Methyl tert-butyl ether (MTBE)	EPA 8021	Volatile Organics	NELAP	10/24/2003
Methyl tert-butyl ether (MTBE)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Methylene chloride	EPA 8260	Volatile Organics	NELAP	10/24/2003
Mevinphos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Molybdenum	EPA 6010	Metals	NELAP	10/24/2003
Naled	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Naphthalene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Naphthalene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Naphthalene	EPA 8310	Extractable Organics	NELAP	10/24/2003
n-Butylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Nickel	EPA 6010	Metals	NELAP	10/24/2003
Nitrate	EPA 9056	General Chemistry	NELAP	10/24/2003
Nitrite	EPA 9056	General Chemistry	NELAP	10/24/2003
Nitrobenzene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Nitrobenzene	EPA 8330	Extractable Organics	NELAP	10/24/2003
n-Nitrosodimethylamine	EPA 8270	Extractable Organics	NELAP	10/24/2003
n-Nitrosodi-n-propylamine	EPA 8270	Extractable Organics	NELAP	10/24/2003
n-Nitrosodiphenylamine	EPA 8270	Extractable Organics	NELAP	10/24/2003
n-Propylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	EPA 8330	Extractable Organics	NELAP	10/24/2003
Oil & Grease	EPA 9070	General Chemistry	NELAP	10/24/2003
Oil & Grease	EPA 9071	General Chemistry	NELAP	10/24/2003
Orthophosphate as P	EPA 9056	General Chemistry	NELAP	10/24/2003
Paint Filter Liquids Test	EPA 9095	General Chemistry	NELAP	10/24/2003
Pentachlorophenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
pH	EPA 9040	General Chemistry	NELAP	10/24/2003
pH	EPA 9045	General Chemistry	NELAP	10/24/2003
Phenanthrene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Phenanthrene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Phenol	EPA 8270	Extractable Organics	NELAP	10/24/2003
Phorate	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003

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Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
p-Isopropyltoluene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Potassium	EPA 6010	Metals	NELAP	10/24/2003
Pyrene	EPA 8270	Extractable Organics	NELAP	10/24/2003
Pyrene	EPA 8310	Extractable Organics	NELAP	10/24/2003
Pyridine	EPA 8270	Extractable Organics	NELAP	10/24/2003
Radium-228	EPA 9320	Radiochemistry	NELAP	1/1/2004
RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)	EPA 8330	Extractable Organics	NELAP	10/24/2003
Reactive cyanide	EPA 7.3.3.2	General Chemistry	NELAP	10/24/2003
Reactive sulfide	EPA 7.3.4.2	General Chemistry	NELAP	10/24/2003
Ronnel	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
sec-Butylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Selenium	EPA 6010	Metals	NELAP	10/24/2003
Silica as SiO2	EPA 6010	Metals	NELAP	10/24/2003
Silver	EPA 6010	Metals	NELAP	10/24/2003
Silvex (2,4,5-TP)	EPA 8151	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Sodium	EPA 6010	Metals	NELAP	10/24/2003
Stirofos	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Strontium	EPA 6010	Metals	NELAP	10/24/2003
Styrene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Sulfate	EPA 9056	General Chemistry	NELAP	10/24/2003
Synthetic Precipitation Leaching Procedure	EPA 1312	General Chemistry	NELAP	10/24/2003
tert-Butylbenzene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Tetrachloroethylene (Perchloroethylene)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Tetryl (methyl-2,4,6-trinitrophenylnitramine)	EPA 8330	Extractable Organics	NELAP	10/24/2003
Thallium	EPA 6010	Metals	NELAP	10/24/2003
Tin	EPA 6010	Metals	NELAP	10/24/2003
Tokuthion (Prothiophos)	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Toluene	EPA 8021	Volatile Organics	NELAP	10/24/2003
Toluene	EPA 8260	Volatile Organics	NELAP	10/24/2003
Total cyanide	EPA 9014	General Chemistry	NELAP	10/24/2003
Total organic carbon	EPA 9060	General Chemistry	NELAP	10/24/2003
Total radium	EPA 9315	Radiochemistry	NELAP	1/1/2004
Toxaphene (Chlorinated camphene)	EPA 8081	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Toxicity Characteristic Leaching Procedure	EPA 1311	General Chemistry	NELAP	10/24/2003
trans-1,2-Dichloroethylene	EPA 8260	Volatile Organics	NELAP	10/24/2003
trans-1,3-Dichloropropylene	EPA 8260	Volatile Organics	NELAP	10/24/2003

Laboratory Scope of Accreditation

Attachment to Certificate #: E87914-06, expiration date June 30, 2009. This listing of accredited analytes should be used only when associated with a valid certificate.

State Laboratory ID: E87914 **EPA Lab Code: CO00078** **(970) 490-1511**

E87914
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: Solid and Chemical Materials

Analyte	Method/Tech	Category	Certification Type	Effective Date
Trichloroethene (Trichloroethylene)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Trichlorofluoromethane	EPA 8260	Volatile Organics	NELAP	10/24/2003
Trichloronate	EPA 8141	Pesticides-Herbicides-PCB's	NELAP	10/24/2003
Vanadium	EPA 6010	Metals	NELAP	10/24/2003
Vinyl acetate	EPA 8260	Volatile Organics	NELAP	10/24/2003
Vinyl chloride	EPA 8260	Volatile Organics	NELAP	10/24/2003
Xylene (total)	EPA 8021	Volatile Organics	NELAP	10/24/2003
Xylene (total)	EPA 8260	Volatile Organics	NELAP	10/24/2003
Zinc	EPA 6010	Metals	NELAP	10/24/2003

FLORIDA DEPARTMENT OF HEALTH

State of Florida
Department of Health, Bureau of Laboratories

This is to certify that

E87914

PARAGON ANALYTICS
225 COMMERCE DRIVE
FORT COLLINS, CO 80524

has complied with Florida Administrative Code 64E-1,
for the examination of Environmental samples in the following categories

NON-POTABLE WATER - EXTRACTABLE ORGANICS, NON-POTABLE WATER - GENERAL CHEMISTRY, NON-POTABLE WATER - METALS, NON-POTABLE WATER - PESTICIDES-HERBICIDES-PCB'S, NON-POTABLE WATER - RADIOCHEMISTRY, NON-POTABLE WATER - VOLATILE ORGANICS, SOLID AND CHEMICAL MATERIALS - EXTRACTABLE ORGANICS, SOLID AND CHEMICAL MATERIALS - GENERAL CHEMISTRY, SOLID AND CHEMICAL MATERIALS - METALS, SOLID AND CHEMICAL MATERIALS - PESTICIDES-HERBICIDES-PCB'S, SOLID AND CHEMICAL MATERIALS - RADIOCHEMISTRY, SOLID AND CHEMICAL MATERIALS - VOLATILE ORGANICS

Continued certification is contingent upon successful on-going compliance with the NELAC Standards and FAC Rule 64E-1 regulations. Specific methods and analytes certified are cited on the Laboratory Scope of Accreditation for this laboratory and are on file at the Bureau of Laboratories, P. O. Box 210, Jacksonville, Florida 32231. Clients and customers are urged to verify with this agency the laboratory's certification status in Florida for particular methods and analytes.

EFFECTIVE July 01, 2008 THROUGH June 30, 2009

Max Salfinger, M.D.
Chief, Bureau of Laboratories
Florida Department of Health
DH Form 1697, 7/04
NON-TRANSFERABLE E87914-06-07/01/2008
Supersedes all previously issued certificates

IDAHO DEPARTMENT OF
HEALTH & WELFARE

C.L. "BUTCH" OTTER - GOVERNOR
RICHARD M. ARMSTRONG - DIRECTOR

JANE S. SMITH - ADMINISTRATOR
DIVISION OF HEALTH
Bureau of Laboratories
2220 Old Penitentiary Road
Boise, ID 83712
PHONE 208-334-2235
FAX 208-334-2382

November 21, 2007

Paragon Analytics, Inc.
225 Commerce Dr.
Fort Collins, CO 80524
Attn: Deb Scheib

Re: Idaho Certification

Ms. Scheib,

We have reviewed the information you submitted in support of renewing your radiology certification for testing drinking water in the State of Idaho. The attached certificate itemizes the specific analytes and methods for which Paragon Analytics, Inc. has been approved which does not go beyond the certification from the Colorado Department of Public Health and Environment.

The radiological certificate expires October 31, 2008. For continuation of future drinking water certification with the state of Idaho please request a renewal application.

If you have any questions, please feel free to contact me.

Sincerely,

Richard Hudson, PhD
Chief, Bureau of Laboratories
Drinking Water Laboratory Certification Authority

C: Jerri Henry, Drinking Water Regulatory Analyst, DEQ

IDAHO DEPARTMENT OF
HEALTH & WELFARE

C.L. "BUTCH" OTTER - GOVERNOR
RICHARD M. ARMSTRONG - DIRECTOR

JANE S. SMITH - ADMINISTRATOR
DIVISION OF HEALTH
Bureau of Laboratories
2220 Old Penitentiary Road
Boise, ID 83712
PHONE 208-334-2235
FAX 208-334-2382

DRINKING WATER LABORATORY CERTIFICATION

Paragon Analytics, Inc.
225 Commerce Dr.
Fort Collins, CO 80524
EPA Lab ID: CO00078
Telephone #: (970) 490-1511

Issued: November 1, 2007
Expiration: October 31, 2008
(or until revised)

List of Analytes	Status [1]	Methods
Gross Alpha	C	EPA-900.0
Gross Beta	C	EPA-900.0
Radium-226	C	EPA-903.0, EPA-903.1
Radium-228	C	EPA-904.0
Uranium	C	DOE-U-02

1) C = Certified, N = Not Certified, P = Provisionally Certified, * = Certification Not Requested

KANSAS

DEPARTMENT OF HEALTH
AND ENVIRONMENT

Division of Environment

Kathleen Sebelius, Governor
Roderick L. Bremby, Secretary

www.kdheks.gov

NELAP-RECOGNIZED

MEMORANDUM

TO: DEB SCHEIB
PARAGON ANALYTICS, A DIVISION OF DATACHEM LABORATORIES, INC.
225 COMMERCE DRIVE
FORT COLLINS, CO 80524

FROM: Jack McKenzie and Aurora Shields
Laboratory Improvement Specialists

Enclosed please find your NELAP certificate of accreditation. Also, note the effective and expiration dates of your new accreditation and be sure to review the parameters listed. It is possible your laboratory applied for parameters not listed on the enclosed accreditation. Those parameters have been denied. If there are any questions concerning the parameters listed, contact this office at (785) 296-1639-Jack or (785) 296-6198-Aurora.

It is essential the laboratory accreditation officer be notified within 30 days of any changes in laboratory director, methods which involve a change in technology, change in ownership, or change in location.

An application packet for re-accreditation will be mailed to you approximately five (5) months prior to the expiration date of your current accreditation.

Enclosure/s

KANSAS DEPARTMENT OF HEALTH AND ENVIRONMENT
ENVIRONMENTAL LABORATORY ACCREDITATION
SAFE DRINKING WATER ACT PROGRAM - DRINKING WATER MATRIX

This certificate supersedes all previous certificates

Paragon Analytics, a Division of DataChem Laboratories, Inc.	**Certificate Number: E-10381**
225 Commerce Drive	**Effective Date: 08/08/2008**
Fort Collins, CO 80524	**Expiration Date: 10/31/2009**
	Reciprocity: UT

The laboratory listed above is hereby approved for environmental laboratory accreditation in accordance with K.S.A. 65-1, 109a for the following:

****RADIOCHEMISTRY**
Radioactive Cesium {EPA 901.1}
Radioactive Strontium 89, 90 {DOE Sr-02}
Radium - 226 {EPA 903.0}
Radium - 226 {EPA 903.1}
Radium - 228 {EPA 904.0}
Tritium {EPA 906.0}
Uranium {ASTM D3972-97}
Uranium {DOE U-02}

End of Parameter List

ACCREDITING AUTHORITY
nelap

NELAP-Recognized

STATE OF KANSAS

DEPARTMENT OF HEALTH AND ENVIRONMENT

CERTIFICATE

NELAP-Recognized

This is to certify that Certificate No. E-10381

Paragon Analytics, a Division of DataChem Laboratories, Inc.
225 Commerce Drive
Fort Collins, CO 80524

has been accredited in accordance with K.S.A. 65-1,109a for performing environmental analyses for the parameters listed on the attached form. Continuous accreditation depends on successful, ongoing participation in the program. Clients are urged to verify with this agency the laboratory's certification status for particular methods and analytes.

EFFECTIVE DATE: 08/08/2008 EXPIRATION DATE: 10/31/2009

Secretary
Department of Health and Environment

Environmental Laboratory Certification Officers

LITHO. IN U.S.A.

ENVIRONMENTAL AND PUBLIC PROTECTION CABINET

Steven L. Beshear
Governor

DEPARTMENT FOR ENVIRONMENTAL PROTECTION
300 FAIR OAKS LANE
FRANKFORT, KENTUCKY 40601
PHONE (502) 564-2150
FAX (502)564-4245
www.dep.ky.gov

Robert D. Vance
Secretary

R. Bruce Scott
Commissioner

January 16, 2008

Ms. Deb Scheib
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

RE: Laboratory Certification 2008

Dear Ms. Scheib,

Please find enclosed your laboratory's Drinking Water Certificate for 2008. Please review the certificate and associated analytes/methods that your laboratory is certified for the analysis of drinking water samples in Kentucky. The certificate is valid until December 31, 2008. Also enclosed is a receipt for your certification fee for 2008.

If you have any comments or questions regarding the enclosed documents please contact Patrick Garrity at (502) 564-3410 extension 574 or by email at patrick.garrity@ky.gov.

Sincerely,

Patrick J. Garrity
Laboratory Certification Officer
Drinking Water Branch
Division of Water

Enclosures

C. DWB Files

COMMONWEALTH OF KENTUCKY

Environmental and Public Protection Cabinet

Drinking Water Laboratory Certification Program
Under The Safe Drinking Water Act and In Accordance with 401 KAR Chapter 8

THIS CERTIFIES THAT

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Laboratory Number: 90137

has fulfilled the requirements governing the Certification of Drinking Water Chemistry Laboratories and is hereby granted certification for the analytes and associated methods listed on the attached table dated 01/01/2008.

Given under our hands this 1st day of January, 2008

at Frankfort, Kentucky. This Certificate expires on December 31, 2008.

Certification Officer

Kentucky UNBRIDLED SPIRIT

Certification Authority

Analyte	Contaminant Code	Method Code	Status	Method Description
Uranium	4006	974	Certified	DOE U-02
Gross Alpha	4109	756	Certified	EPA 900.0
Gross Beta	4100	756	Certified	EPA 900.0
Cesium-134	4270	940	Certified	EPA 901.1
Cesium-137	4276	940	Certified	EPA 901.1
Radium-226	4020	926	Certified	EPA 903.0
Radium-226	4020	757	Certified	EPA 903.1
Radium-228	4030	927	Certified	EPA 904.0
Tritium	4102	764	Certified	EPA 906.0

MARYLAND DEPARTMENT OF THE ENVIRONMENT

1800 Washington Boulevard • Baltimore MD 21230
410-537-3000 • 1-800-633-6101

Martin O'Malley
Governor

Anthony G. Brown
Lieutenant Governor

Shari T. Wilson
Secretary

Robert M. Summers, Ph.D.
Deputy Secretary

9/26/2008

Kenneth D. Campbell
PARAGON ANALYTICS A Division Of Data Chem Laboratories Inc.
225 Commerce Drive
Fort Collins, CO 80524

Subject: **EXTENSION OF WATER QUALITY LABORATORY CERTIFICATION**
PARAGON ANALYTICS A Division Of Data Chem Laboratories Inc. 285

Dear Mr. Campbell:

Your laboratory was originally due to be re-certified for Microbiology and /or Chemistry by September 30, 2008. However, it is not possible to meet that scheduled deadline. It is necessary for us to extend your certification with a new expiration date of December 30, 2008.

We have received your laboratory certification and payment. The documents are currently under review. Thank you for your cooperation.

If you have any questions, please contact me at lames@mde.state.md.us or 410-537-3712.

Sincerely,

Linda Ames

Linda Ames
Laboratory Certification Officer
MDE - Water Supply Program

MARYLAND DEPARTMENT OF THE ENVIRONMENT

1800 Washington Boulevard • Baltimore MD 21230
410-537-3000 • 1-800-633-6101

Martin O'Malley
Governor

Anthony G. Brown
Lieutenant Governor

Shari T. Wilson
Secretary

Robert M. Summers, Ph.D.
Deputy Secretary

CERTIFIED & STANDARD MAIL

7/1/2008

Ken Campbell
PARAGON ANALYTICS A Division Of Data Chem Laboratories Inc.
225 Commerce Drive
Fort Collins, CO 80524

RE: **CURRENT MARYLAND WATER QUALITY CERTIFICATE**
PARAGON ANALYTICS A Division Of Data Chem Laboratories Inc. 285

Dear Mr. Campbell:

Enclosed please find your certificate of reciprocity for drinking water laboratory certification in the State of Maryland. The reciprocity is good for a period of three (3) years. The certificate and fees are renewable annually.

If you have any changes in methods, supervisory personnel, major equipment, ownership, location, or your home state certification status, during the year, you are required to advise this office within 30 days.

If you have any questions, please do not hesitate to call me at 410-537-3712.

Sincerely,

Linda Ames

Linda Ames
Laboratory Certification Officer
Water Supply Program

Enclosure (certificate)

Issued Date: June 24, 2008
Expiration Date: September 30, 2008

MARYLAND DEPARTMENT OF THE ENVIRONMENT
1800 Washington Boulevard • Baltimore MD 21230
410-537-3000 • 1-800-633-6101

Martin O'Malley
Governor

Anthony G. Brown
Lieutenant Governor

Shari T. Wilson
Secretary

Robert M. Summers, Ph.D.
Deputy Secretary

SDWA ANNUAL CERTIFIED PARAMETER LIST

Paragon Analytics, a Division of DataChem Laboratories, Inc.
225 Commerce Drive
Fort Collins, CO 80524

Ken Campbell
Certificate # 285
EPA ID # CO00078

ANALYTE	METHOD	STATUS
Cesium 134	EPA 901.1	Certified
Cesium 137	EPA 901.1	Certified
Cobalt 60	EPA 901.1	Certified
Gross alpha	EPA 900.0	Certified
Gross beta	EPA 900.0	Certified
Radium 226	EPA 903.0	Certified
Radium 226	EPA 903.1	Certified
Radium 228	EPA 904.0	Certified
Tritium	EPA 906.0	Certified
Uranium	DOE U-02	Certified

DEPARTMENT OF THE ENVIRONMENT
WATER SUPPLY PROGRAM

Certifies That

PARAGON ANALYTICS, A DIVISION OF DATACHEM LABORATORIES, INC.
225 Commerce Drive, Fort Collins, CO 80524

Having duly met the requirements of the
Regulations Governing Laboratory Certification
And Standards of Performance In Accordance With
The Annotated Code of Maryland,
is hereby approved as a

State Certified Water Quality Laboratory

To perform the analyses indicated on the Annual Certified Parameter List,
which must accompany this certificate.

Certification # 285

Date Issued June 24, 2008

Expiration Date September 30, 2008
(Not Transferable)

Administrator, Water Supply Program

This certification is subject to unannounced laboratory inspections

CONSPICUOUSLY DISPLAY IN THE LABORATORY WITH THE ANNUAL CERTIFIED PARAMETER LIST. MDE00303

STATE OF MISSOURI

Matt Blunt, Governor • Doyle Childers, Director

DEPARTMENT OF NATURAL RESOURCES

www.dnr.mo.gov

July 20, 2007

Ms Deb Scheib
Paragon Analytics, Inc
225 Commerce Drive
Fort Collins CO 80524

Lab #175

Dear Ms Scheib:

Based upon an evaluation of laboratory data by staff of the Missouri Department of Natural Resources' Environmental Services Program and the on-site evaluation performed by the Utah Department of Health, Division of Epidemiology and Laboratory Services, Paragon Analytics, Inc, is certified under the provisions of the Missouri Public Drinking Water Regulations to perform chemical analysis for public water systems in the State of Missouri.

Enclosed is a certificate of approval and a certified parameter list for your laboratory. Please reference the certified parameter list for parameters and methods of analysis that have been approved by the State of Missouri to complete chemical testing for public water systems. **Your certification will expire at the same time your certification from the State of Utah expires and is contingent upon no changes being made with the approved methods or equipment.** Please notify this office within 30 days of changes, which occur in these specified areas before the June 30, 2008 expiration date.

Sincerely,

WATER PROTECTION PROGRAM

Steven W. Sturgess, Chief,
Public Drinking Water Branch

SWS:lv

Enclosures

c: Mr. Ron Heckman, MDNR-ESP

MISSOURI DEPARTMENT OF NATURAL RESOURCES

DRINKING WATER LABORATORY

CERTIFIED PARAMETER LIST

This is to certify that

Paragon Analytics, Inc

located at

225 Commerce Drive, Fort Collins, CO 80524

has been approved to perform the indicated procedures on drinking water under the Missouri Public Drinking Water Regulations (10 CSR 60-5.020). Specific method numbers or references are included in parenthesis when appropriate.

RADIOACTIVITY

Gross Alpha (EPA 900.0), Gross Beta (EPA 900.0), Gross Alpha & Beta Radioactivity in Drinking Water Evaporation Technique (EPA 900.0), Cesium 134 (EPA 901.1), Gamma Emitters (EPA 901.1), Alpha Emitting Radium Isotopes (EPA 903.0), Radium 226 (EPA 903.0), Total Radium (EPA 903.0), Radium 226 in Drinking Water Radon Emanation Technique (EPA 903.1), Radium 228 in Drinking Water Radiochemical Technique (EPA 904.0), Tritium in Drinking Water Liquid Scintillation Technique (EPA 906.0), Strontium-90 (ASTM D5811-95), Strontium-89/90 Radiochemical Technique (DOE-Sr-01), Strontium-89/90 Radiochemical Technique (DOE-Sr-02), Uranium Alpha Spectrometry Technique (ASTM D-3972-90), Uranium Alpha Spectrometry Technique (DOE-U-02)

Expiration Date: June 30, 2008
Certificate No.: 175
Original Certifying State: Utah

State of Missouri
Department of Natural Resources

Certificate of Approval
for Chemical Laboratory Service

This is to certify that

Paragon Analytics, Inc

is hereby approved to perform the analysis of drinking water as specified on the Certified Parameter List, which must accompany this certificate to be valid.

Certification No. 175

Date Issued July 20, 2007

Expiration Date June 30, 2008

Chief, Public Drinking Water Branch
Water Protection Program
Department of Natural Resources

Director, Environmental Services Program
Department of Natural Resources

Evaluation Officer, Environmental Services Program
Department of Natural Resources

NORTH DAKOTA DEPARTMENT OF HEALTH
LABORATORY SERVICES DIVISION - CHEMISTRY
2635 East Main Avenue, P.O. Box 937
Bismarck, North Dakota 58502-0937
(701) 328-6140 FAX (701) 328-6280

September 10, 2008

Debra Scheib
Paragon Analytics, Inc.
225 Commerce Drive
Fort Collins, CO 80524

Dear Ms. Scheib:

Paragon Analytics' State of Utah Department of Health certification for the Clean Water Act, Resource Conservation and Recovery Act and Safe Drinking Water Act parameters by the methods on the enclosed list of certified parameters for the laboratory is being recognized by the North Dakota Environmental Laboratory Certification Program (NDELCP) for the period July 01, 2008 through June 30, 2009. The main requirements for maintaining this recognition of certification are (1) that I be notified, in writing, within thirty days of any changes in the status of Paragon Analytics' Utah certification for the parameters by the methods on the enclosed list during the effective period of this recognition of certification; and (2) that I be sent copies of the reports of Paragon Analytics' participation in water pollution, RCRA, water supply and radiochemistry proficiency test studies for the parameters by the methods on the enclosed list during the effective period of this recognition of certification.

If Paragon Analytics desires to renew certification with North Dakota when this recognition of certification expires, an authorized representative will need to contact me to initiate the renewal process. Anyone having questions about this recognition of Paragon Analytics Utah certification by the NDELCP should call me at 701-328-6172.

Sincerely,

Errol Erickson

Errol Erickson
Laboratory Certification Officer for Chemical Parameters

Copies to: Derek Hall, NDSDH Waste Management Division
Marty Haroldson, NDSDH Water Quality Division
Lydia Fewless, NDSDH Municipal Facilities Division

Certified Parameters for
Paragon Analytics, Inc.
225 Commerce Drive, Fort Collins, CO
Issued by
North Dakota Department of Health
Laboratory Services Division - Chemistry
September 10, 2008
Certification Period: July 01, 2008 through June 30, 2009
Lab Certification No: R-057
Based on Certificate No: ATL2
From the State of Utah Department of Health

Program	*Parameter*	*Method*	*Source #*	*Status*
Clean Water Act				
	Alkalinity	2320 B	6	Certified
	Hardness (Total)	2340 B	6	Certified
	Conductivity	2510 B	6	Certified
	Total Solids	2540 B	6	Certified
	Filterable Residue (Total Dissolved Solids)	2540 C	6	Certified
	Non-filterable Residue (Total Suspended Solids)	2540 D	6	Certified
	Chromium (Hexavalent)	3500-Cr D	5	Certified
	Cyanide	4500-CN- E	6	Certified
	Cyanides Amenable to Chlorination	4500-CN- G	6	Certified
	Fluoride	4500-F- C	6	Certified
	pH	4500-H+ B	6	Certified
	Ammonia as N	4500-NH3 H	4	Certified
	Orthophosphate	4500-P E	6	Certified
	Phosphorus (Total)	4500-P E	6	Certified
	Sulfide	4500-S(2-) F	6	Certified
	Total Organic Carbon (TOC)	5310 C	6	Certified
	Conductivity	EPA 120.1	70	Certified
	Oil and Grease	EPA 1664 A	72	Certified
	Aluminum	EPA 200.7	2	Certified
	Antimony	EPA 200.7	2	Certified
	Arsenic	EPA 200.7	2	Certified
	Barium	EPA 200.7	2	Certified
	Beryllium	EPA 200.7	2	Certified
	Boron	EPA 200.7	2	Certified
	Cadmium	EPA 200.7	2	Certified
	Calcium	EPA 200.7	2	Certified
	Chromium	EPA 200.7	2	Certified
	Cobalt	EPA 200.7	2	Certified
	Copper	EPA 200.7	2	Certified
	Iron	EPA 200.7	2	Certified
	Lead	EPA 200.7	2	Certified
	Magnesium	EPA 200.7	2	Certified

Program	Parameter	Method	Source #	Status
Clean Water Act				
	Manganese	EPA 200.7	2	Certified
	Molybdenum	EPA 200.7	2	Certified
	Nickel	EPA 200.7	2	Certified
	Potassium	EPA 200.7	2	Certified
	Selenium	EPA 200.7	2	Certified
	Silica	EPA 200.7	2	Certified
	Silver	EPA 200.7	2	Certified
	Sodium	EPA 200.7	2	Certified
	Thallium	EPA 200.7	2	Certified
	Tin	EPA 200.7	2	Certified
	Vanadium	EPA 200.7	2	Certified
	Zinc	EPA 200.7	2	Certified
	Aluminum	EPA 200.8	2	Certified
	Antimony	EPA 200.8	2	Certified
	Arsenic	EPA 200.8	2	Certified
	Cadmium	EPA 200.8	2	Certified
	Copper	EPA 200.8	2	Certified
	Lead	EPA 200.8	2	Certified
	Molybdenum	EPA 200.8	2	Certified
	Selenium	EPA 200.8	2	Certified
	Silver	EPA 200.8	2	Certified
	Thallium	EPA 200.8	2	Certified
	Vanadium	EPA 200.8	2	Certified
	Mercury	EPA 245.1	2	Certified
	Bromide	EPA 300.0	9	Certified
	Chloride	EPA 300.0	9	Certified
	Fluoride	EPA 300.0	9	Certified
	Nitrate	EPA 300.0	9	Certified
	Nitrite	EPA 300.0	9	Certified
	Orthophosphate	EPA 300.0	9	Certified
	Sulfate	EPA 300.0	9	Certified
	Ammonia as N	EPA 350.1	9	Certified
	Nitrate + Nitrite	EPA 353.2	9	Certified
	4,4'-DDD	EPA 608	65	Certified
	4,4'-DDE	EPA 608	65	Certified
	4,4'-DDT	EPA 608	65	Certified
	Aldrin	EPA 608	65	Certified
	alpha-BHC	EPA 608	65	Certified
	Aroclor 1016	EPA 608	65	Certified
	Aroclor 1221	EPA 608	65	Certified
	Aroclor 1232	EPA 608	65	Certified
	Aroclor 1242	EPA 608	65	Certified
	Aroclor 1248	EPA 608	65	Certified
	Aroclor 1254	EPA 608	65	Certified
	Aroclor 1260	EPA 608	65	Certified
	beta-BHC	EPA 608	65	Certified
	Chlordane (Technical)	EPA 608	65	Certified
	delta-BHC	EPA 608	65	Certified
	Dieldrin	EPA 608	65	Certified

Program	Parameter	Method	Source #	Status
Clean Water Act				
	Endosulfan I	EPA 608	65	Certified
	Endosulfan II	EPA 608	65	Certified
	Endosulfan Sulfate	EPA 608	65	Certified
	Endrin	EPA 608	65	Certified
	Endrin Aldehyde	EPA 608	65	Certified
	gamma-BHC (Lindane)	EPA 608	65	Certified
	Heptachlor	EPA 608	65	Certified
	Heptachlor Epoxide	EPA 608	65	Certified
	Toxaphene	EPA 608	65	Certified
	2,4-D	EPA 615	92	Certified
	2,4-DB	EPA 615	92	Certified
	Dichloroprop	EPA 615	92	Certified
	Dinoseb	EPA 615	92	Certified
	MCPA	EPA 615	92	Certified
	MCPP	EPA 615	92	Certified
	1,1,1-Trichloroethane	EPA 624	65	Certified
	1,1,2,2-Tetrachloroethane	EPA 624	65	Certified
	1,1,2-Trichloroethane	EPA 624	65	Certified
	1,1-Dichloroethane	EPA 624	65	Certified
	1,1-Dichloroethene	EPA 624	65	Certified
	1,2-Dichlorobenzene	EPA 624	65	Certified
	1,2-Dichloroethane	EPA 624	65	Certified
	1,2-Dichloropropane	EPA 624	65	Certified
	1,3-Dichlorobenzene	EPA 624	65	Certified
	1,4-Dichlorobenzene	EPA 624	65	Certified
	2-Chloroethyl vinyl ether	EPA 624	65	Certified
	Acrolein	EPA 624	65	Certified
	Acrylonitrile	EPA 624	65	Certified
	Benzene	EPA 624	65	Certified
	Bromodichloromethane	EPA 624	65	Certified
	Bromoform	EPA 624	65	Certified
	Bromomethane	EPA 624	65	Certified
	Carbon Tetrachloride	EPA 624	65	Certified
	Chlorobenzene	EPA 624	65	Certified
	Chloroethane	EPA 624	65	Certified
	Chloroform	EPA 624	65	Certified
	Chloromethane	EPA 624	65	Certified
	Cis-1,3-Dichloropropene	EPA 624	65	Certified
	Dibromochloromethane	EPA 624	65	Certified
	Ethylbenzene	EPA 624	65	Certified
	Methylene chloride	EPA 624	65	Certified
	Tetrachloroethene	EPA 624	65	Certified
	Toluene	EPA 624	65	Certified
	Trans-1,2-Dichloroethene	EPA 624	65	Certified
	Trans-1,3-Dichloropropene	EPA 624	65	Certified
	Trichloroethene	EPA 624	65	Certified
	Trichlorofluoromethane	EPA 624	65	Certified
	Vinyl chloride (chloroethene)	EPA 624	65	Certified
	1,2,4-Trichlorobenzene	EPA 625	65	Certified

Program	Parameter	Method	Source #	Status
Clean Water Act				
	2,4,6-Trichlorophenol	EPA 625	65	Certified
	2,4-Dichlorophenol	EPA 625	65	Certified
	2,4-Dimethylphenol	EPA 625	65	Certified
	2,4-Dinitrotoluene	EPA 625	65	Certified
	2,6-Dinitrotoluene	EPA 625	65	Certified
	2-Chloronaphthalene	EPA 625	65	Certified
	2-Chlorophenol	EPA 625	65	Certified
	2-Methyl-4,6-dinitrophenol	EPA 625	65	Certified
	2-Nitrophenol	EPA 625	65	Certified
	3,3'-Dichlorobenzidine	EPA 625	65	Certified
	4-Bromophenyl Phenyl Ether	EPA 625	65	Certified
	4-Chloro-3-methylphenol	EPA 625	65	Certified
	4-Chlorophenyl Phenyl Ether	EPA 625	65	Certified
	4-Nitrophenol	EPA 625	65	Certified
	Acenaphthene	EPA 625	65	Certified
	Acenaphthylene	EPA 625	65	Certified
	Anthracene	EPA 625	65	Certified
	Benzidine	EPA 625	65	Certified
	Benzo(a)anthracene	EPA 625	65	Certified
	Benzo(a)pyrene	EPA 625	65	Certified
	Benzo(b)fluoranthene	EPA 625	65	Certified
	Benzo(g,h,i)perylene	EPA 625	65	Certified
	Benzo(k)fluoranthene	EPA 625	65	Certified
	Benzyl Butyl Phthalate	EPA 625	65	Certified
	bis(2-chloroethoxy)methane	EPA 625	65	Certified
	bis(2-Chloroethyl)ether	EPA 625	65	Certified
	bis(2-Chloroisopropyl)ether	EPA 625	65	Certified
	bis(2-Ethylhexyl)phthalate	EPA 625	65	Certified
	Chrysene	EPA 625	65	Certified
	Dibenzo(a,h)anthracene	EPA 625	65	Certified
	Diethyl phthalate	EPA 625	65	Certified
	Dimethyl phthalate	EPA 625	65	Certified
	Di-n-butyl phthalate	EPA 625	65	Certified
	Di-n-octyl phthalate	EPA 625	65	Certified
	Fluoranthene	EPA 625	65	Certified
	Fluorene	EPA 625	65	Certified
	Hexachlorobenzene	EPA 625	65	Certified
	Hexachlorobutadiene	EPA 625	65	Certified
	Hexachlorocyclopentadiene	EPA 625	65	Certified
	Hexachloroethane	EPA 625	65	Certified
	Indeno(1,2,3-cd)pyrene	EPA 625	65	Certified
	Isophorone	EPA 625	65	Certified
	Naphthalene	EPA 625	65	Certified
	Nitrobenzene	EPA 625	65	Certified
	N-Nitrosodimethylamine	EPA 625	65	Certified
	N-Nitrosodi-n-propylamine	EPA 625	65	Certified
	N-Nitrosodiphenylamine	EPA 625	65	Certified
	Pentachlorophenol	EPA 625	65	Certified
	Phenanthrene	EPA 625	65	Certified

Program	Parameter	Method	Source #	Status
Clean Water Act				
	Phenol	EPA 625	65	Certified
	Pyrene	EPA 625	65	Certified
	Alpha-Total, pCi per liter	EPA 900.0	15	Certified
	Beta-Total, pCi per liter	EPA 900.0	15	Certified
	Radium Total pCi per liter	EPA 903.0	15	Certified
Resource Conservation and Recovery Act				
	Ignitability	SW846 1010A	85	Certified
	TCLP Metals Extraction	SW846 1311	81	Certified
	TCLP Semi-Volatiles Extraction	SW846 1311	81	Certified
	TCLP Volatiles Extraction	SW846 1311	81	Certified
	Synthetic Precipitation Leaching Procedure (SPLP)	SW846 1312	82	Certified
	Aluminum	SW846 6010B	84	Certified
	Antimony	SW846 6010B	84	Certified
	Arsenic	SW846 6010B	84	Certified
	Barium	SW846 6010B	84	Certified
	Beryllium	SW846 6010B	84	Certified
	Boron	SW846 6010B	84	Certified
	Cadmium	SW846 6010B	84	Certified
	Calcium	SW846 6010B	84	Certified
	Chromium	SW846 6010B	84	Certified
	Cobalt	SW846 6010B	84	Certified
	Copper	SW846 6010B	84	Certified
	Iron	SW846 6010B	84	Certified
	Lead	SW846 6010B	84	Certified
	Lithium	SW846 6010B	84	Certified
	Magnesium	SW846 6010B	84	Certified
	Manganese	SW846 6010B	84	Certified
	Molybdenum	SW846 6010B	84	Certified
	Nickel	SW846 6010B	84	Certified
	Potassium	SW846 6010B	84	Certified
	Selenium	SW846 6010B	84	Certified
	Silica	SW846 6010B	84	Certified
	Silver	SW846 6010B	84	Certified
	Sodium	SW846 6010B	84	Certified
	Strontium	SW846 6010B	84	Certified
	Thallium	SW846 6010B	84	Certified
	Tin	SW846 6010B	84	Certified
	Titanium	SW846 6010B	84	Certified
	Vanadium	SW846 6010B	84	Certified
	Zinc	SW846 6010B	84	Certified
	Aluminum	SW846 6020A	96	Certified
	Antimony	SW846 6020A	96	Certified
	Arsenic	SW846 6020A	96	Certified
	Cadmium	SW846 6020A	96	Certified
	Copper	SW846 6020A	96	Certified
	Lead	SW846 6020A	96	Certified
	Molybdenum	SW846 6020A	96	Certified
	Selenium	SW846 6020A	96	Certified

Program	Parameter	Method	Source #	Status
Resource Conservation and Recovery Act				
	Silver	SW846 6020A	96	Certified
	Thallium	SW846 6020A	96	Certified
	Uranium	SW846 6020A	96	Certified
	Vanadium	SW846 6020A	96	Certified
	Chromium (Hexavalent)	SW846 7196A	81	Certified
	Mercury	SW846 7470A	82	Certified
	Mercury	SW846 7471A	82	Certified
	Diesel Range Organics	SW846 8015B	84	Certified
	Gasoline Range Organics	SW846 8015B	84	Certified
	1,2-Dichlorobenzene	SW846 8021B	84	Certified
	1,3-Dichlorobenzene	SW846 8021B	84	Certified
	1,4-Dichlorobenzene	SW846 8021B	84	Certified
	Benzene	SW846 8021B	84	Certified
	Chlorobenzene	SW846 8021B	84	Certified
	Ethylbenzene	SW846 8021B	84	Certified
	meta-Xylene	SW846 8021B	84	Certified
	o-xylene	SW846 8021B	84	Certified
	para-Xylene	SW846 8021B	84	Certified
	Toluene	SW846 8021B	84	Certified
	Xylenes (Total)	SW846 8021B	84	Certified
	4,4'-DDD	SW846 8081A	84	Certified
	4,4'-DDE	SW846 8081A	84	Certified
	4,4'-DDT	SW846 8081A	84	Certified
	Aldrin	SW846 8081A	84	Certified
	alpha-BHC	SW846 8081A	84	Certified
	alpha-chlordane	SW846 8081A	84	Certified
	beta-BHC	SW846 8081A	84	Certified
	Chlordane (Technical)	SW846 8081A	84	Certified
	delta-BHC	SW846 8081A	84	Certified
	Dieldrin	SW846 8081A	84	Certified
	Endosulfan I	SW846 8081A	84	Certified
	Endosulfan II	SW846 8081A	84	Certified
	Endosulfan Sulfate	SW846 8081A	84	Certified
	Endrin	SW846 8081A	84	Certified
	Endrin Aldehyde	SW846 8081A	84	Certified
	Endrin Ketone	SW846 8081A	84	Certified
	gamma-BHC (Lindane)	SW846 8081A	84	Certified
	gamma-chlordane	SW846 8081A	84	Certified
	Heptachlor	SW846 8081A	84	Certified
	Heptachlor Epoxide	SW846 8081A	84	Certified
	Methoxychlor	SW846 8081A	84	Certified
	Toxaphene	SW846 8081A	84	Certified
	Aroclor 1016	SW846 8082	84	Certified
	Aroclor 1221	SW846 8082	84	Certified
	Aroclor 1232	SW846 8082	84	Certified
	Aroclor 1242	SW846 8082	84	Certified
	Aroclor 1248	SW846 8082	84	Certified
	Aroclor 1254	SW846 8082	84	Certified
	Aroclor 1260	SW846 8082	84	Certified

Program	Parameter	Method	Source #	Status
Resource Conservation and Recovery Act				
	Azinphos-methyl (Guthion)	SW846 8141A	82	Certified
	Bolstar (Sulprofos)	SW846 8141A	82	Certified
	Chlorpyrifos	SW846 8141A	82	Certified
	Coumaphos	SW846 8141A	82	Certified
	Demeton-O	SW846 8141A	82	Certified
	Demeton-S	SW846 8141A	82	Certified
	Diazinon	SW846 8141A	82	Certified
	Dichlorovos (DDVP)	SW846 8141A	82	Certified
	Disulfoton	SW846 8141A	82	Certified
	Ethoprop	SW846 8141A	82	Certified
	Fensulfothion	SW846 8141A	82	Certified
	Fenthion	SW846 8141A	82	Certified
	Malathion	SW846 8141A	82	Certified
	Merphos	SW846 8141A	82	Certified
	Mevinphos	SW846 8141A	82	Certified
	Naled	SW846 8141A	82	Certified
	Parathion, methyl	SW846 8141A	82	Certified
	Phorate	SW846 8141A	82	Certified
	Ronnel	SW846 8141A	82	Certified
	Tetrachlorovinphos	SW846 8141A	82	Certified
	Tokuthion	SW846 8141A	82	Certified
	Trichloronate	SW846 8141A	82	Certified
	2,4,5-T	SW846 8151A	84	Certified
	2,4,5-TP (Silvex)	SW846 8151A	84	Certified
	2,4-D	SW846 8151A	84	Certified
	2,4-DB	SW846 8151A	84	Certified
	Dalapon	SW846 8151A	84	Certified
	Dicamba	SW846 8151A	84	Certified
	Dichloroprop	SW846 8151A	84	Certified
	Dinoseb	SW846 8151A	84	Certified
	MCPA	SW846 8151A	84	Certified
	MCPP	SW846 8151A	84	Certified
	1,1,1,2-Tetrachloroethane	SW846 8260B	84	Certified
	1,1,1-Trichloroethane	SW846 8260B	84	Certified
	1,1,2,2-Tetrachloroethane	SW846 8260B	84	Certified
	1,1,2-Trichloroethane	SW846 8260B	84	Certified
	1,1-Dichloroethane	SW846 8260B	84	Certified
	1,1-Dichloroethene	SW846 8260B	84	Certified
	1,1-Dichloropropene	SW846 8260B	84	Certified
	1,2,3-Trichlorobenzene	SW846 8260B	84	Certified
	1,2,3-Trichloropropane	SW846 8260B	84	Certified
	1,2,4-Trichlorobenzene	SW846 8260B	84	Certified
	1,2,4-Trimethylbenzene	SW846 8260B	84	Certified
	1,2-Dibromo-3-Chloropropane (DBCP)	SW846 8260B	84	Certified
	1,2-Dibromoethane	SW846 8260B	84	Certified
	1,2-Dichlorobenzene	SW846 8260B	84	Certified
	1,2-Dichloroethane	SW846 8260B	84	Certified
	1,2-Dichloropropane	SW846 8260B	84	Certified
	1,3,5-Trimethylbenzene	SW846 8260B	84	Certified

Program	Parameter	Method	Source #	Status
Resource Conservation and Recovery Act				
	1,3-Dichlorobenzene	SW846 8260B	84	Certified
	1,3-Dichloropropane	SW846 8260B	84	Certified
	1,4-Dichlorobenzene	SW846 8260B	84	Certified
	1-Chlorohexane	SW846 8260B	84	Certified
	2,2-Dichloropropane	SW846 8260B	84	Certified
	2-Chloroethyl vinyl ether	SW846 8260B	84	Certified
	2-Chlorotoluene	SW846 8260B	84	Certified
	2-hexanone	SW846 8260B	84	Certified
	4-Chlorotoluene	SW846 8260B	84	Certified
	4-methyl 2-pentanone (MIBK)	SW846 8260B	84	Certified
	Acetone	SW846 8260B	84	Certified
	Acetonitrile	SW846 8260B	84	Certified
	Acrolein	SW846 8260B	84	Certified
	Acrylonitrile	SW846 8260B	84	Certified
	Benzene	SW846 8260B	84	Certified
	Bromobenzene	SW846 8260B	84	Certified
	Bromochloromethane	SW846 8260B	84	Certified
	Bromodichloromethane	SW846 8260B	84	Certified
	Bromoform	SW846 8260B	84	Certified
	Bromomethane	SW846 8260B	84	Certified
	Carbon Disulfide	SW846 8260B	84	Certified
	Carbon Tetrachloride	SW846 8260B	84	Certified
	Chlorobenzene	SW846 8260B	84	Certified
	Chlorodibromomethane	SW846 8260B	84	Certified
	Chloroethane	SW846 8260B	84	Certified
	Chloroform	SW846 8260B	84	Certified
	Chloromethane	SW846 8260B	84	Certified
	Cis-1,2-Dichloroethene	SW846 8260B	84	Certified
	Cis-1,3-Dichloropropene	SW846 8260B	84	Certified
	Dibromomethane	SW846 8260B	84	Certified
	Dichlorodifluoromethane	SW846 8260B	84	Certified
	Ethylbenzene	SW846 8260B	84	Certified
	Hexachlorobutadiene	SW846 8260B	84	Certified
	Iodomethane	SW846 8260B	84	Certified
	Isopropylbenzene	SW846 8260B	84	Certified
	meta-Xylene	SW846 8260B	84	Certified
	Methyl ethyl ketone (MEK)	SW846 8260B	84	Certified
	Methyl tert butyl ether	SW846 8260B	84	Certified
	Methylene chloride	SW846 8260B	84	Certified
	Naphthalene	SW846 8260B	84	Certified
	n-Butylbenzene	SW846 8260B	84	Certified
	N-Propylbenzene	SW846 8260B	84	Certified
	o-xylene	SW846 8260B	84	Certified
	para-Xylene	SW846 8260B	84	Certified
	p-Isopropyltoluene	SW846 8260B	84	Certified
	sec-Butylbenzene	SW846 8260B	84	Certified
	Styrene	SW846 8260B	84	Certified
	Tert-Butylbenzene	SW846 8260B	84	Certified
	Tetrachloroethene	SW846 8260B	84	Certified

Program	Parameter	Method	Source #	Status
Resource Conservation and Recovery Act				
	Toluene	SW846 8260B	84	Certified
	Trans-1,2-Dichloroethene	SW846 8260B	84	Certified
	Trans-1,3-Dichloropropene	SW846 8260B	84	Certified
	Trichloroethene	SW846 8260B	84	Certified
	Trichlorofluoromethane	SW846 8260B	84	Certified
	Vinyl Acetate	SW846 8260B	84	Certified
	Vinyl chloride (chloroethene)	SW846 8260B	84	Certified
	Xylenes (Total)	SW846 8260B	84	Certified
	1,2,4-Trichlorobenzene	SW846 8270D	96	Certified
	1,2-Dichlorobenzene	SW846 8270D	96	Certified
	1,3-Dichlorobenzene	SW846 8270D	96	Certified
	1,4-Dichlorobenzene	SW846 8270D	96	Certified
	2,3,4,6-Tetrachlorophenol	SW846 8270D	96	Certified
	2,4,5-Trichlorophenol	SW846 8270D	96	Certified
	2,4,6-Trichlorophenol	SW846 8270D	96	Certified
	2,4-Dichlorophenol	SW846 8270D	96	Certified
	2,4-Dimethylphenol	SW846 8270D	96	Certified
	2,4-Dinitrophenol	SW846 8270D	96	Certified
	2,4-Dinitrotoluene	SW846 8270D	96	Certified
	2,6-Dinitrotoluene	SW846 8270D	96	Certified
	2-Chloronaphthalene	SW846 8270D	96	Certified
	2-Methyl-4,6-dinitrophenol	SW846 8270D	96	Certified
	2-Methylnaphthalene	SW846 8270D	96	Certified
	2-Methylphenol (o-Cresol)	SW846 8270D	96	Certified
	2-Nitroaniline	SW846 8270D	96	Certified
	2-Nitrophenol	SW846 8270D	96	Certified
	3,3'-Dichlorobenzidine	SW846 8270D	96	Certified
	3-Methylphenol	SW846 8270D	96	Certified
	3-Nitroaniline	SW846 8270D	96	Certified
	4-Bromophenyl Phenyl Ether	SW846 8270D	96	Certified
	4-Chloro-3-methylphenol	SW846 8270D	96	Certified
	4-Chloroaniline	SW846 8270D	96	Certified
	4-Chlorophenyl Phenyl Ether	SW846 8270D	96	Certified
	4-Methylphenol (p-Cresol)	SW846 8270D	96	Certified
	4-Nitroaniline	SW846 8270D	96	Certified
	4-Nitrophenol	SW846 8270D	96	Certified
	Acenaphthene	SW846 8270D	96	Certified
	Acenaphthylene	SW846 8270D	96	Certified
	Aniline	SW846 8270D	96	Certified
	Anthracene	SW846 8270D	96	Certified
	Benzo(a)anthracene	SW846 8270D	96	Certified
	Benzo(a)pyrene	SW846 8270D	96	Certified
	Benzo(b)fluoranthene	SW846 8270D	96	Certified
	Benzo(g,h,i)perylene	SW846 8270D	96	Certified
	Benzo(k)fluoranthene	SW846 8270D	96	Certified
	Benzoic Acid	SW846 8270D	96	Certified
	Benzyl Alcohol	SW846 8270D	96	Certified
	bis(2-chloroethoxy)methane	SW846 8270D	96	Certified
	bis(2-Chloroethyl)ether	SW846 8270D	96	Certified

Program	Parameter	Method	Source #	Status
Resource Conservation and Recovery Act				
	bis(2-Chloroisopropyl)ether	SW846 8270D	96	Certified
	bis(2-Ethylhexyl)phthalate	SW846 8270D	96	Certified
	Butyl benzyl phthalate	SW846 8270D	96	Certified
	Chrysene	SW846 8270D	96	Certified
	Dibenzo(a,h)anthracene	SW846 8270D	96	Certified
	Dibenzofuran	SW846 8270D	96	Certified
	Diethyl phthalate	SW846 8270D	96	Certified
	Dimethyl phthalate	SW846 8270D	96	Certified
	Di-n-butyl phthalate	SW846 8270D	96	Certified
	Di-n-octyl phthalate	SW846 8270D	96	Certified
	Fluoranthene	SW846 8270D	96	Certified
	Fluorene	SW846 8270D	96	Certified
	Hexachlorobenzene	SW846 8270D	96	Certified
	Hexachlorobutadiene	SW846 8270D	96	Certified
	Hexachlorocyclopentadiene	SW846 8270D	96	Certified
	Hexachloroethane	SW846 8270D	96	Certified
	Indeno(1,2,3-cd)pyrene	SW846 8270D	96	Certified
	Isophorone	SW846 8270D	96	Certified
	Naphthalene	SW846 8270D	96	Certified
	Nitrobenzene	SW846 8270D	96	Certified
	N-Nitrosodimethylamine	SW846 8270D	96	Certified
	N-nitroso-di-n-propylamine	SW846 8270D	96	Certified
	N-Nitrosodiphenylamine	SW846 8270D	96	Certified
	Pentachlorophenol	SW846 8270D	96	Certified
	Phenanthrene	SW846 8270D	96	Certified
	Phenol	SW846 8270D	96	Certified
	Pyrene	SW846 8270D	96	Certified
	1,3,5-Trinitrobenzene	SW846 8330	82	Certified
	1,3-Dinitrobenzene	SW846 8330	82	Certified
	2,4,6-Trinitrotoluene	SW846 8330	82	Certified
	2,4-Dinitrotoluene	SW846 8330	82	Certified
	2,6-Dinitrotoluene	SW846 8330	82	Certified
	2-Amino-4,6-Dinitrotoluene	SW846 8330	82	Certified
	2-Nitrotoluene	SW846 8330	82	Certified
	3-Nitrotoluene	SW846 8330	82	Certified
	4-Amino-2,6-Dinitrotoluene	SW846 8330	82	Certified
	4-Nitrotoluene	SW846 8330	82	Certified
	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	SW846 8330	82	Certified
	Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	SW846 8330	82	Certified
	Nitrobenzene	SW846 8330	82	Certified
	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	SW846 8330	82	Certified
	Cyanide	SW846 9014	84	Certified
	pH	SW846 9040B	69	Certified
	pH	SW846 9045C	69	Certified
	Specific Conductance	SW846 9050A	84	Certified
	Bromide	SW846 9056	82	Certified
	Chloride	SW846 9056	82	Certified
	Fluoride	SW846 9056	82	Certified
	Nitrate	SW846 9056	82	Certified

Program	Parameter	Method	Source #	Status
Resource Conservation and Recovery Act				
	Nitrite	SW846 9056	82	Certified
	Orthophosphate	SW846 9056	82	Certified
	Sulfate	SW846 9056	82	Certified
	Total Organic Carbon (TOC)	SW846 9060	69	Certified
	n-Hexane Extractable Material (HEM)	SW846 9071B	86	Certified
	Paint Filter Liquids Test	SW846 9095A	69	Certified
	Fluoride	SW846 9214	84	Certified
	Gross Alpha and Gross Beta	SW846 9310	69	Certified
	Alpha Emitting Radium Isotopes	SW846 9315	69	Certified
	Radium 228	SW846 9320	69	Certified
Safe Drinking Water Act				
	Filterable Residue (Total Dissolved Solids)	2540 C	6	Certified
	Total Organic Carbon (TOC)	5310 C	6	Certified
	Aluminum	EPA 200.7	2	Certified
	Barium	EPA 200.7	2	Certified
	Beryllium	EPA 200.7	2	Certified
	Cadmium	EPA 200.7	2	Certified
	Chromium	EPA 200.7	2	Certified
	Copper	EPA 200.7	2	Certified
	Iron	EPA 200.7	2	Certified
	Manganese	EPA 200.7	2	Certified
	Silver	EPA 200.7	2	Certified
	Zinc	EPA 200.7	2	Certified
	Aluminum	EPA 200.8	2	Certified
	Antimony	EPA 200.8	2	Certified
	Arsenic	EPA 200.8	2	Certified
	Cadmium	EPA 200.8	2	Certified
	Copper	EPA 200.8	2	Certified
	Lead	EPA 200.8	2	Certified
	Selenium	EPA 200.8	2	Certified
	Silver	EPA 200.8	2	Certified
	Thallium	EPA 200.8	2	Certified
	Uranium	EPA 200.8	2	Certified
	Mercury	EPA 245.1	2	Certified
	Bromide	EPA 300.0	9	Certified
	Chloride	EPA 300.0	9	Certified
	Fluoride	EPA 300.0	9	Certified
	Nitrate	EPA 300.0	9	Certified
	Nitrite	EPA 300.0	9	Certified
	Sulfate	EPA 300.0	9	Certified
	Gross Alpha	EPA 900.0	15	Certified
	Gross Beta	EPA 900.0	15	Certified
	Gamma Emitting Radionuclides	EPA 901.1	15	Certified
	Radium 226	EPA 903.0	15	Certified
	Radium 226	EPA 903.1	15	Certified
	Radium 228	EPA 904.0	15	Certified
	Tritium	EPA 906.0	15	Certified
	Strontium 89	SR-01	22	Certified

Program	Parameter	Method	Source #	Status
Safe Drinking Water Act				
	Strontium 90	SR-01	22	Certified
	Strontium 89	SR-02	22	Certified
	Strontium 90	SR-02	22	Certified
	Uranium	U 02	22	Certified

Source Reference

2	"Methods for the Determination of Metals in Environmental Samples - Supplement I", EPA/600/R-94/111, May 1994
4	Standard Methods for the Examination of Water and Wastewater, 18th edition (1992), American Public Health Association
5	Standard Methods for the Examination of Water and Wastewater, 19th edition (1995), American Public Health Association
6	Standard Methods for the Examination of Water and Wastewater, 20th edition (1998), American Public Health Association
9	"Methods for the Determination of Inorganic Substances in Environmental Samples", EPA/600/R-93-100, August 1993
15	"Prescribed Procedures for the Measurement of Radioactivity in Drinking Water", EPA 600/4-80-032, August 1980
22	"EML Procedures Manual", 28th (1997) or 27th (1990) Editions, Volumes 1 and 2, Environmental Measurements Laboratory, U.S. Department of Energy, New York, NY
65	40 CFR Part 136, Appendix A
69	Test Methods for Evaluating Solid Waste Physical Chemical Methods (SW846) Third Edition, EPA-SW-846-03-03B, EPA Office of Solid Waste and Emergency Response
70	"Methods for Chemical Analysis of Water and Wastes" Environmental Protection Agency, EPA-600/4-79-020, revised March 1983 and 1979 where applicable
72	USEPA Office of Water, EPA-821-R-98-002, PB99-121949, February 1999
81	Test Methods for Evaluating Solid Waste Physical Chemical Methods (SW846) Third Edition, as amended by Update I, July 1992, EPA Office of Solid Waste and Emergency Response
82	Test Methods for Evaluating Solid Waste Physical Chemical Methods (SW846) Third Edition, as amended by Update II, September 1994, EPA Office of Solid Waste and Emergency Response
84	Test Methods for Evaluating Solid Waste Physical Chemical Methods (SW846) Third Edition, as amended by Update III, December 1996, EPA Office of Solid Waste and Emergency Response
85	Test Methods for Evaluating Solid Waste Physical Chemical Methods (SW846) Third Edition, as amended by Final Update IIIB, November 2004, EPA Office of Solid Waste and Emergency Response
86	SW846 Method 9071B, n-Hexane Extractable Material (HEM) for Sludge, Sediment and Solid Samples (Revision 2, April 1998)
92	Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater - Volume I - EPA-821-R-93-010-A August 1993, Revision 1
96	Test Methods for Evaluating Solid Waste Physical Chemical Methods (SW846) Third Edition, as amended by Final Update IV, February 2007, EPA Office of Solid Waste and Emergency Response

NORTH DAKOTA STATE DEPARTMENT OF HEALTH
RECOGNITION OF CERTIFICATION OR ACCREDITATION

The North Dakota State Department of Health recognizes the certification or accreditation of

Paragon Analytics, Inc. - 225 Commerce Drive - Fort Collins, CO

by

State of Utah Department of Health

for

All Clean Water Act, Resource Conservation and Recovery Act and Safe Drinking Water Act chemical parameters by the methods on the accompanying list of certified parameters for this laboratory

Certification Number: R-057

Date of Issue: September 10, 2008 Expiration Date: June 30, 2009 Covers: 7/1/2008 - 6/30/2009

This certificate remains the property of the North Dakota State Department of Health and may be recalled, for cause, at any time, by the Department. Recognition of a laboratory's certification or accreditation from another state's certification or accreditation program by the North Dakota State Department of Health is neither an endorsement of the results reported by the laboratory nor a guarantee of the validity or accuracy of the results reported by the laboratory.

Myra Kosse
Director, Division of Chemistry

Erol Erickson
Certification Officer

State of New Jersey
DEPARTMENT OF ENVIRONMENTAL PROTECTION
Office of Quality Assurance
9 Ewing Street, 2nd Floor, P.O. Box 424
Trenton, New Jersey 08625
Tel: (609) 292-3950
Fax: (609) 777-1774

JON S. CORZINE
Governor

LISA P. JACKSON
Commissioner

July 30, 2008

Deb Scheib
Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Dear Ms. Scheib:

Re: Application Modification Request
Laboratory Certification ID# CO003

Based on your request for certification for the parameter(s) listed below and a review of your supporting documentation, enclosed is an up-dated annual certified parameter list (ACPL). This will replace the current ACPL your laboratory holds. Please review it carefully and notify this office immediately if any discrepancies are noted.

Parameter Code	Parameter	Method	Status
SHW04.47300	Uranium	SW-846 6020	Certified

If this office can be of any further assistance, please call Vas Komanduri at (609) 292-3950.

Sincerely,

Joseph F. Aiello, Chief

Enclosure
C: File

New Jersey Department of Environmental Protection

National Environmental Laboratory Accreditation Program

ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

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Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SDW07 -- Radiochem.: Radioactivity / Radionuclide

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SDW07.01000	DW	Proportional or Scintillation	[EPA 900.0]	Gross - alpha-beta
Certified	Yes	UT	SDW07.03000	DW	Gamma Spectrometry - Radiochemistry	[EPA 901.0]	Cesium 134/137
Certified	Yes	UT	SDW07.03900	DW	Radiochemical	[EPA 903.0]	Radium - 226
Certified	Yes	UT	SDW07.04000	DW	Radon Emanation	[EPA 903.1]	Radium - 226
Certified	Yes	UT	SDW07.04100	DW	Precipitation	[EPA 904.0]	Radium - 228
Certified	Yes	UT	SDW07.05000	DW	Precipitation	[EPA 903.0]	Radium - total
Certified	Yes	UT	SDW07.06000	DW	Total Sr & Strontium 90	[DOE 1990 Sr-02]	Strontium - 89, 90
Certified	Yes	UT	SDW07.07000	DW	Distillation/Liquid Scintillation	[EPA 906.0]	Tritium
Certified	Yes	UT	SDW07.08300	DW	Alpha Spectrometry	[ASTM D 3972-97]	Uranium

Category: SHW02 -- Characteristics of Hazardous Waste

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW02.01000	NPW	Pensky Martens	[SW-846 1010A]	Ignitability

Category: SHW04 -- Inorganic Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW04.01000	NPW	Acid Digestion/Surface and Groundwater, ICP, FLAA	[SW-846 3005A, Rev. 1, 7/92]	Metals, Total Rec and Dissolved
Certified	Yes	UT	SHW04.01500	NPW	Acid Digestion/Aqueous Samples, ICP, FLAA	[SW-846 3010A, Rev. 1, 7/92]	Metals, Total
Certified	Yes	UT	SHW04.33000	NPW	AA, Manual Cold Vapor	[SW-846 7470A, Rev. 1, 9/94]	Mercury - liquid waste

Category: SHW05 -- Organic Parameters, Prep. / Screening

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW05.01000	NPW	Separatory Funnel Extraction	[SW-846 3510C, Rev. 3, 12/96]	Semivolatile organics
Certified	Yes	UT	SHW05.02000	NPW	Continuous Liquid-Liquid Extraction	[SW-846 3520C, Rev. 3, 12/96]	Semivolatile organics

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Category: SHW05 -- Organic Parameters, Prep. / Screening

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW05.07000	NPW	Purge & Trap Aqueous	[SW-846 5030B, Rev. 2, 12/96]	Volatile organics

Category: SHW06 -- Organic Parameters, Chromatography

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW06.02010	NPW	Microextraction, GC, ECD	[SW-846 8011, Rev. 0, 7/92]	Dibromoethane (1,2-) (EDB)
Certified	Yes	UT	SHW06.02020	NPW	Microextraction, GC, ECD	[SW-846 8011, Rev. 0, 7/92]	Dibromo-3-chloropropane (1,2-)

Category: SHW09 -- Miscellaneous Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW09.14000	NPW	Electrometric	[SW-846 9040B, Rev. 2, 1/95]	pH - waste, >20% water
Certified	Yes	UT	SHW09.17000	NPW	Wheatstone Bridge	[SW-846 9050A, Rev. 1, 12/96]	Specific conductance
Certified	Yes	UT	SHW09.19000	NPW	Infrared Spectrometry or FID	[SW-846 9060, Rev. 0, 9/86]	Total organic carbon (TOC)
Certified	Yes	UT	SHW09.24100	NPW	Extraction & Gravimetric - LL or SPE	[SW-846 1664A, Rev. 1, 2/99]	Oil & grease - hem
Applied	No	UT	SHW09.34100	NPW	Aqueous, Ion-Selective Electrode	[SW-846 9214, Rev. 0, 12/96]	Fluoride

Category: WPP02 -- Inorg. Parameters, Nutrients and Demands

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Applied	No	UT	WPP02.01500	NPW	Electrometric or Color Titration	[SM 2320 B]	Alkalinity as CaCO3
Certified	Yes	UT	WPP02.04000	NPW	Automated Phenate	[EPA 350.1] [SM 4500-NH3 B+H (18th ed)]	Ammonia
Certified	Yes	UT	WPP02.06000	NPW	ICP	[EPA 200.7]	Boron
Certified	Yes	UT	WPP02.07100	NPW	Ion Chromatography	[EPA 300.0]	Bromide
Certified	Yes	UT	WPP02.08000	NPW	Digestion, ICP	[EPA 200.7]	Calcium
Certified	Yes	UT	WPP02.12600	NPW	Ion Chromatography	[EPA 300.0]	Chloride
Certified	Yes	UT	WPP02.16500	NPW	Distillation + Electrode, Manual	[SM 4500-F B, C]	Fluoride
Certified	Yes	UT	WPP02.18100	NPW	Ion Chromatography	[EPA 300.0]	Fluoride

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225 COMMERCE DR
FORT COLLINS, CO 80524

Category: WPP02 -- Inorg. Parameters, Nutrients and Demands

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP02.19000	NPW	Titrimetric, EDTA	[SM 2340 B or C]	Hardness - total as CaCO3
Certified	Yes	UT	WPP02.20100	NPW	Ca + Mg Carbonates, ICP	[EPA 200.7]	Hardness - total as CaCO3
Certified	Yes	UT	WPP02.24000	NPW	Digestion, ICP	[EPA 200.7]	Magnesium
Certified	Yes	UT	WPP02.26100	NPW	Ion Chromatography	[EPA 300.0]	Nitrate
Certified	Yes	UT	WPP02.27000	NPW	Cadmium Reduction, Automated	[EPA 353.2]	Nitrate - nitrite
Certified	Yes	UT	WPP02.28000	NPW	Spectrophotometric, Manual	[SM 4500-NO2 B]	Nitrite
Certified	Yes	UT	WPP02.28600	NPW	Ion Chromatography	[EPA 300.0]	Nitrite
Certified	Yes	UT	WPP02.30000	NPW	Combustion or Oxidation	[SM 5310 B, C or D]	Total organic carbon (TOC)
Certified	Yes	UT	WPP02.32100	NPW	Ion Chromatography	[EPA 300.0]	Orthophosphate
Certified	Yes	UT	WPP02.36500	NPW	Digestion, ICP	[EPA 200.7]	Potassium
Certified	Yes	UT	WPP02.38000	NPW	Gravimetric, 103-105 Degrees C	[SM 2540 B]	Residue - total
Certified	Yes	UT	WPP02.38500	NPW	Gravimetric, 180 Degrees C	[SM 2540 C]	Residue - filterable (TDS)
Certified	Yes	UT	WPP02.39000	NPW	Gravimetric, 103-105 Degrees C, Post Washing	[SM 2540 D]	Residue - nonfilterable (TSS)
Certified	Yes	UT	WPP02.42500	NPW	0.45u Filtration + ICP	[EPA 200.7]	Silica - dissolved
Certified	Yes	UT	WPP02.44000	NPW	Digestion, ICP	[EPA 200.7]	Sodium
Certified	Yes	UT	WPP02.45500	NPW	Wheatstone Bridge	[SM 2510 B]	Specific conductance
Certified	Yes	UT	WPP02.45600	NPW	Continuous	[EPA 120.1]	Specific conductance
Certified	Yes	UT	WPP02.47100	NPW	Ion Chromatography	[EPA 300.0]	Sulfate
Certified	Yes	UT	WPP02.47500	NPW	Titrimetric, Iodine	[SM 4500-S F (19/20th ed)]	Sulfides

Category: WPP03 -- Analyze-Immediately Inorganic Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP03.09000	NPW	Electrometric	[SM 4500-H B]	pH

Category: WPP04 -- Inorganic Parameters, Metals

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP04.02000	NPW	Digestion, ICP	[EPA 200.7]	Aluminum

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225 COMMERCE DR
FORT COLLINS, CO 80524

Category: WPP04 -- Inorganic Parameters, Metals

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP04.02100	NPW	ICP/MS	[EPA 200.8]	Aluminum
Certified	Yes	UT	WPP04.04500	NPW	Digestion, ICP	[EPA 200.7]	Antimony
Certified	Yes	UT	WPP04.04600	NPW	ICP/MS	[EPA 200.8]	Antimony
Certified	Yes	UT	WPP04.05600	NPW	Digestion, ICP	[EPA 200.7]	Arsenic
Certified	Yes	UT	WPP04.05700	NPW	ICP/MS	[EPA 200.8]	Arsenic
Certified	Yes	UT	WPP04.08000	NPW	Digestion, ICP	[EPA 200.7]	Barium
Certified	Yes	UT	WPP04.11000	NPW	Digestion, ICP	[EPA 200.7]	Beryllium
Certified	Yes	UT	WPP04.13500	NPW	Digestion, ICP	[EPA 200.7]	Cadmium
Certified	Yes	UT	WPP04.13600	NPW	ICP/MS	[EPA 200.8]	Cadmium
Certified	Yes	UT	WPP04.15000	NPW	0.45u Filter, Colorimetric DPC	[SM 3500-Cr D]	Chromium (VI)
Certified	Yes	UT	WPP04.18000	NPW	Digestion, ICP	[EPA 200.7]	Chromium
Certified	Yes	UT	WPP04.19500	NPW	Digestion, ICP	[EPA 200.7]	Cobalt
Certified	Yes	UT	WPP04.21500	NPW	Digestion, ICP	[EPA 200.7]	Copper
Certified	Yes	UT	WPP04.21600	NPW	ICP/MS	[EPA 200.8]	Copper
Certified	Yes	UT	WPP04.26500	NPW	Digestion, ICP	[EPA 200.7]	Iron
Certified	Yes	UT	WPP04.28000	NPW	Digestion, ICP	[EPA 200.7]	Lead
Certified	Yes	UT	WPP04.28100	NPW	ICP/MS	[EPA 200.8]	Lead
Certified	Yes	UT	WPP04.31000	NPW	Digestion, ICP	[EPA 200.7]	Manganese
Certified	Yes	UT	WPP04.33000	NPW	Manual Cold Vapor	[EPA 245.1]	Mercury
Certified	Yes	UT	WPP04.35000	NPW	Digestion, ICP	[EPA 200.7]	Molybdenum
Certified	Yes	UT	WPP04.35200	NPW	ICP/MS	[EPA 200.8]	Molybdenum
Certified	Yes	UT	WPP04.37500	NPW	Digestion, ICP	[EPA 200.7]	Nickel
Certified	Yes	UT	WPP04.45500	NPW	Digestion, ICP	[EPA 200.7]	Selenium
Certified	Yes	UT	WPP04.45600	NPW	ICP/MS	[EPA 200.8]	Selenium
Certified	Yes	UT	WPP04.48000	NPW	Digestion, ICP	[EPA 200.7]	Silver
Certified	Yes	UT	WPP04.48200	NPW	ICP/MS	[EPA 200.8]	Silver
Certified	Yes	UT	WPP04.50000	NPW	Digestion, ICP	[EPA 200.7]	Thallium
Certified	Yes	UT	WPP04.50100	NPW	ICP/MS	[EPA 200.8]	Thallium
Certified	Yes	UT	WPP04.51100	NPW	Digestion, ICP	[EPA 200.7]	Tin
Certified	Yes	UT	WPP04.52050	NPW	Digestion, ICP	[EPA 200.7]	Titanium
Certified	Yes	UT	WPP04.52500	NPW	ICP/MS	[EPA 200.8]	Uranium
Certified	Yes	UT	WPP04.54000	NPW	Digestion, ICP	[EPA 200.7]	Vanadium

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225 COMMERCE DR
FORT COLLINS, CO 80524

Category: WPP04 -- Inorganic Parameters, Metals

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP04.54100	NPW	ICP/MS	[EPA 200.8]	Vanadium
Certified	Yes	UT	WPP04.56500	NPW	Digestion, ICP	[EPA 200.7]	Zinc

Category: WPP05 -- Organic Parameters, Chromatography

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP05.09010	NPW	Extract/GC (ECD)	[EPA 608]	Aldrin
Certified	Yes	UT	WPP05.09020	NPW	Extract/GC (ECD)	[EPA 608]	Alpha BHC
Certified	Yes	UT	WPP05.09030	NPW	Extract/GC (ECD)	[EPA 608]	Beta BHC
Certified	Yes	UT	WPP05.09040	NPW	Extract/GC (ECD)	[EPA 608]	Delta BHC
Certified	Yes	UT	WPP05.09050	NPW	Extract/GC (ECD)	[EPA 608]	Lindane (gamma BHC)
Certified	Yes	UT	WPP05.09060	NPW	Extract/GC (ECD)	[EPA 608]	Chlordane
Certified	Yes	UT	WPP05.09070	NPW	Extract/GC (ECD)	[EPA 608]	DDD (4,4'-)
Certified	Yes	UT	WPP05.09080	NPW	Extract/GC (ECD)	[EPA 608]	DDE (4,4'-)
Certified	Yes	UT	WPP05.09090	NPW	Extract/GC (ECD)	[EPA 608]	DDT (4,4'-)
Certified	Yes	UT	WPP05.09100	NPW	Extract/GC (ECD)	[EPA 608]	Dieldrin
Certified	Yes	UT	WPP05.09110	NPW	Extract/GC (ECD)	[EPA 608]	Endosulfan I
Certified	Yes	UT	WPP05.09120	NPW	Extract/GC (ECD)	[EPA 608]	Endosulfan II
Certified	Yes	UT	WPP05.09130	NPW	Extract/GC (ECD)	[EPA 608]	Endosulfan sulfate
Certified	Yes	UT	WPP05.09140	NPW	Extract/GC (ECD)	[EPA 608]	Endrin
Certified	Yes	UT	WPP05.09150	NPW	Extract/GC (ECD)	[EPA 608]	Endrin aldehyde
Certified	Yes	UT	WPP05.09160	NPW	Extract/GC (ECD)	[EPA 608]	Endrin ketone
Certified	Yes	UT	WPP05.09170	NPW	Extract/GC (ECD)	[EPA 608]	Heptachlor
Certified	Yes	UT	WPP05.09180	NPW	Extract/GC (ECD)	[EPA 608]	Heptachlor epoxide
Certified	Yes	UT	WPP05.09190	NPW	Extract/GC (ECD)	[EPA 608]	Methoxychlor
Certified	Yes	UT	WPP05.09200	NPW	Extract/GC (ECD)	[EPA 608]	Toxaphene
Certified	Yes	UT	WPP05.09350	NPW	Extraction, GC, ECD	[EPA 615]	D (2,4-)
Certified	Yes	UT	WPP05.09380	NPW	Extraction, GC, NPD or FPD	[EPA 615]	Dichlorprop
Certified	Yes	UT	WPP05.11010	NPW	Extract/GC (ECD)	[EPA 608]	PCB 1016
Certified	Yes	UT	WPP05.11020	NPW	Extract/GC (ECD)	[EPA 608]	PCB 1221

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Category: WPP05 -- Organic Parameters, Chromatography

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP05.11030	NPW	Extract/GC (ECD)	[EPA 608]	PCB 1232
Certified	Yes	UT	WPP05.11040	NPW	Extract/GC (ECD)	[EPA 608]	PCB 1242
Certified	Yes	UT	WPP05.11050	NPW	Extract/GC (ECD)	[EPA 608]	PCB 1248
Certified	Yes	UT	WPP05.11060	NPW	Extract/GC (ECD)	[EPA 608]	PCB 1254
Certified	Yes	UT	WPP05.11070	NPW	Extract/GC (ECD)	[EPA 608]	PCB 1260

Category: WPP06 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP06.02007	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Acrolein
Certified	Yes	UT	WPP06.02009	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Acrylonitrile
Certified	Yes	UT	WPP06.02010	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Benzene
Certified	Yes	UT	WPP06.02020	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Bromodichloromethane
Certified	Yes	UT	WPP06.02030	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Bromoform
Certified	Yes	UT	WPP06.02040	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Bromomethane
Certified	Yes	UT	WPP06.02050	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Carbon tetrachloride
Certified	Yes	UT	WPP06.02060	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Chlorobenzene
Certified	Yes	UT	WPP06.02070	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Chloroethane
Certified	Yes	UT	WPP06.02080	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Chloroethyl vinyl ether (2-)
Certified	Yes	UT	WPP06.02090	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Chloroform
Certified	Yes	UT	WPP06.02100	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Chloromethane
Certified	Yes	UT	WPP06.02107	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dibromo-3-chloropropane (1,2-)
Certified	Yes	UT	WPP06.02110	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dibromochloromethane
Certified	Yes	UT	WPP06.02115	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dibromoethane (1,2-) (EDB)
Certified	Yes	UT	WPP06.02116	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dibromomethane
Certified	Yes	UT	WPP06.02120	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichlorobenzene (1,2-)
Certified	Yes	UT	WPP06.02130	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichlorobenzene (1,3-)
Certified	Yes	UT	WPP06.02140	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichlorobenzene (1,4-)
Certified	Yes	UT	WPP06.02150	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichloroethane (1,1-)
Certified	Yes	UT	WPP06.02160	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichloroethane (1,2-)

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New Jersey Department of Environmental Protection

National Environmental Laboratory Accreditation Program

ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: WPP06 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP06.02170	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichloroethene (1,1-)
Certified	Yes	UT	WPP06.02180	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichloroethene (trans-1,2-)
Certified	Yes	UT	WPP06.02190	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichloropropane (1,2-)
Certified	Yes	UT	WPP06.02200	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichloropropene (cis-1,3-)
Certified	Yes	UT	WPP06.02210	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Dichloropropene (trans-1,3-)
Certified	Yes	UT	WPP06.02220	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Ethylbenzene
Certified	Yes	UT	WPP06.02230	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Methylene chloride (Dichloromethane)
Certified	Yes	UT	WPP06.02240	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Tetrachloroethane (1,1,2,2-)
Certified	Yes	UT	WPP06.02245	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Tetrachloroethane (1,1,1,2-)
Certified	Yes	UT	WPP06.02250	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Tetrachloroethene
Certified	Yes	UT	WPP06.02260	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Toluene
Certified	Yes	UT	WPP06.02270	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Trichloroethane (1,1,1-)
Certified	Yes	UT	WPP06.02280	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Trichloroethane (1,1,2-)
Certified	Yes	UT	WPP06.02290	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Trichloroethene
Certified	Yes	UT	WPP06.02300	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Trichlorofluoromethane
Certified	Yes	UT	WPP06.02310	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Vinyl chloride
Certified	Yes	UT	WPP06.02312	NPW	GC/MS, P & T, Capillary Column	[EPA 624]	Xylenes (total)
Certified	Yes	UT	WPP06.03010	NPW	Extract, GC/MS	[EPA 625]	Acenaphthene
Certified	Yes	UT	WPP06.03020	NPW	Extract, GC/MS	[EPA 625]	Acenaphthylene
Certified	Yes	UT	WPP06.03030	NPW	Extract, GC/MS	[EPA 625]	Anthracene
Certified	Yes	UT	WPP06.03040	NPW	Extract, GC/MS	[EPA 625]	Benzo(a)anthracene
Certified	Yes	UT	WPP06.03050	NPW	Extract, GC/MS	[EPA 625]	Benzo(b)fluoranthene
Certified	Yes	UT	WPP06.03060	NPW	Extract, GC/MS	[EPA 625]	Benzo(k)fluoranthene
Certified	Yes	UT	WPP06.03070	NPW	Extract, GC/MS	[EPA 625]	Benzo(a)pyrene
Certified	Yes	UT	WPP06.03080	NPW	Extract, GC/MS	[EPA 625]	Benzo(ghi)perylene
Certified	Yes	UT	WPP06.03090	NPW	Extract, GC/MS	[EPA 625]	Butyl benzyl phthalate
Certified	Yes	UT	WPP06.03100	NPW	Extract, GC/MS	[EPA 625]	Bis (2-chloroethyl) ether
Certified	Yes	UT	WPP06.03110	NPW	Extract, GC/MS	[EPA 625]	Bis (2-chloroethoxy) methane
Certified	Yes	UT	WPP06.03120	NPW	Extract, GC/MS	[EPA 625]	Bis (2-ethylhexyl) phthalate
Certified	Yes	UT	WPP06.03130	NPW	Extract, GC/MS	[EPA 625]	Bis (2-chloroisopropyl) ether
Certified	Yes	UT	WPP06.03140	NPW	Extract, GC/MS	[EPA 625]	Bromophenyl-phenyl ether (4-)
Certified	Yes	UT	WPP06.03150	NPW	Extract, GC/MS	[EPA 625]	Chloronaphthalene (2-)

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ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

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Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: WPP06 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP06.03160	NPW	Extract, GC/MS	[EPA 625]	Chlorophenyl-phenyl ether (4-)
Certified	Yes	UT	WPP06.03170	NPW	Extract, GC/MS	[EPA 625]	Chrysene
Certified	Yes	UT	WPP06.03180	NPW	Extract, GC/MS	[EPA 625]	Dibenzo(a,h)anthracene
Certified	Yes	UT	WPP06.03186	NPW	Extract, GC/MS	[EPA 625]	Dibenzofuran
Certified	Yes	UT	WPP06.03190	NPW	Extract, GC/MS	[EPA 625]	Di-n-butyl phthalate
Certified	No	UT	WPP06.03200	NPW	Extract, GC/MS	[USER DEFINED EPA 625]	Dichlorobenzene (1,3-)
Certified	No	UT	WPP06.03210	NPW	Extract, GC/MS	[USER DEFINED EPA 625]	Dichlorobenzene (1,2-)
Certified	No	UT	WPP06.03220	NPW	Extract, GC/MS	[USER DEFINED EPA 625]	Dichlorobenzene (1,4-)
Certified	Yes	UT	WPP06.03230	NPW	Extract, GC/MS	[EPA 625]	Dichlorobenzidine (3,3'-)
Certified	Yes	UT	WPP06.03240	NPW	Extract, GC/MS	[EPA 625]	Diethyl phthalate
Certified	Yes	UT	WPP06.03250	NPW	Extract, GC/MS	[EPA 625]	Dimethyl phthalate
Certified	Yes	UT	WPP06.03260	NPW	Extract, GC/MS	[EPA 625]	Dinitrotoluene (2,4-)
Certified	Yes	UT	WPP06.03270	NPW	Extract, GC/MS	[EPA 625]	Dinitrotoluene (2,6-)
Certified	Yes	UT	WPP06.03280	NPW	Extract, GC/MS	[EPA 625]	Di-n-octyl phthalate
Certified	Yes	UT	WPP06.03290	NPW	Extract, GC/MS	[EPA 625]	Fluoranthene
Certified	Yes	UT	WPP06.03300	NPW	Extract, GC/MS	[EPA 625]	Fluorene
Certified	Yes	UT	WPP06.03310	NPW	Extract, GC/MS	[EPA 625]	Hexachlorobenzene
Certified	Yes	UT	WPP06.03320	NPW	Extract, GC/MS	[EPA 625]	Hexachlorobutadiene (1,3-)
Certified	Yes	UT	WPP06.03330	NPW	Extract, GC/MS	[EPA 625]	Hexachloroethane
Certified	Yes	UT	WPP06.03340	NPW	Extract, GC/MS	[EPA 625]	Indeno(1,2,3-cd)pyrene
Certified	Yes	UT	WPP06.03350	NPW	Extract, GC/MS	[EPA 625]	Isophorone
Certified	Yes	UT	WPP06.03358	NPW	Extract, GC/MS	[EPA 625]	Methylnaphthalene (2-)
Certified	Yes	UT	WPP06.03360	NPW	Extract, GC/MS	[EPA 625]	Naphthalene
Certified	Yes	UT	WPP06.03366	NPW	Extract, GC/MS	[EPA 625]	Chloroaniline (4-)
Certified	Yes	UT	WPP06.03367	NPW	Extract, GC/MS	[EPA 625]	Nitroaniline (2-)
Certified	Yes	UT	WPP06.03368	NPW	Extract, GC/MS	[EPA 625]	Nitroaniline (3-)
Certified	Yes	UT	WPP06.03369	NPW	Extract, GC/MS	[EPA 625]	Nitroaniline (4-)
Certified	Yes	UT	WPP06.03370	NPW	Extract, GC/MS	[EPA 625]	Nitrobenzene
Certified	Yes	UT	WPP06.03380	NPW	Extract, GC/MS	[EPA 625]	N-Nitroso-di-n-propylamine
Certified	Yes	UT	WPP06.03390	NPW	Extract, GC/MS	[EPA 625]	Phenanthrene
Certified	Yes	UT	WPP06.03400	NPW	Extract, GC/MS	[EPA 625]	Pyrene
Certified	Yes	UT	WPP06.03410	NPW	Extract, GC/MS	[EPA 625]	Trichlorobenzene (1,2,4-)

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225 COMMERCE DR
FORT COLLINS, CO 80524

Category: WPP06 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP06.03420	NPW	Extract, GC/MS	[EPA 625]	Methyl phenol (4-chloro-3-)
Certified	Yes	UT	WPP06.03430	NPW	Extract, GC/MS	[EPA 625]	Chlorophenol (2-)
Certified	Yes	UT	WPP06.03440	NPW	Extract, GC/MS	[EPA 625]	Dichlorophenol (2,4-)
Certified	Yes	UT	WPP06.03450	NPW	Extract, GC/MS	[EPA 625]	Dimethylphenol (2,4-)
Certified	Yes	UT	WPP06.03460	NPW	Extract, GC/MS	[EPA 625]	Dinitrophenol (2,4-)
Certified	Yes	UT	WPP06.03470	NPW	Extract, GC/MS	[EPA 625]	Dinitrophenol (2-methyl-4,6-)
Certified	Yes	UT	WPP06.03480	NPW	Extract, GC/MS	[EPA 625]	Nitrophenol (2-)
Certified	Yes	UT	WPP06.03490	NPW	Extract, GC/MS	[EPA 625]	Nitrophenol (4-)
Certified	Yes	UT	WPP06.03500	NPW	Extract, GC/MS	[EPA 625]	Pentachlorophenol
Certified	Yes	UT	WPP06.03510	NPW	Extract, GC/MS	[EPA 625]	Phenol
Certified	Yes	UT	WPP06.03518	NPW	Extract, GC/MS	[EPA 625]	Trichlorophenol (2,4,5-)
Certified	Yes	UT	WPP06.03520	NPW	Extract, GC/MS	[EPA 625]	Trichlorophenol (2,4,6-)
Certified	Yes	UT	WPP06.03540	NPW	Extract, GC/MS	[EPA 625]	Methylphenol (4-)
Certified	Yes	UT	WPP06.03570	NPW	Extract, GC/MS	[EPA 625]	Aniline
Certified	Yes	UT	WPP06.03580	NPW	Extract, GC/MS	[EPA 625]	Benzidine
Certified	Yes	UT	WPP06.03590	NPW	Extract, GC/MS	[EPA 625]	Carbazole
Certified	Yes	UT	WPP06.03610	NPW	Extract, GC/MS	[EPA 625]	Methylphenol (2-)
Certified	Yes	UT	WPP06.03612	NPW	Extract, GC/MS	[EPA 625]	Methylphenol (3-)
Certified	Yes	UT	WPP06.03660	NPW	Extract, GC/MS	[EPA 625]	Hexachlorocyclopentadiene
Certified	Yes	UT	WPP06.03680	NPW	Extract, GC/MS	[EPA 625]	N-Nitrosodimethylamine
Certified	Yes	UT	WPP06.03690	NPW	Extract, GC/MS	[EPA 625]	N-Nitrosodiphenylamine

Category: WPP07 -- Organic Parameters, Individual Pesticide

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP07.23100	NPW	GC	[EPA 615]	DB (2,4-)
Certified	Yes	UT	WPP07.33000	NPW	GC	[EPA 615]	Dicamba
Certified	Yes	UT	WPP07.38200	NPW	GC	[EPA 615]	Dinoseb
Certified	Yes	UT	WPP07.60200	NPW	GC	[EPA 615]	MCPA
Certified	Yes	UT	WPP07.60210	NPW	GC	[EPA 615]	MCPP

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Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: WPP09 -- Radiochem.: Radioactivity / Radionuclide

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	WPP09.01000	NPW	Proportional or Scintillation	[EPA 900.0]	Gross - alpha
Certified	Yes	UT	WPP09.03000	NPW	Proportional Counter	[EPA 900.0]	Gross - beta
Certified	Yes	UT	WPP09.03100	NPW	Gamma Spectrometry	[EPA 901.1]	Cesium 134/137
Certified	Yes	UT	WPP09.05000	NPW	Precipitation	[EPA 903.0]	Radium - total
Certified	Yes	UT	WPP09.05010	NPW	Proportional	[EPA 903.0]	Radium - 226
Certified	Yes	UT	WPP09.06000	NPW	Radiochemical	[EPA 903.1]	Radium - 226
Certified	Yes	UT	WPP09.06020	NPW	Co-Precipitation / Beta Counting	[EPA 904.0]	Radium - 228
Certified	Yes	UT	WPP09.07000	NPW	Gamma Spectrometry	[EPA 901.1]	Photon Emitters
Certified	Yes	UT	WPP09.08000	NPW	Precipitation / Beta Counting	[DOE 1990 Sr-02]	Strontium - 89, 90
Certified	Yes	UT	WPP09.09010	NPW	Isotopic Analysis / Alpha Spectrometry	[ASTM D 3972-97]	Uranium
Certified	Yes	UT	WPP09.10000	NPW	Distillation/Liquid Scintillation	[EPA 906.0]	Tritium

Category: SHW04 -- Inorganic Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW04.05000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Aluminum
Certified	Yes	UT	SHW04.05500	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Aluminum
Certified	Yes	UT	SHW04.06500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Antimony
Certified	Yes	UT	SHW04.07000	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Antimony
Certified	Yes	UT	SHW04.09000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Arsenic
Certified	Yes	UT	SHW04.09500	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Arsenic
Certified	Yes	UT	SHW04.11500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Barium
Certified	Yes	UT	SHW04.13500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Beryllium
Certified	Yes	UT	SHW04.15100	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Boron
Certified	Yes	UT	SHW04.15500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Cadmium
Certified	Yes	UT	SHW04.16000	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Cadmium
Certified	Yes	UT	SHW04.17500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Calcium
Certified	Yes	UT	SHW04.18500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Chromium
Certified	Yes	UT	SHW04.21000	NPW, SCM	Colorimetric	[SW-846 7196A, Rev. 1, 7/92]	Chromium (VI)
Certified	Yes	UT	SHW04.22500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Cobalt

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Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW04 -- Inorganic Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW04.24500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Copper
Certified	Yes	UT	SHW04.25000	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Copper
Certified	Yes	UT	SHW04.26000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Iron
Certified	Yes	UT	SHW04.27500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Lead
Certified	Yes	UT	SHW04.28000	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Lead
Certified	Yes	UT	SHW04.29500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Lithium
Certified	Yes	UT	SHW04.30500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Magnesium
Certified	Yes	UT	SHW04.31500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Manganese
Certified	Yes	UT	SHW04.34000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Molybdenum
Certified	Yes	UT	SHW04.34005	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Molybdenum
Certified	Yes	UT	SHW04.35500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Nickel
Certified	Yes	UT	SHW04.38000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Potassium
Certified	Yes	UT	SHW04.39000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Selenium
Certified	Yes	UT	SHW04.40600	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Selenium
Certified	Yes	UT	SHW04.41000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Silver
Certified	Yes	UT	SHW04.41500	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Silver
Certified	Yes	UT	SHW04.43000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Sodium
Certified	Yes	UT	SHW04.44000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Strontium
Certified	Yes	UT	SHW04.45000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Thallium
Certified	Yes	UT	SHW04.45500	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Thallium
Certified	Yes	UT	SHW04.47100	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Tin
Certified	Yes	UT	SHW04.47145	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Titanium
Certified	Yes	UT	SHW04.47300	NPW, SCM	ICP/MS	[SW-846 6020]	Uranium
Certified	Yes	UT	SHW04.47500	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Vanadium
Certified	Yes	UT	SHW04.47505	NPW, SCM	ICP/MS	[SW-846 6020, Rev. 0, 9/94]	Vanadium
Certified	Yes	UT	SHW04.49000	NPW, SCM	ICP	[SW-846 6010B, Rev. 2, 12/96]	Zinc

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225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW05 -- Organic Parameters, Prep. / Screening

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW05.12000	NPW, SCM	Cleanup-Florisil	[SW-846 3620C]	Semivolatile organics
Certified	Yes	UT	SHW05.13000	NPW, SCM	Cleanup-Silica Gel	[SW-846 3630C]	Semivolatile organics
Certified	Yes	UT	SHW05.14000	NPW, SCM	Cleanup-Gel Permeation	[SW-846 3640A]	Semivolatile organics
Certified	Yes	UT	SHW05.16000	NPW, SCM	Cleanup-Sulfur Removal	[SW-846 3660B]	Semivolatile organics

Category: SHW06 -- Organic Parameters, Chromatography

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW06.04010	NPW, SCM	GC P&T, FID	[SW-846 8015B, Rev. 2, 12/96]	Gasoline range organic
Certified	Yes	UT	SHW06.04500	NPW, SCM	Extraction, GC, FID	[SW-846 8015B, Rev. 2, 12/96]	Diesel range organic
Certified	Yes	UT	SHW06.05010	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Benzene
Certified	Yes	UT	SHW06.05020	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Chlorobenzene
Certified	Yes	UT	SHW06.05030	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Dichlorobenzene (1,2-)
Certified	Yes	UT	SHW06.05040	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Dichlorobenzene (1,3-)
Certified	Yes	UT	SHW06.05050	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Dichlorobenzene (1,4-)
Certified	Yes	UT	SHW06.05060	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Ethylbenzene
Certified	Yes	UT	SHW06.05070	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Toluene
Certified	Yes	UT	SHW06.05080	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Xylene (o-)
Certified	Yes	UT	SHW06.05090	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Xylene (m-)
Certified	Yes	UT	SHW06.05100	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Xylene (p-)
Certified	Yes	UT	SHW06.05360	NPW, SCM	GC, Direct Injection or P & T, PID-HECD	[SW-846 8021B, Rev. 2, 12/96]	Methyl tert-butyl ether
Certified	Yes	UT	SHW06.12010	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Aldrin
Certified	Yes	UT	SHW06.12020	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Alpha BHC
Certified	Yes	UT	SHW06.12030	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Beta BHC
Certified	Yes	UT	SHW06.12040	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Delta BHC
Certified	Yes	UT	SHW06.12050	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Lindane (gamma BHC)
Certified	Yes	UT	SHW06.12070	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Chlordane (alpha)
Certified	Yes	UT	SHW06.12080	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Chlordane (gamma)
Certified	Yes	UT	SHW06.12090	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	DDD (4,4'-)
Certified	Yes	UT	SHW06.12100	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	DDE (4,4'-)

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New Jersey Department of Environmental Protection

National Environmental Laboratory Accreditation Program

ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW06 -- Organic Parameters, Chromatography

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW06.12110	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	DDT (4,4'-)
Certified	Yes	UT	SHW06.12120	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Dieldrin
Certified	Yes	UT	SHW06.12130	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Endosulfan I
Certified	Yes	UT	SHW06.12140	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Endosulfan II
Certified	Yes	UT	SHW06.12150	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Endosulfan sulfate
Certified	Yes	UT	SHW06.12160	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Endrin
Certified	Yes	UT	SHW06.12170	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Endrin aldehyde
Certified	Yes	UT	SHW06.12180	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Endrin ketone
Certified	Yes	UT	SHW06.12190	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Heptachlor
Certified	Yes	UT	SHW06.12200	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Heptachlor epoxide
Certified	Yes	UT	SHW06.12210	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Methoxychlor
Certified	Yes	UT	SHW06.12220	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8081A, Rev. 1, 12/96]	Toxaphene
Certified	Yes	UT	SHW06.13110	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8082, Rev. 0, 12/96]	PCB 1016
Certified	Yes	UT	SHW06.13120	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8082, Rev. 0, 12/96]	PCB 1221
Certified	Yes	UT	SHW06.13130	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8082, Rev. 0, 12/96]	PCB 1232
Certified	Yes	UT	SHW06.13140	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8082, Rev. 0, 12/96]	PCB 1242
Certified	Yes	UT	SHW06.13150	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8082, Rev. 0, 12/96]	PCB 1248
Certified	Yes	UT	SHW06.13160	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8082, Rev. 0, 12/96]	PCB 1254
Certified	Yes	UT	SHW06.13170	NPW, SCM	GC, Extraction, ECD or HECD, Capillary	[SW-846 8082, Rev. 0, 12/96]	PCB 1260
Certified	Yes	UT	SHW06.21010	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Azinphos methyl
Certified	Yes	UT	SHW06.21012	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Bolstar
Certified	Yes	UT	SHW06.21015	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Chloropyrifos
Certified	Yes	UT	SHW06.21017	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Coumaphos
Certified	Yes	UT	SHW06.21020	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Demeton (o-)
Certified	Yes	UT	SHW06.21030	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Demeton (s-)
Certified	Yes	UT	SHW06.21040	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Diazinon
Certified	Yes	UT	SHW06.21043	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Dichlorvos
Certified	Yes	UT	SHW06.21050	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Disulfoton
Certified	Yes	UT	SHW06.21054	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Ethoprop
Certified	Yes	UT	SHW06.21056	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Fensulfothion
Certified	Yes	UT	SHW06.21058	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Fenthion
Certified	Yes	UT	SHW06.21060	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Malathion

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ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW06 -- Organic Parameters, Chromatography

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW06.21062	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A]	Merphos
Certified	Yes	UT	SHW06.21064	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Mevinphos
Certified	Yes	UT	SHW06.21066	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Naled
Certified	Yes	UT	SHW06.21080	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Parathion methyl
Certified	Yes	UT	SHW06.21085	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Phorate
Certified	Yes	UT	SHW06.21090	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Ronnel
Certified	Yes	UT	SHW06.21095	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Stirofos
Certified	Yes	UT	SHW06.21108	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Tokuthion [Protothiofos]
Certified	Yes	UT	SHW06.21112	NPW, SCM	GC, Extract or Dir Inj, NPD or FPD,Cap	[SW-846 8141A, Rev. 1, 9/94]	Trichloronate
Certified	Yes	UT	SHW06.23010	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	Dalapon
Certified	Yes	UT	SHW06.23020	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	Dicamba
Certified	Yes	UT	SHW06.23021	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	Dichlorprop
Certified	Yes	UT	SHW06.23030	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	Dinoseb
Certified	Yes	UT	SHW06.23040	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	D (2,4-)
Certified	Yes	UT	SHW06.23041	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	DB (2,4-)
Certified	Yes	UT	SHW06.23050	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	T (2,4,5-)
Certified	Yes	UT	SHW06.23060	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	TP (2,4,5-) (Silvex)
Certified	Yes	UT	SHW06.23063	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	MCPA
Certified	Yes	UT	SHW06.23064	NPW, SCM	GC, Extraction, ECD, Capillary	[SW-846 8151A, Rev. 1, 9/96]	MCPP
Certified	Yes	UT	SHW06.28010	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	HMX
Certified	Yes	UT	SHW06.28020	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	RDX
Certified	Yes	UT	SHW06.28030	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Trinitrobenzene (1,3,5-)
Certified	Yes	UT	SHW06.28040	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Dinitrobenzene (1,3-)
Certified	Yes	UT	SHW06.28045	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	PETN
Certified	Yes	UT	SHW06.28050	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Tetryl
Certified	Yes	UT	SHW06.28060	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Nitrobenzene
Certified	Yes	UT	SHW06.28070	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Trinitrotoluene (2,4,6-)
Certified	Yes	UT	SHW06.28080	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Dinitrotoluene (4-amino-2,6-)
Certified	Yes	UT	SHW06.28090	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Dinitrotoluene (2-amino-4,6-)
Certified	Yes	UT	SHW06.28100	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Dinitrotoluene (2,4-)
Certified	Yes	UT	SHW06.28110	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Dinitrotoluene (2,6-)
Certified	Yes	UT	SHW06.28120	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Nitrotoluene (2-)

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ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW06 -- Organic Parameters, Chromatography

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW06.28130	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Nitrotoluene (3-)
Certified	Yes	UT	SHW06.28140	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Nitrotoluene (4-)
Certified	Yes	UT	SHW06.29100	NPW, SCM	HPLC, UV Detector	[SW-846 8330, Rev. 0, 9/94]	Nitroglycerine

Category: SHW07 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW07.04010	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Benzene
Certified	Yes	UT	SHW07.04011	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Bromobenzene
Certified	Yes	UT	SHW07.04012	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Butyl benzene (n-)
Certified	Yes	UT	SHW07.04013	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Sec-butylbenzene
Certified	Yes	UT	SHW07.04014	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Tert-butylbenzene
Certified	Yes	UT	SHW07.04020	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Chlorobenzene
Certified	Yes	UT	SHW07.04022	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Chlorotoluene (2-)
Certified	Yes	UT	SHW07.04023	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Chlorotoluene (4-)
Certified	Yes	UT	SHW07.04030	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichlorobenzene (1,2-)
Certified	Yes	UT	SHW07.04040	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichlorobenzene (1,3-)
Certified	Yes	UT	SHW07.04050	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichlorobenzene (1,4-)
Certified	Yes	UT	SHW07.04060	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Ethylbenzene
Certified	Yes	UT	SHW07.04065	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Isopropylbenzene
Certified	Yes	UT	SHW07.04067	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Propylbenzene (n-)
Certified	Yes	UT	SHW07.04070	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Toluene
Certified	Yes	UT	SHW07.04071	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B]	Isopropyltoluene (4-)
Certified	Yes	UT	SHW07.04072	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trichlorobenzene (1,2,3-)
Certified	Yes	UT	SHW07.04073	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trimethylbenzene (1,2,4-)
Certified	Yes	UT	SHW07.04074	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trimethylbenzene (1,3,5-)
Certified	Yes	UT	SHW07.04080	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Xylenes (total)
Certified	Yes	UT	SHW07.04081	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Xylene (m-)
Certified	Yes	UT	SHW07.04082	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Xylene (o-)
Certified	Yes	UT	SHW07.04083	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Xylene (p-)

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New Jersey Department of Environmental Protection

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ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW07 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW07.04089	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Bromochloromethane
Certified	Yes	UT	SHW07.04090	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Bromodichloromethane
Certified	Yes	UT	SHW07.04100	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Bromoform
Certified	Yes	UT	SHW07.04110	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Bromomethane
Certified	Yes	UT	SHW07.04120	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Carbon tetrachloride
Certified	Yes	UT	SHW07.04130	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Chloroethane
Certified	Yes	UT	SHW07.04140	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Chloroethyl vinyl ether (2-)
Certified	Yes	UT	SHW07.04150	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Chloroform
Certified	Yes	UT	SHW07.04160	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Chloromethane
Certified	Yes	UT	SHW07.04170	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloropropene (trans-1,3-)
Certified	Yes	UT	SHW07.04180	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dibromochloromethane
Certified	Yes	UT	SHW07.04185	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dibromoethane (1,2-) (EDB)
Certified	Yes	UT	SHW07.04186	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dibromomethane
Certified	Yes	UT	SHW07.04187	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dibromo-3-chloropropane (1,2-)
Certified	Yes	UT	SHW07.04190	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichlorodifluoromethane
Certified	Yes	UT	SHW07.04200	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloroethane (1,1-)
Certified	Yes	UT	SHW07.04210	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloroethane (1,2-)
Certified	Yes	UT	SHW07.04220	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloroethene (1,1-)
Certified	Yes	UT	SHW07.04230	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloroethene (trans-1,2-)
Certified	Yes	UT	SHW07.04235	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloroethene (cis-1,2-)
Certified	Yes	UT	SHW07.04240	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloropropane (1,2-)
Certified	Yes	UT	SHW07.04241	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloropropane (1,3-)
Certified	Yes	UT	SHW07.04242	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloropropane (2,2-)
Certified	Yes	UT	SHW07.04249	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloropropene (1,1-)
Certified	Yes	UT	SHW07.04250	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Dichloropropene (cis-1,3-)
Certified	Yes	UT	SHW07.04259	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B]	Ethanol
Certified	Yes	UT	SHW07.04260	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Methylene chloride (Dichloromethane)
Certified	Yes	UT	SHW07.04270	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Tetrachloroethane (1,1,2,2-)
Certified	Yes	UT	SHW07.04280	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Tetrachloroethene
Certified	Yes	UT	SHW07.04290	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trichloroethane (1,1,1-)
Certified	Yes	UT	SHW07.04300	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trichloroethane (1,1,2-)
Certified	Yes	UT	SHW07.04310	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trichloroethene

KEY: AE = Air and Emissions, BT = Biological Tissues, DW = Drinking Water, NPW = Non-Potable Water, SCM = Solid and Chemical Materials

New Jersey Department of Environmental Protection

National Environmental Laboratory Accreditation Program

ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW07 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW07.04320	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trichlorofluoromethane
Certified	Yes	UT	SHW07.04325	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trichloropropane (1,2,3-)
Certified	Yes	UT	SHW07.04327	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Vinyl acetate
Certified	Yes	UT	SHW07.04330	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Vinyl chloride
Certified	Yes	UT	SHW07.04340	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Acetone
Certified	Yes	UT	SHW07.04350	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Carbon disulfide
Certified	Yes	UT	SHW07.04360	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Butanone (2-)
Certified	Yes	UT	SHW07.04370	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Hexanone (2-)
Certified	Yes	UT	SHW07.04375	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Methyl iodide
Certified	Yes	UT	SHW07.04380	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Pentanone (4-methyl-2-)
Certified	Yes	UT	SHW07.04390	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Methyl tert-butyl ether
Certified	Yes	UT	SHW07.04398	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Acetonitrile
Certified	Yes	UT	SHW07.04400	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Acrolein
Certified	Yes	UT	SHW07.04410	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Acrylonitrile
Certified	Yes	UT	SHW07.04500	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Hexachlorobutadiene (1,3-)
Certified	Yes	UT	SHW07.04540	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Naphthalene
Certified	Yes	UT	SHW07.04550	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Styrene
Certified	Yes	UT	SHW07.04560	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Tetrachloroethane (1,1,1,2-)
Certified	Yes	UT	SHW07.04570	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B, Rev. 2, 12/96]	Trichlorobenzene (1,2,4-)
Certified	Yes	UT	SHW07.04590	NPW, SCM	GC/MS, P & T or Direct Injection, Capillary	[SW-846 8260B]	Dioxane (1,4-)
Applied	No	UT	SHW07.04710	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Chloronaphthalene (1-)
Certified	Yes	UT	SHW07.04980	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Tetrachlorophenol (2,3,4,6-)
Certified	Yes	UT	SHW07.05005	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	N-Nitrosodimethylamine
Certified	Yes	UT	SHW07.05006	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	N-Nitroso-di-n-propylamine
Certified	Yes	UT	SHW07.05010	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	N-Nitrosodiphenylamine
Certified	Yes	UT	SHW07.05030	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Carbazole
Applied	No	UT	SHW07.05038	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzidine
Certified	Yes	UT	SHW07.05040	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dichlorobenzidine (3,3'-)
Certified	Yes	UT	SHW07.05048	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Aniline
Certified	Yes	UT	SHW07.05050	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Chloraniline (4-)
Certified	Yes	UT	SHW07.05060	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Nitroaniline (2-)
Certified	Yes	UT	SHW07.05062	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Nitroaniline (3-)

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ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW07 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW07.05063	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Nitroaniline (4-)
Certified	Yes	UT	SHW07.05070	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Chloronaphthalene (2-)
Certified	Yes	UT	SHW07.05080	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Hexachlorobenzene
Certified	Yes	UT	SHW07.05090	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Hexachlorobutadiene (1,3-)
Certified	Yes	UT	SHW07.05100	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Hexachlorocyclopentadiene
Certified	Yes	UT	SHW07.05110	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Hexachloroethane
Certified	Yes	UT	SHW07.05120	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Trichlorobenzene (1,2,4-)
Certified	Yes	UT	SHW07.05130	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Bis (2-chloroethoxy) methane
Certified	Yes	UT	SHW07.05132	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Bis (2-chloroethyl) ether
Certified	Yes	UT	SHW07.05140	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Bis (2-chloroisopropyl) ether
Certified	Yes	UT	SHW07.05150	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Chlorophenyl-phenyl ether (4-)
Certified	Yes	UT	SHW07.05160	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Bromophenyl-phenyl ether (4-)
Certified	Yes	UT	SHW07.05170	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dinitrotoluene (2,4-)
Certified	Yes	UT	SHW07.05180	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dinitrotoluene (2,6-)
Certified	Yes	UT	SHW07.05190	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Isophorone
Certified	Yes	UT	SHW07.05200	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Nitrobenzene
Certified	Yes	UT	SHW07.05210	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Butyl benzyl phthalate
Certified	Yes	UT	SHW07.05220	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Bis (2-ethylhexyl) phthalate
Certified	Yes	UT	SHW07.05230	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Diethyl phthalate
Certified	Yes	UT	SHW07.05240	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dimethyl phthalate
Certified	Yes	UT	SHW07.05250	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Di-n-butyl phthalate
Certified	Yes	UT	SHW07.05260	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Di-n-octyl phthalate
Certified	Yes	UT	SHW07.05270	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Acenaphthene
Certified	Yes	UT	SHW07.05280	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Anthracene
Certified	Yes	UT	SHW07.05290	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Acenaphthylene
Certified	Yes	UT	SHW07.05300	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzo(a)anthracene
Certified	Yes	UT	SHW07.05310	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzo(a)pyrene
Certified	Yes	UT	SHW07.05320	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzo(b)fluoranthene
Certified	Yes	UT	SHW07.05330	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzo(ghi)perylene
Certified	Yes	UT	SHW07.05340	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzo(k)fluoranthene
Certified	Yes	UT	SHW07.05350	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Chrysene
Certified	Yes	UT	SHW07.05360	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dibenzo(a,h)anthracene

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National Environmental Laboratory Accreditation Program

ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW07 -- Organic Parameters, Chromatography/MS

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW07.05370	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Fluoranthene
Certified	Yes	UT	SHW07.05380	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Fluorene
Certified	Yes	UT	SHW07.05390	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Indeno(1,2,3-cd)pyrene
Certified	Yes	UT	SHW07.05400	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Methylnaphthalene (2-)
Certified	Yes	UT	SHW07.05410	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Naphthalene
Certified	Yes	UT	SHW07.05420	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Phenanthrene
Certified	Yes	UT	SHW07.05430	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Pyrene
Certified	Yes	UT	SHW07.05440	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Methyl phenol (4-chloro-3-)
Certified	Yes	UT	SHW07.05450	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Chlorophenol (2-)
Certified	Yes	UT	SHW07.05460	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dichlorophenol (2,4-)
Certified	Yes	UT	SHW07.05470	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dimethylphenol (2,4-)
Certified	Yes	UT	SHW07.05480	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dinitrophenol (2,4-)
Certified	Yes	UT	SHW07.05490	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dinitrophenol (2-methyl-4,6-)
Certified	Yes	UT	SHW07.05500	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Methylphenol (2-)
Certified	Yes	UT	SHW07.05510	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Methylphenol (4-)
Certified	Yes	UT	SHW07.05520	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Nitrophenol (2-)
Certified	Yes	UT	SHW07.05530	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Nitrophenol (4-)
Certified	Yes	UT	SHW07.05540	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Pentachlorophenol
Certified	Yes	UT	SHW07.05550	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Phenol
Certified	Yes	UT	SHW07.05560	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Trichlorophenol (2,4,5-)
Certified	Yes	UT	SHW07.05570	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Trichlorophenol (2,4,6-)
Certified	Yes	UT	SHW07.05590	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Methylphenol (3-)
Certified	Yes	UT	SHW07.05600	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dibenzofuran
Certified	Yes	UT	SHW07.05691	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dichlorobenzene (1,2-)
Certified	Yes	UT	SHW07.05692	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dichlorobenzene (1,3-)
Certified	Yes	UT	SHW07.05700	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Dichlorobenzene (1,4-)
Certified	Yes	UT	SHW07.05710	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzoic acid
Certified	Yes	UT	SHW07.05720	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Benzyl alcohol
Certified	Yes	UT	SHW07.05750	NPW, SCM	GC/MS, Extract or Dir Inj, Capillary	[SW-846 8270C, Rev. 3, 12/96]	Pyridine

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ANNUAL CERTIFIED PARAMETER LIST AND CURRENT STATUS

Effective as of 07/29/2008 until 06/30/2009

Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW09 -- Miscellaneous Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW09.02000	NPW, SCM	Distillation	[SW-846 9010B, Rev. 2, 12/96]	Cyanide
Applied	No	UT	SHW09.03000	NPW, SCM	Distillation	[SW-846 9010B, Rev. 2, 12/96]	Cyanide - amenable to Cl2
Certified	No	UT	SHW09.05000	NPW, SCM	Colorimetric, Automated	[SW-846 9012B]	Cyanide
Certified	Yes	UT	SHW09.13050	NPW, SCM	Ion Chromatography	[SW-846 9056, Rev. 0, 9/94]	Sulfate
Certified	Yes	UT	SHW09.29150	NPW, SCM	Ion Chromatography	[SW-846 9056, Rev. 0, 12/94]	Nitrite
Certified	Yes	UT	SHW09.30150	NPW, SCM	Ion Chromatography	[SW-846 9056, Rev. 0, 12/94]	Nitrate
Certified	Yes	UT	SHW09.30250	NPW, SCM	Ion Chromatography	[SW-846 9056, Rev. 0, 12/96]	Bromide
Certified	Yes	UT	SHW09.33100	NPW, SCM	Ion Chromatography	[SW-846 9056, Rev. 0, 12/96]	Chloride
Certified	Yes	UT	SHW09.34150	NPW, SCM	Ion Chromatography	[SW-846 9056, Rev. 0, 12/96]	Fluoride
Certified	Yes	UT	SHW09.54150	NPW, SCM	Ion Chromatography	[SW-846 9056, Rev. 0, 12/94]	Orthophosphate
Certified	Yes	UT	SHW09.60000	NPW, SCM	Proportional Counter	[SW-846 9310, Rev. 0, 9/86]	Gross - alpha-beta
Certified	Yes	UT	SHW09.60100	NPW, SCM	Precipitation	[SW-846 9315, Rev. 0, 9/86]	Alpha Emitting Radium Isotopes
Certified	Yes	UT	SHW09.60110	NPW, SCM	Precipitation	[SW-846 9320, Rev. 0, 9/86]	Radium - 228

Category: SHW02 -- Characteristics of Hazardous Waste

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW02.06900	SCM	TCLP, Toxicity Procedure, ZHE	[SW-846 1311]	Volatile organics
Certified	Yes	UT	SHW02.07000	SCM	TCLP, Toxicity Procedure, Shaker	[SW-846 1311]	Metals - semi volatile organics
Certified	Yes	UT	SHW02.08000	SCM	Synthetic PPT Leachate Procedure	[SW-846 1312]	Metals - organics

Category: SHW04 -- Inorganic Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW04.03000	SCM	Acid Digestion, Soil Sediment & Sludge	[SW-846 3050B, Rev. 2, 12/96]	Metals
Certified	Yes	UT	SHW04.03700	SCM	Chromium VI Digestion	[SW-846 3060A, Rev. 1, 12/96]	Metals
Certified	Yes	UT	SHW04.33500	SCM	AA, Manual Cold Vapor	[SW-846 7471A, Rev. 1, 9/94]	Mercury - solid waste

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Laboratory Name: PARAGON ANALYTICS Laboratory Number: CO003 Activity ID: NLC080002
225 COMMERCE DR
FORT COLLINS, CO 80524

Category: SHW05 -- Organic Parameters, Prep. / Screening

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW05.03000	SCM	Soxhlet Extraction	[SW-846 3540C, Rev. 3, 12/96]	Semivolatile organics
Certified	Yes	UT	SHW05.06000	SCM	Waste Dilution	[SW-846 3580A, Rev. 1, 7/92]	Organics
Certified	Yes	UT	SHW05.07300	SCM	Closed System Purge & Trap	[SW-846 5035L, Rev. 0, 12/96]	Volatile organics - low conc.

Category: SHW09 -- Miscellaneous Parameters

Status	Eligible to Report NJ Data	State	Code	Matrix	Technique Description	Approved Method	Parameter Description
Certified	Yes	UT	SHW09.04000	SCM	Extraction, Oils and Solids	[SW-846 9013, Rev. 0, 7/92]	Cyanide
Certified	Yes	UT	SHW09.04100	SCM	Titrimetric/Manual Spectrophotometric	[SW-846 9014, Rev. 0, 12/96]	Cyanide
Certified	Yes	UT	SHW09.16000	SCM	Mix with Water or Calcium Chloride	[SW-846 9045C, Rev. 3, 1/95]	pH - soil and waste
Certified	Yes	UT	SHW09.25000	SCM	Extraction & Gravimetric	[SW-846 9071 B, Rev. 2, 5/99]	Oil & grease - sludge-hem
Certified	Yes	UT	SHW09.29000	SCM	Flow-Through Paint Filter, Observation	[SW-846 9095]	Free liquid

Joseph F. Aiello, Chief

KEY: AE = Air and Emissions, BT = Biological Tissues, DW = Drinking Water, NPW = Non-Potable Water, SCM = Solid and Chemical Materials

State of New Jersey
Department of Environmental Protection

Certifies That

Paragon Analytics

Laboratory Certification ID # CO003

having duly met the requirements of the

Regulations Governing The Certification Of
Laboratories And Environmental Measurements N.J.A.C. 7:18 et. seq.

and

having been found compliant with the standard approved by the

National Environmental Laboratory Accreditation Conference

is hereby approved as a

Nationally Accredited Environmental Laboratory

to perform the analyses as indicated on the Annual Certified Parameter List
which must accompany this certificate to be valid

Expiration Date June 30, 2009

NJDEP is a NELAP Recognized Accrediting Authority

Joseph F. Aiello, Chief
Office of Quality Assurance

THIS CERTIFICATE IS TO BE CONSPICUOUSLY DISPLAYED AT THE LABORATORY WITH THE ANNUAL CERTIFIED PARAMETER LIST IN A LOCATION ON THE PREMISES VISIBLE TO THE PUBLIC

ndep
NEVADA DIVISION OF ENVIRONMENTAL PROTECTION
protecting the future for generations

STATE OF NEVADA

Department of Conservation & Natural Resources
DIVISION OF ENVIRONMENTAL PROTECTION

Jim Gibbons, Governor
Allen Biaggi, Director
Leo M. Drozdoff, P.E., Administrator

July 31, 2008

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

RE: Nevada Environmental Laboratory Certification Extension.

Dear Paragon Analytics:

Your 2006-2007 Nevada scope (including any approved additions) has been **extended** until July 31, 2009.

This will serve as notice to you and your clients.

We are still processing 2007-2008 applications. We will be processing your 2007-2008 and 2008-2009 applications simultaneously. Your patience is appreciated.

If you or your clients have any questions please contact Donald LaFara at 775-687-9491.

Sincerely,

Don LaFara

Donald LaFara, Program Manager
Environmental Laboratory Services

ndep
NEVADA DIVISION OF ENVIRONMENTAL PROTECTION
protecting the future for generations

STATE OF NEVADA
Department of Conservation & Natural Resources
DIVISION OF ENVIRONMENTAL PROTECTION

Jim Gibbons, Governor
Allen Biaggi, Director
Leo M. Drozdoff, P.E., Administrator

July 31, 2007

PARAGON ANALYTICS
225 COMMERCE DR
FORT COLLINS CO 80524

RE: Environmental Laboratory Certification Extension.

Dear PARAGON ANALYTICS:

Your laboratory is paid in full for the FY07 (August 1, 2006-July 31, 2007) and your certification has been **extended**.

Either your FY06 (August 1, 2005-July 31, 2006) scope or your FY07 (August 1, 2006-July 31, 2007) scope is in effect until receipt of your FY08 (August 1, 2007-July 31, 2008) scope and certificate from the State of Nevada; Department of Conservation and Natural Resources; Division of Environmental Protection.. However, your continued certification is dependent on receipt of your FY08 application.

This will serve as notice to you and your clients.

If you or your clients have any questions please contact Donald LaFara at 775-687-9491.

Sincerely,

Don LaFara

Donald LaFara, Program Manager
Environmental Laboratory Services

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***SDWA (potable)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Demands**				
SM 5310C 18th,19th & 20th	Total Organic Carbon	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Metals**				
EPA 200.7	Aluminum	8/1/2006	7/31/2007	Certified
EPA 200.7	Barium	8/1/2006	7/31/2007	Certified
EPA 200.7	Beryllium	8/1/2006	7/31/2007	Certified
EPA 200.7	Boron	8/1/2006	7/31/2007	Certified
EPA 200.7	Cadmium	8/1/2005	7/31/2007	Certified
EPA 200.7	Calcium	8/1/2006	7/31/2007	Certified
EPA 200.7	Chromium	8/1/2006	7/31/2007	Certified
EPA 200.7	Copper	8/1/2005	7/31/2007	Certified
EPA 200.7	Iron	8/1/2006	7/31/2007	Certified
EPA 200.7	Magnesium	8/1/2006	7/31/2007	Certified
EPA 200.7	Manganese	8/1/2006	7/31/2007	Certified
EPA 200.7	Nickel	8/1/2006	7/31/2007	Certified
EPA 200.7	Silver	8/1/2005	7/31/2007	Certified
EPA 200.7	Sodium	8/1/2006	7/31/2007	Certified
EPA 200.7	Vanadium	8/1/2005	7/31/2007	Certified
EPA 200.7	Zinc	8/1/2005	7/31/2007	Certified
EPA 200.7*	Lithium	8/1/2006	7/31/2007	Nevada Approved
EPA 200.7*	Molybdenum	8/1/2006	7/31/2007	Certified
EPA 200.7*	Potassium	8/1/2005	7/31/2007	Certified
EPA 200.8	Aluminum	8/1/2005	7/31/2007	Certified

Disclaimer: A laboratory that is certified or approved has established that they have the ability to implement a quality control program in accordance with the appropriate Federal or State regulations or statutes. It is the certified laboratory's responsibility to provide the client with their current certified parameter list. Contact ELS to verify certification status. *Not for compliance purposes.

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***SDWA (potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 200.8	Antimony	8/1/2005	7/31/2007	Certified
EPA 200.8	Arsenic	8/1/2005	7/31/2007	Certified
EPA 200.8	Cadmium	8/1/2005	7/31/2007	Certified
EPA 200.8	Copper	8/1/2005	7/31/2007	Certified
EPA 200.8	Lead	8/1/2005	7/31/2007	Certified
EPA 200.8	Molybdenum	8/1/2005	7/31/2007	Certified
EPA 200.8	Selenium	8/1/2005	7/31/2007	Certified
EPA 200.8	Silver	8/1/2005	7/31/2007	Certified
EPA 200.8	Thallium	8/1/2005	7/31/2007	Certified
EPA 245.1	Mercury	8/1/2005	7/31/2007	Certified
Discipline/Category: **Chemistry/Minerals**				
EPA 300.0	Chloride	8/1/2006	7/31/2007	Certified
EPA 300.0	Fluoride	8/1/2006	7/31/2007	Certified
EPA 300.0	Sulfate	8/1/2006	7/31/2007	Certified
SM 2320B 18th,19th & 20th	Alkalinity	8/1/2006	7/31/2007	Certified
SM 2340B 18th,19th & 20th	Calcium Hardness as CaCO3	8/1/2006	7/31/2007	Nevada Approved
SM 2510B 18th,19th & 20th	Conductivity	8/1/2006	7/31/2007	Certified
SM 2540C 18th,19th & 20th	Residue Filterable (TDS)	8/1/2006	7/31/2007	Nevada Approved
SM 4500-F C 18th,19th & 20th	Fluoride	8/1/2006	7/31/2007	Certified
SM 4500-S2 F	Sulfide	8/1/2006	7/31/2007	Nevada Approved
Discipline/Category: **Chemistry/Miscellaneous**				
EPA 150.1	pH (Hydrogen ion)	8/1/2006	7/31/2007	Certified
EPA 200.7*	Silica as SiO2	8/1/2005	7/31/2007	Certified

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State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***SDWA (potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 300.0	Bromide	8/1/2006	7/31/2007	Certified
EPA 314.0	Perchlorate	8/1/2005	7/31/2007	Certified
SM 4500-H+ B 18th,19th & 20th	pH (Hydrogen ion)	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Nutrients**				
EPA 300.0	Nitrate-N	8/1/2006	7/31/2007	Certified
EPA 300.0	Nitrite-N	8/1/2006	7/31/2007	Certified
EPA 300.0	Ortho-phosphate as P	8/1/2006	7/31/2007	Certified
SM 4500-NO2 B 18th,19th & 20th	Nitrite-N	8/1/2006	7/31/2007	Certified
SM 4500-P E	Ortho-phosphate as P	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Radiochemistry**				
ASTM D3972	Uranium	8/1/2005	7/31/2007	Certified
EPA 200.8	Uranium	8/1/2005	7/31/2007	Certified
Discipline/Category: **RadioChemistry/Radiochemistry**				
DOE Sr-01	Strontium 89, 90	8/1/2006	7/31/2007	Nevada Approved
DOE Sr-02	Strontium-90	8/1/2006	7/31/2007	Certified
DOE U-02	Uranium	8/1/2006	7/31/2007	Certified
EPA 900.0	Gross Alpha	8/1/2005	7/31/2007	Certified
EPA 900.0	Gross Beta	8/1/2005	7/31/2007	Certified
EPA 901.1	Cesium 134	8/1/2005	7/31/2007	Certified
EPA 901.1	Cesium 137	8/1/2006	7/31/2007	Certified
EPA 901.1	Gamma Emitters	8/1/2006	7/31/2007	Certified
EPA 903.0	Radium-226	8/1/2005	7/31/2007	Certified
EPA 903.1	Radium-226	8/1/2006	7/31/2007	Certified

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State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

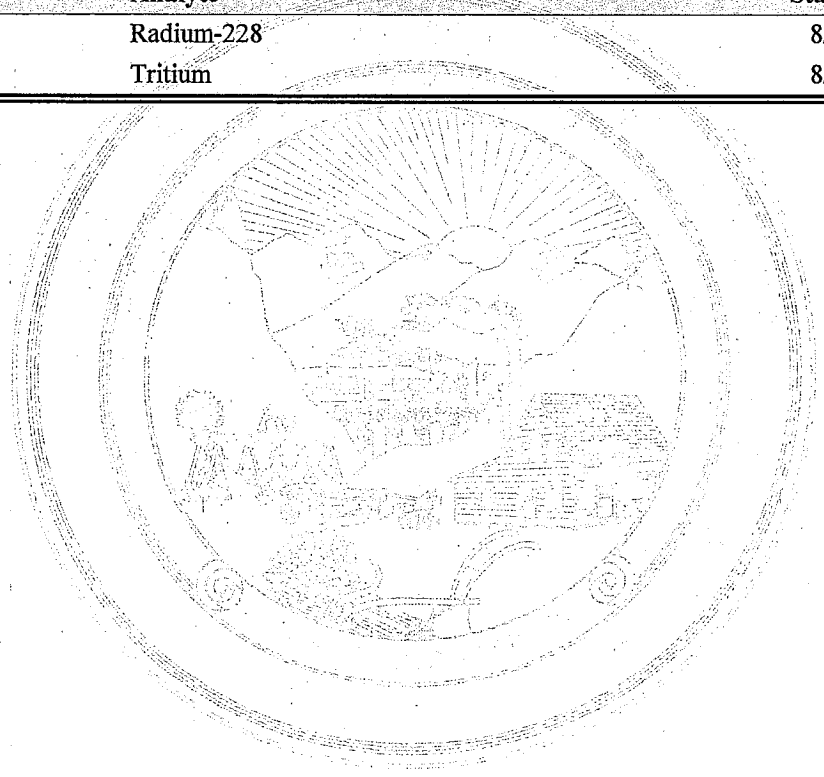
EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***SDWA (potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 904.0	Radium-228	8/1/2006	7/31/2007	Certified
EPA 906.0	Tritium	8/1/2005	7/31/2007	Certified



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State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Demands**				
EPA 415.1	Total Organic Carbon	8/1/2006	7/31/2007	Certified
SM 5310C	Total Organic Carbon	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Herbicides**				
EPA 615	2,4,5-T	8/1/2006	7/31/2007	Certified
EPA 615	2,4,5-TP (Silvex)	8/1/2006	7/31/2007	Certified
EPA 615	2,4-D	8/1/2006	7/31/2007	Certified
EPA 615	2,4-DB	8/1/2006	7/31/2007	Certified
EPA 615	Dicamba	8/1/2006	7/31/2007	Certified
EPA 615	Dichloroprop	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Metals**				
EPA 200.7	Aluminum	8/1/2006	7/31/2007	Certified
EPA 200.7	Antimony	8/1/2006	7/31/2007	Certified
EPA 200.7	Arsenic	8/1/2006	7/31/2007	Certified
EPA 200.7	Barium	8/1/2006	7/31/2007	Certified
EPA 200.7	Beryllium	8/1/2006	7/31/2007	Certified
EPA 200.7	Boron	8/1/2006	7/31/2007	Certified
EPA 200.7	Cadmium	8/1/2006	7/31/2007	Certified
EPA 200.7	Calcium	8/1/2006	7/31/2007	Certified
EPA 200.7	Chromium	8/1/2006	7/31/2007	Certified
EPA 200.7	Cobalt	8/1/2006	7/31/2007	Certified
EPA 200.7	Copper	8/1/2006	7/31/2007	Certified
EPA 200.7	Iron	8/1/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 200.7	Lead	8/1/2006	7/31/2007	Certified
EPA 200.7	Magnesium	8/1/2006	7/31/2007	Certified
EPA 200.7	Manganese	8/1/2006	7/31/2007	Certified
EPA 200.7	Molybdenum	8/1/2006	7/31/2007	Certified
EPA 200.7	Nickel	8/1/2006	7/31/2007	Certified
EPA 200.7	Potassium	8/1/2006	7/31/2007	Certified
EPA 200.7	Selenium	8/1/2006	7/31/2007	Certified
EPA 200.7	Silver	8/1/2006	7/31/2007	Certified
EPA 200.7	Sodium	8/1/2006	7/31/2007	Certified
EPA 200.7	Strontium	8/1/2006	7/31/2007	Certified
EPA 200.7	Thallium	8/1/2006	7/31/2007	Certified
EPA 200.7	Tin	8/1/2006	7/31/2007	Certified
EPA 200.7	Titanium	8/1/2006	7/31/2007	Certified
EPA 200.7	Vanadium	8/1/2006	7/31/2007	Certified
EPA 200.7	Zinc	8/1/2006	7/31/2007	Certified
EPA 200.8	Aluminum	8/1/2006	7/31/2007	Certified
EPA 200.8	Antimony	8/1/2006	7/31/2007	Certified
EPA 200.8	Arsenic	8/1/2006	7/31/2007	Certified
EPA 200.8	Cadmium	8/1/2006	7/31/2007	Certified
EPA 200.8	Copper	8/1/2006	7/31/2007	Certified
EPA 200.8	Lead	8/1/2006	7/31/2007	Certified
EPA 200.8	Molybdenum	8/1/2006	7/31/2007	Certified
EPA 200.8	Selenium	8/1/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 200.8	Thallium	8/1/2006	7/31/2007	Certified
EPA 245.1	Mercury	8/1/2006	7/31/2007	Certified
SM 3500-Cr D 18th & 19th	Hexavalent Chromium (Cr-VI)	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Minerals**				
EPA 120.1	Conductivity	8/1/2006	7/31/2007	Certified
EPA 160.1	Residue Filterable (TDS)	8/1/2006	7/31/2007	Certified
EPA 300.0	Chloride	8/1/2006	7/31/2007	Certified
EPA 300.0	Fluoride	8/1/2006	7/31/2007	Certified
EPA 300.0	Sulfate	8/1/2006	7/31/2007	Certified
EPA 310.1	Alkalinity	8/1/2006	7/31/2007	Certified
EPA 325.3	Chloride	8/1/2006	7/31/2007	Certified
EPA 340.2	Fluoride	8/1/2006	7/31/2007	Certified
EPA 376.1	Sulfide	8/1/2006	7/31/2007	Certified
SM 2510B	Conductivity	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Miscellaneous**				
EPA 150.1	pH (Hydrogen ion)	8/1/2006	7/31/2007	Certified
EPA 200.7	Silica as SiO2	8/1/2006	7/31/2007	Certified
EPA 300.0	Bromide	8/1/2006	7/31/2007	Certified
EPA 335.2	Cyanide, Total	8/1/2006	7/31/2007	Certified
SM 2340B	Hardness (calculation)	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Nutrients**				
EPA 300.0	Nitrate-N	8/1/2006	7/31/2007	Certified
EPA 300.0	Nitrite-N	8/1/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 300.0	Ortho-phosphate as P	8/1/2006	7/31/2007	Certified
EPA 350.1	Ammonia as N	8/1/2006	7/31/2007	Certified
EPA 353.2	Nitrate-Nitrite as N	8/1/2006	7/31/2007	Certified
EPA 354.1	Nitrite-N	8/1/2006	7/31/2007	Certified
EPA 365.2	Ortho-phosphate as P	8/1/2006	7/31/2007	Certified
EPA 365.2	Phosphorus, Total	8/1/2006	7/31/2007	Certified
SM 4500-NH3 H 18th	Ammonia as N	8/1/2006	7/31/2007	Certified
SM 4500-NO2 B 18th,19th & 20th	Nitrite-N	8/1/2006	7/31/2007	Certified
SM 4500-P E	Ortho-phosphate as P	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/PCBs as aroclors**				
EPA 608	Aroclor 1016	8/1/2006	7/31/2007	Certified
EPA 608	Aroclor 1221	8/1/2006	7/31/2007	Certified
EPA 608	Aroclor 1232	8/1/2006	7/31/2007	Certified
EPA 608	Aroclor 1242	8/1/2006	7/31/2007	Certified
EPA 608	Aroclor 1248	8/1/2006	7/31/2007	Certified
EPA 608	Aroclor 1254	8/1/2006	7/31/2007	Certified
EPA 608	Aroclor 1260	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Pesticides**				
EPA 608	4,4'-DDD	8/1/2006	7/31/2007	Certified
EPA 608	4,4'-DDE	8/1/2006	7/31/2007	Certified
EPA 608	4,4'-DDT	8/1/2006	7/31/2007	Certified
EPA 608	Aldrin	8/1/2006	7/31/2007	Certified
EPA 608	alpha-BHC	8/1/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 608	beta-BHC	8/1/2006	7/31/2007	Certified
EPA 608	Chlordane (total)	8/1/2006	7/31/2007	Certified
EPA 608	Chlordane, technical	8/1/2006	7/31/2007	Certified
EPA 608	delta-BHC	8/1/2006	7/31/2007	Certified
EPA 608	Dieldrin	8/1/2006	7/31/2007	Certified
EPA 608	Endosulfan I	8/1/2006	7/31/2007	Certified
EPA 608	Endosulfan II	8/1/2006	7/31/2007	Certified
EPA 608	Endosulfan sulfate	8/1/2006	7/31/2007	Certified
EPA 608	Endrin	8/1/2006	7/31/2007	Certified
EPA 608	Endrin aldehyde	8/1/2006	7/31/2007	Certified
EPA 608	Endrin ketone	8/1/2006	7/31/2007	Certified
EPA 608	gamma-BHC (Lindane)	8/1/2006	7/31/2007	Certified
EPA 608	Heptachlor	8/1/2006	7/31/2007	Certified
EPA 608	Heptachlor Epoxide	8/1/2006	7/31/2007	Certified
EPA 608	Methoxychlor	8/1/2006	7/31/2007	Certified
EPA 608	Toxaphene	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Radiochemistry**				
EPA 200.8	Uranium	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Residue**				
EPA 160.2	Residue Non-filterable (TSS)	8/1/2006	7/31/2007	Certified
EPA 160.3	Residue Total	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Semi-Volatile - BNAs**				
EPA 625	2,4,6-Trichlorophenol	8/1/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 625	2,4-Dichlorophenol	8/1/2006	7/31/2007	Certified
EPA 625	2,4-Dimethylphenol	8/1/2006	7/31/2007	Certified
EPA 625	2,4-Dinitrophenol	8/1/2006	7/31/2007	Certified
EPA 625	2,4-Dinitrotoluene (2,4-DNT)	8/1/2006	7/31/2007	Certified
EPA 625	2,6-Dinitrotoluene (2,6-DNT)	8/1/2006	7/31/2007	Certified
EPA 625	2-Chloronaphthalene	8/1/2006	7/31/2007	Certified
EPA 625	2-Chlorophenol	8/1/2006	7/31/2007	Certified
EPA 625	2-Methyl-4,6-dinitrophenol	8/1/2006	7/31/2007	Certified
EPA 625	2-Nitrophenol	8/1/2006	7/31/2007	Certified
EPA 625	4-Bromophenyl phenyl ether	8/1/2006	7/31/2007	Certified
EPA 625	4-Chloro-3-methylphenol	8/1/2006	7/31/2007	Certified
EPA 625	4-Chlorophenyl phenyl ether	8/1/2006	7/31/2007	Certified
EPA 625	4-Nitrophenol	8/1/2006	7/31/2007	Certified
EPA 625	Acenaphthene	8/1/2006	7/31/2007	Certified
EPA 625	Acenaphthylene	8/1/2006	7/31/2007	Certified
EPA 625	Anthracene	8/1/2006	7/31/2007	Certified
EPA 625	Benzidine	8/1/2006	7/31/2007	Certified
EPA 625	Benzo(a)anthracene	8/1/2006	7/31/2007	Certified
EPA 625	Benzo(a)pyrene	8/1/2006	7/31/2007	Certified
EPA 625	Benzo(b)fluoranthene	8/1/2006	7/31/2007	Certified
EPA 625	Benzo(g,h,i)perylene	8/1/2006	7/31/2007	Certified
EPA 625	Benzo(k)fluoranthene	8/1/2006	7/31/2007	Certified
EPA 625	Benzyl butyl phthalate	8/1/2006	7/31/2007	Certified

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

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Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 625	bis(2-chloroethoxy) methane	8/1/2006	7/31/2007	Certified
EPA 625	bis(2-chloroethyl) ether	8/1/2006	7/31/2007	Certified
EPA 625	bis(2-chloroisopropyl) ether	8/1/2006	7/31/2007	Certified
EPA 625	bis(2-ethylhexyl) phthalate (DEHD)	8/1/2006	7/31/2007	Certified
EPA 625	Chrysene	8/1/2006	7/31/2007	Certified
EPA 625	Dibenzo(a,h)anthracene	8/1/2006	7/31/2007	Certified
EPA 625	Diethyl phthalate	8/1/2006	7/31/2007	Certified
EPA 625	Dimethyl phthalate	8/1/2006	7/31/2007	Certified
EPA 625	Di-n-butyl phthalate	8/1/2006	7/31/2007	Certified
EPA 625	Di-n-octyl phthalate	8/1/2006	7/31/2007	Certified
EPA 625	Fluoranthene	8/1/2006	7/31/2007	Certified
EPA 625	Fluorene	8/1/2006	7/31/2007	Certified
EPA 625	Hexachlorobenzene	8/1/2006	7/31/2007	Certified
EPA 625	Hexachlorocyclopentadiene	8/1/2006	7/31/2007	Certified
EPA 625	Indeno(1,2,3-cd)pyrene	8/1/2006	7/31/2007	Certified
EPA 625	Isophorone	8/1/2006	7/31/2007	Certified
EPA 625	N-Nitroso-dimethylamine (NDMA)	8/1/2006	7/31/2007	Certified
EPA 625	N-Nitroso-di-n-propylamine (NDPA)	8/1/2006	7/31/2007	Certified
EPA 625	Pentachlorophenol	8/1/2006	7/31/2007	Certified
EPA 625	Phenanthrene	8/1/2006	7/31/2007	Certified
EPA 625	Phenol	8/1/2006	7/31/2007	Certified
EPA 625	Pyrene	8/1/2006	7/31/2007	Certified
EPA 625*	2,4,5-Trichlorophenol	8/1/2006	7/31/2007	Certified

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Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 625*	2-Methylphenol (o-Cresol)	8/1/2006	7/31/2007	Certified
EPA 625*	3,3'-Dichlorobenzidine	8/1/2006	7/31/2007	Certified
EPA 625*	4-Methylphenol (p-Cresol)	8/1/2006	7/31/2007	Certified
EPA 625*	Aniline	8/1/2006	7/31/2007	Certified
EPA 625*	Benzyl alcohol	8/1/2006	7/31/2007	Certified
EPA 625*	Dibenzofuran	8/1/2006	7/31/2007	Certified
EPA 625*	N-Nitroso-diphenylamine	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Trihalomethanes**				
EPA 624	Bromodichloromethane	8/1/2006	7/31/2007	Certified
EPA 624	Bromoform	8/1/2006	7/31/2007	Certified
EPA 624	Chlorodibromomethane	8/1/2006	7/31/2007	Certified
EPA 624	Chloroform	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Volatile**				
EPA 624	1,1,1-Trichloroethane	8/1/2006	7/31/2007	Certified
EPA 624	1,1,2,2-Tetrachloroethane	8/1/2006	7/31/2007	Certified
EPA 624	1,1,2-Trichloroethane	8/1/2006	7/31/2007	Certified
EPA 624	1,1-Dichloroethane	8/1/2006	7/31/2007	Certified
EPA 624	1,1-Dichloroethene (1,1-DCE)	8/1/2006	7/31/2007	Certified
EPA 624	1,2-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 624	1,2-Dichloroethane	8/1/2006	7/31/2007	Certified
EPA 624	1,2-Dichloropropane	8/1/2006	7/31/2007	Certified
EPA 624	1,3-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 624	1,4-Dichlorobenzene	8/1/2006	7/31/2007	Certified

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Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 624	2-Chloroethyl vinyl ether	8/1/2006	7/31/2007	Certified
EPA 624	Benzene	8/1/2006	7/31/2007	Certified
EPA 624	Bromomethane	8/1/2006	7/31/2007	Certified
EPA 624	Carbon tetrachloride	8/1/2006	7/31/2007	Certified
EPA 624	Chlorobenzene	8/1/2006	7/31/2007	Certified
EPA 624	Chloroethane	8/1/2006	7/31/2007	Certified
EPA 624	Chloromethane	8/1/2006	7/31/2007	Certified
EPA 624	cis-1,3-Dichloropropene	8/1/2006	7/31/2007	Certified
EPA 624	Dichlorodifluoromethane	8/1/2006	7/31/2007	Certified
EPA 624	Ethylbenzene	8/1/2006	7/31/2007	Certified
EPA 624	Methylene chloride (Dichloromethane)	8/1/2006	7/31/2007	Certified
EPA 624	Tetrachloroethene (Perchloroethene, PCE)	8/1/2006	7/31/2007	Certified
EPA 624	Toluene	8/1/2006	7/31/2007	Certified
EPA 624	Total xylenes	8/1/2006	7/31/2007	Certified
EPA 624	trans-1,2-Dichloroethene	8/1/2006	7/31/2007	Certified
EPA 624	trans-1,3-Dichloropropene	8/1/2006	7/31/2007	Certified
EPA 624	Trichloroethene	8/1/2006	7/31/2007	Certified
EPA 624	Trichlorofluoromethane (Freon 11)	8/1/2006	7/31/2007	Certified
EPA 624	Vinyl Chloride	8/1/2006	7/31/2007	Certified
EPA 625	1,2,4-Trichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 625	1,2-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 625	1,3-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 625	1,4-Dichlorobenzene	8/1/2006	7/31/2007	Certified

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Matrix: ***CWA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 625	Hexachlorobutadiene	8/1/2006	7/31/2007	Certified
EPA 625	Hexachloroethane	8/1/2006	7/31/2007	Certified
EPA 625	Naphthalene	8/1/2006	7/31/2007	Certified
EPA 625	Nitrobenzene	8/1/2006	7/31/2007	Certified
Discipline/Category: **RadioChemistry/Radiochemistry**				
DOE Sr-02	Strontium-90	8/1/2006	7/31/2007	Nevada Approved
DOE U-02	Uranium	8/1/2006	7/31/2007	Nevada Approved
EPA 900.0	Gross Alpha	8/1/2006	7/31/2007	Certified
EPA 900.0	Gross Beta	8/1/2006	7/31/2007	Certified
EPA 903.0	Radium-226	8/1/2006	7/31/2007	Certified
EPA 903.1	Radium-226	8/1/2006	7/31/2007	Certified
EPA 904.0	Radium-228	8/1/2006	7/31/2007	Nevada Approved
EPA 906.0	Tritium	8/1/2006	7/31/2007	Nevada Approved

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Characteristics**				
EPA 1311	Toxicity Characteristic Leaching Procedure (TCLP)	8/1/2006	7/31/2007	Nevada Approved
Discipline/Category: **Chemistry/Demands**				
EPA 9060A	Total Organic Carbon	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Herbicides**				
EPA 8141A	Dichlorvos (DDVP)	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4,5-T	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4,5-TP (Silvex)	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4-D	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4-DB	8/1/2006	7/31/2007	Certified
EPA 8151A	Dicamba	8/1/2006	7/31/2007	Certified
EPA 8151A	Dichloroprop	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Metals**				
EPA 6010B	Aluminum	8/1/2006	7/31/2007	Certified
EPA 6010B	Antimony	8/1/2006	7/31/2007	Certified
EPA 6010B	Arsenic	8/1/2006	7/31/2007	Certified
EPA 6010B	Barium	8/1/2006	7/31/2007	Certified
EPA 6010B	Beryllium	8/1/2006	7/31/2007	Certified
EPA 6010B	Boron	8/1/2006	7/31/2007	Certified
EPA 6010B	Cadmium	8/1/2006	7/31/2007	Certified
EPA 6010B	Calcium	8/1/2006	7/31/2007	Certified
EPA 6010B	Chromium	8/1/2006	7/31/2007	Certified
EPA 6010B	Cobalt	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 6010B	Copper	8/1/2006	7/31/2007	Certified
EPA 6010B	Iron	8/1/2006	7/31/2007	Certified
EPA 6010B	Lead	8/1/2006	7/31/2007	Certified
EPA 6010B	Lithium	8/1/2006	7/31/2007	Certified
EPA 6010B	Magnesium	8/1/2006	7/31/2007	Certified
EPA 6010B	Manganese	8/1/2006	7/31/2007	Certified
EPA 6010B	Molybdenum	8/1/2006	7/31/2007	Certified
EPA 6010B	Nickel	8/1/2006	7/31/2007	Certified
EPA 6010B	Potassium	8/1/2006	7/31/2007	Certified
EPA 6010B	Selenium	8/1/2006	7/31/2007	Certified
EPA 6010B	Silver	8/1/2006	7/31/2007	Certified
EPA 6010B	Sodium	8/1/2006	7/31/2007	Certified
EPA 6010B	Strontium	8/1/2006	7/31/2007	Certified
EPA 6010B	Thallium	8/1/2006	7/31/2007	Certified
EPA 6010B	Tin	8/1/2006	7/31/2007	Certified
EPA 6010B	Titanium	8/1/2006	7/31/2007	Certified
EPA 6010B	Vanadium	8/1/2006	7/31/2007	Certified
EPA 6010B	Zinc	8/1/2006	7/31/2007	Certified
EPA 6020A	Aluminum	8/1/2006	7/31/2007	Certified
EPA 6020A	Antimony	8/1/2006	7/31/2007	Certified
EPA 6020A	Arsenic	8/1/2006	7/31/2007	Certified
EPA 6020A	Cadmium	8/1/2006	7/31/2007	Certified
EPA 6020A	Copper	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 6020A	Lead	8/1/2006	7/31/2007	Certified
EPA 6020A	Molybdenum	8/1/2006	7/31/2007	Certified
EPA 6020A	Selenium	8/1/2006	7/31/2007	Certified
EPA 6020A	Silver	8/1/2006	7/31/2007	Certified
EPA 6020A	Thallium	8/1/2006	7/31/2007	Certified
EPA 6020A	Vanadium	8/1/2006	7/31/2007	Certified
EPA 7196A	Hexavalent Chromium (Cr-VI)	8/1/2006	7/31/2007	Certified
EPA 7470A	Mercury	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Minerals**				
EPA 9056	Chloride	8/1/2006	7/31/2007	Certified
EPA 9056	Fluoride	8/1/2006	7/31/2007	Certified
EPA 9056	Sulfate	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Miscellaneous**				
EPA 6010B	Silica as SiO2	8/1/2006	7/31/2007	Certified
EPA 9010B	Cyanide, Amenable (Available cyanide)	8/1/2006	7/31/2007	Certified
EPA 9010B	Cyanide, Total	8/1/2006	7/31/2007	Certified
EPA 9014	Cyanide	8/1/2006	7/31/2007	Certified
EPA 9040B	pH (Hydrogen ion)	8/1/2006	7/31/2007	Certified
EPA 9056	Bromide	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Nutrients**				
EPA 9056	Nitrate-N	8/1/2006	7/31/2007	Certified
EPA 9056	Nitrite-N	8/1/2006	7/31/2007	Certified
EPA 9056	Ortho-phosphate as P	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Oxygenate**				
EPA 8021B	Methyl t-butyl ether (MTBE)	8/1/2006	7/31/2007	Certified
EPA 8260B	Methyl t-butyl ether (MTBE)	11/17/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/PCB**				
EPA 8082	PCBs in Oil	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/PCBs as aroclors**				
EPA 8082	Aroclor 1016	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1221	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1232	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1242	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1248	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1254	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1260	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Pesticides**				
EPA 8081A	4,4'-DDD	8/1/2006	7/31/2007	Certified
EPA 8081A	4,4'-DDE	8/1/2006	7/31/2007	Certified
EPA 8081A	4,4'-DDT	8/1/2006	7/31/2007	Certified
EPA 8081A	Aldrin	8/1/2006	7/31/2007	Certified
EPA 8081A	alpha-BHC	8/1/2006	7/31/2007	Certified
EPA 8081A	alpha-Chlordane	8/1/2006	7/31/2007	Certified
EPA 8081A	beta-BHC	8/1/2006	7/31/2007	Certified
EPA 8081A	delta-BHC	8/1/2006	7/31/2007	Certified
EPA 8081A	Dieldrin	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8081A	Endosulfan I	8/1/2006	7/31/2007	Certified
EPA 8081A	Endosulfan II	8/1/2006	7/31/2007	Certified
EPA 8081A	Endosulfan sulfate	8/1/2006	7/31/2007	Certified
EPA 8081A	Endrin	8/1/2006	7/31/2007	Certified
EPA 8081A	Endrin aldehyde	8/1/2006	7/31/2007	Certified
EPA 8081A	Endrin ketone	8/1/2006	7/31/2007	Certified
EPA 8081A	gamma-BHC (Lindane)	8/1/2006	7/31/2007	Certified
EPA 8081A	gamma-Chlordane	8/1/2006	7/31/2007	Certified
EPA 8081A	Heptachlor	8/1/2006	7/31/2007	Certified
EPA 8081A	Heptachlor Epoxide	8/1/2006	7/31/2007	Certified
EPA 8081A	Methoxychlor	8/1/2006	7/31/2007	Certified
EPA 8081A	Toxaphene	8/1/2006	7/31/2007	Certified
EPA 8141A	Azinphos-methyl	8/1/2006	7/31/2007	Certified
EPA 8141A	Chlorfenvinphos	8/1/2006	7/31/2007	Certified
EPA 8141A	Diazinon	8/1/2006	7/31/2007	Certified
EPA 8141A	Disulfoton	8/1/2006	7/31/2007	Certified
EPA 8141A	Ethoprop	8/1/2006	7/31/2007	Certified
EPA 8141A	Malathion	8/1/2006	7/31/2007	Certified
EPA 8141A	Parathion, methyl	8/1/2006	7/31/2007	Certified
EPA 8141A	Phorate	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Petroleum Hydrocarbons**				
EPA 8015B	Diesel Range Organics	8/1/2006	7/31/2007	Certified
EPA 8015M	Gasoline Range Organics	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Properties**				
EPA 1312	Synthetic precipitation leaching procedure	8/1/2006	7/31/2007	Nevada Approved
Discipline/Category: **Chemistry/Radiochemistry**				
EPA 6020A	Uranium	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Semi-Volatile - BNAs**				
EPA 8270C	2,4,5-Trichlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4,6-Trichlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dichlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dimethylphenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dinitrophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dinitrotoluene (2,4-DNT)	8/1/2006	7/31/2007	Certified
EPA 8270C	2,6-Dinitrotoluene (2,6-DNT)	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Chloronaphthalene	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Chlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Methylnaphthalene	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Methylphenol (o-Cresol)	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Nitroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Nitrophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	3 & 4-Methylphenol (m & p-Cresol)	8/1/2006	7/31/2007	Certified
EPA 8270C	3,3'-Dichlorobenzidine	8/1/2006	7/31/2007	Certified
EPA 8270C	3-Nitroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	4,6-Dinitro-2-methylphenol	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Bromophenyl phenyl ether	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8270C	4-Chloro-3-methylphenol	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Chloroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Chlorophenyl phenyl ether	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Nitroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Nitrophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	Acenaphthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Acenaphthylene	8/1/2006	7/31/2007	Certified
EPA 8270C	Aniline	8/1/2006	7/31/2007	Certified
EPA 8270C	Anthracene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzidine	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(a)anthracene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(a)pyrene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(b)fluoranthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(g,h,i)perylene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(k)fluoranthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzoic acid	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzyl alcohol	8/1/2006	7/31/2007	Certified
EPA 8270C	bis(2-chloroethoxy) methane	8/1/2006	7/31/2007	Certified
EPA 8270C	bis(2-chloroethyl) ether	8/1/2006	7/31/2007	Certified
EPA 8270C	bis(2-chloroisopropyl) ether	8/1/2006	7/31/2007	Certified
EPA 8270C	bis(2-ethylhexyl) phthalate (DEHD)	8/1/2006	7/31/2007	Certified
EPA 8270C	Butyl benzyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Carbazole	8/1/2006	7/31/2007	Certified

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EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

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Method	Analyte	Start Date	Date Expires	Status
EPA 8270C	Chrysene	8/1/2006	7/31/2007	Certified
EPA 8270C	Dibenzo(a,h)anthracene	8/1/2006	7/31/2007	Certified
EPA 8270C	Dibenzofuran	8/1/2006	7/31/2007	Certified
EPA 8270C	Diethyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Dimethyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Di-n-butyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Di-n-octyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Fluoranthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Fluorene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachlorocyclopentadiene	8/1/2006	7/31/2007	Certified
EPA 8270C	Indeno(1,2,3-cd)pyrene	8/1/2006	7/31/2007	Certified
EPA 8270C	Isophorone	8/1/2006	7/31/2007	Certified
EPA 8270C	N-Nitroso-dimethylamine (NDMA)	8/1/2006	7/31/2007	Certified
EPA 8270C	N-Nitroso-di-n-propylamine (NDPA)	8/1/2006	7/31/2007	Certified
EPA 8270C	N-Nitroso-diphenylamine	8/1/2006	7/31/2007	Certified
EPA 8270C	Pentachlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	Phenanthrene	8/1/2006	7/31/2007	Certified
EPA 8270C	Phenol	8/1/2006	7/31/2007	Certified
EPA 8270C	Pyrene	8/1/2006	7/31/2007	Certified
EPA 8330	2,4-Dinitrotoluene (2,4-DNT)	8/1/2006	7/31/2007	Certified
EPA 8330	2,6-Dinitrotoluene (2,6-DNT)	8/1/2006	7/31/2007	Certified
EPA 8330	Methyl-2,4,6-trinitrophenylnitramine (Tetyrl)	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Semi-Volatile - NOS**				
EPA 8330	1,3,5-Trinitrobenzene	8/1/2006	7/31/2007	Certified
EPA 8330	1,3-Dinitrobenzene (1,3-DNB)	8/1/2006	7/31/2007	Certified
EPA 8330	2,4,6-Trinitrotoluene (2,4,6-TNT)	8/1/2006	7/31/2007	Certified
EPA 8330	2-Amino-4, 6-dinitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	2-Nitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	3-Nitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	4-Amino-2,6-dinitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	4-Nitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	8/1/2006	7/31/2007	Certified
EPA 8330	Nitroglycerin	8/1/2006	7/31/2007	Nevada Approved
EPA 8330	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	8/1/2006	7/31/2007	Certified
EPA 8332	Nitroglycerin	8/1/2006	7/31/2007	Nevada Approved
EPA 8332	Pentaerythritol tetranitrate (PETN)	8/1/2006	7/31/2007	Nevada Approved
Discipline/Category: **Chemistry/Trihalomethanes**				
EPA 8260B	Bromodichloromethane	8/1/2006	7/31/2007	Certified
EPA 8260B	Bromoform	8/1/2006	7/31/2007	Certified
EPA 8260B	Chlorodibromomethane	8/1/2006	7/31/2007	Certified
EPA 8260B	Chloroform	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Volatile**				
EPA 8015B	Ethylene glycol	8/1/2006	7/31/2007	Nevada Approved
EPA 8015B	Ethylene glycol monobutyl ether (EGBE) (2-Butoxyethanol)	8/1/2006	7/31/2007	Nevada Approved
EPA 8021B	Benzene	8/1/2006	7/31/2007	Certified

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Method	Analyte	Start Date	Date Expires	Status
EPA 8021B	Chlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8021B	Ethylbenzene	8/1/2006	7/31/2007	Certified
EPA 8021B	Toluene	8/1/2006	7/31/2007	Certified
EPA 8021B	Total xylenes	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,1,2-Tetrachloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,1-Trichloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,2,2-Tetrachloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,2-Trichloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1-Dichloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1-Dichloroethene (1,1-DCE)	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2,3-Trichloropropane (TCP)	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2,4-Trimethylbenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2-Dibromo-3-chloropropane (DBCP)	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2-Dibromoethane (EDB, Ethylene Dibromide)	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2-Dichloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2-Dichloropropane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,3,5-Trimethylbenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	1,3-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	1,4-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	2-Butanone (Methyl ethyl ketone, MEK)	8/1/2006	7/31/2007	Certified
EPA 8260B	2-Chloroethyl vinyl ether	8/1/2006	7/31/2007	Certified
EPA 8260B	2-Hexanone	8/1/2006	7/31/2007	Certified

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Method	Analyte	Start Date	Date Expires	Status
EPA 8260B	4-Methyl-2-pentanone (MIBK)	8/1/2006	7/31/2007	Certified
EPA 8260B	Acetone	8/1/2006	7/31/2007	Certified
EPA 8260B	Acetonitrile	8/1/2006	7/31/2007	Certified
EPA 8260B	Acrolein (Propenal)	8/1/2006	7/31/2007	Certified
EPA 8260B	Acrylonitrile	8/1/2006	7/31/2007	Certified
EPA 8260B	Benzene	8/1/2006	7/31/2007	Certified
EPA 8260B	Bromomethane	8/1/2006	7/31/2007	Certified
EPA 8260B	Carbon disulfide	8/1/2006	7/31/2007	Certified
EPA 8260B	Carbon tetrachloride	8/1/2006	7/31/2007	Certified
EPA 8260B	Chlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	Chloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	Chloromethane	8/1/2006	7/31/2007	Certified
EPA 8260B	cis-1,2-Dichloroethene	8/1/2006	7/31/2007	Certified
EPA 8260B	cis-1,3-Dichloropropene	8/1/2006	7/31/2007	Certified
EPA 8260B	Dibromomethane	8/1/2006	7/31/2007	Certified
EPA 8260B	Dichlorodifluoromethane	8/1/2006	7/31/2007	Certified
EPA 8260B	Ethylbenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	Methylene chloride (Dichloromethane)	8/1/2006	7/31/2007	Certified
EPA 8260B	m-Xylene	8/1/2006	7/31/2007	Certified
EPA 8260B	Naphthalene	8/1/2006	7/31/2007	Certified
EPA 8260B	o-Xylene	8/1/2006	7/31/2007	Certified
EPA 8260B	p-Xylene	8/1/2006	7/31/2007	Certified
EPA 8260B	Styrene	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8260B	Tetrachloroethene (Perchloroethene, PCE)	8/1/2006	7/31/2007	Certified
EPA 8260B	Toluene	8/1/2006	7/31/2007	Certified
EPA 8260B	Total xylenes	8/1/2006	7/31/2007	Certified
EPA 8260B	trans-1,2-Dichloroethene	8/1/2006	7/31/2007	Certified
EPA 8260B	trans-1,3-Dichloropropene	8/1/2006	7/31/2007	Certified
EPA 8260B	Trichloroethene	8/1/2006	7/31/2007	Certified
EPA 8260B	Trichlorofluoromethane (Freon 11)	8/1/2006	7/31/2007	Certified
EPA 8260B	Vinyl acetate	8/1/2006	7/31/2007	Certified
EPA 8260B	Vinyl Chloride	8/1/2006	7/31/2007	Certified
EPA 8270C	1,2,4-Trichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	1,2-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	1,3-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	1,4-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachlorobutadiene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachloroethane	8/1/2006	7/31/2007	Certified
EPA 8270C	Naphthalene	8/1/2006	7/31/2007	Certified
EPA 8270C	Nitrobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	Pyridine	8/1/2006	7/31/2007	Certified
EPA 8330	Nitrobenzene	8/1/2006	7/31/2007	Certified
Discipline/Category: **RadioChemistry/Radiochemistry**				
DOE Sr-01, Sr-02	Strontium 89, 90	8/1/2006	7/31/2007	Certified
DOE U-02	Uranium	8/1/2006	7/31/2007	Certified
SM 9310	Gross Alpha	8/1/2006	7/31/2007	Certified

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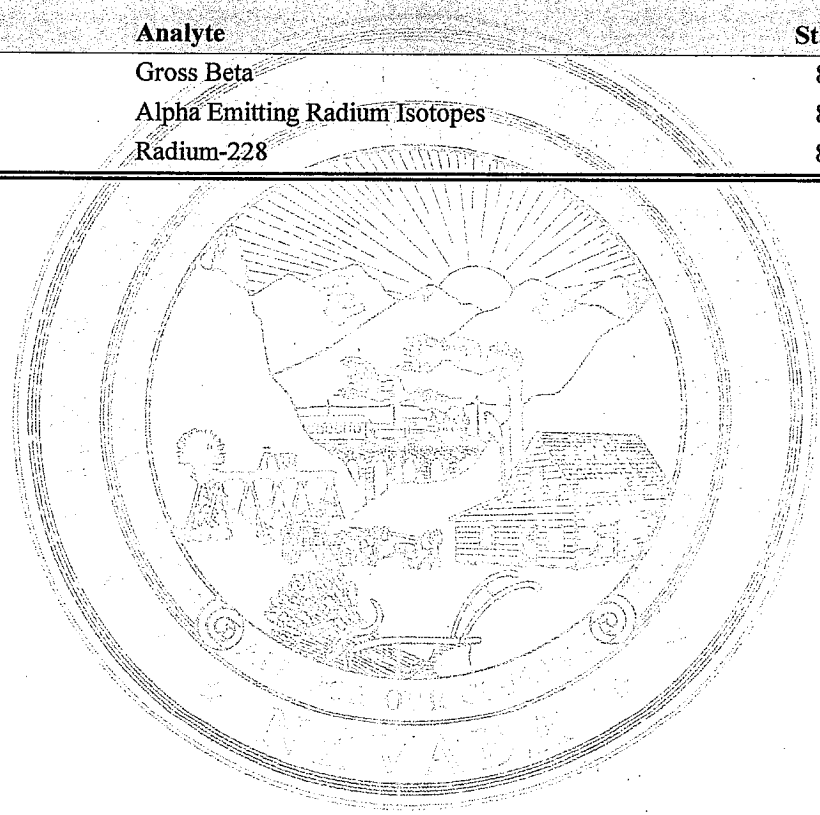
Matrix: ***RCRA (non-potable)***

Method	Analyte	Start Date	Date Expires	Status
SM 9310	Gross Beta	8/1/2006	7/31/2007	Certified
SM 9315	Alpha Emitting Radium Isotopes	8/1/2006	7/31/2007	Certified
SM 9320	Radium-228	8/1/2006	7/31/2007	Certified



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Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Characteristics**				
EPA 1311	Toxicity Characteristic Leaching Procedure (TCLP)	8/1/2006	7/31/2007	Nevada Approved
EPA 9095B	Paint Filter Liquids Test	8/1/2006	7/31/2007	Nevada Approved
Discipline/Category: **Chemistry/Herbicides**				
EPA 8141A	Dichlorvos (DDVP)	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4,5-T	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4,5-TP (Silvex)	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4-D	8/1/2006	7/31/2007	Certified
EPA 8151A	2,4-DB	8/1/2006	7/31/2007	Certified
EPA 8151A	Dalapon	8/1/2006	7/31/2007	Certified
EPA 8151A	Dicamba	8/1/2006	7/31/2007	Certified
EPA 8151A	Dinoseb	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Metals**				
EPA 6010B	Aluminum	8/1/2006	7/31/2007	Certified
EPA 6010B	Antimony	8/1/2006	7/31/2007	Certified
EPA 6010B	Arsenic	8/1/2006	7/31/2007	Certified
EPA 6010B	Barium	8/1/2006	7/31/2007	Certified
EPA 6010B	Beryllium	8/1/2006	7/31/2007	Certified
EPA 6010B	Boron	8/1/2006	7/31/2007	Certified
EPA 6010B	Cadmium	8/1/2006	7/31/2007	Certified
EPA 6010B	Calcium	8/1/2006	7/31/2007	Certified
EPA 6010B	Chromium	8/1/2006	7/31/2007	Certified
EPA 6010B	Cobalt	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 6010B	Copper	8/1/2006	7/31/2007	Certified
EPA 6010B	Iron	8/1/2006	7/31/2007	Certified
EPA 6010B	Lead	8/1/2006	7/31/2007	Certified
EPA 6010B	Lithium	8/1/2006	7/31/2007	Certified
EPA 6010B	Magnesium	8/1/2006	7/31/2007	Certified
EPA 6010B	Manganese	8/1/2006	7/31/2007	Certified
EPA 6010B	Molybdenum	8/1/2006	7/31/2007	Certified
EPA 6010B	Nickel	8/1/2006	7/31/2007	Certified
EPA 6010B	Potassium	8/1/2006	7/31/2007	Certified
EPA 6010B	Selenium	8/1/2006	7/31/2007	Certified
EPA 6010B	Silver	8/1/2006	7/31/2007	Certified
EPA 6010B	Sodium	8/1/2006	7/31/2007	Certified
EPA 6010B	Strontium	8/1/2006	7/31/2007	Certified
EPA 6010B	Thallium	8/1/2006	7/31/2007	Certified
EPA 6010B	Tin	8/1/2006	7/31/2007	Certified
EPA 6010B	Titanium	8/1/2006	7/31/2007	Certified
EPA 6010B	Vanadium	8/1/2006	7/31/2007	Certified
EPA 6010B	Zinc	8/1/2006	7/31/2007	Certified
EPA 6020A	Aluminum	8/1/2006	7/31/2007	Certified
EPA 6020A	Antimony	8/1/2006	7/31/2007	Certified
EPA 6020A	Arsenic	8/1/2006	7/31/2007	Certified
EPA 6020A	Cadmium	8/1/2006	7/31/2007	Certified
EPA 6020A	Copper	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 6020A	Lead	8/1/2006	7/31/2007	Certified
EPA 6020A	Molybdenum	8/1/2006	7/31/2007	Certified
EPA 6020A	Selenium	8/1/2006	7/31/2007	Certified
EPA 6020A	Silver	8/1/2006	7/31/2007	Certified
EPA 6020A	Thallium	8/1/2006	7/31/2007	Certified
EPA 6020A	Vanadium	8/1/2006	7/31/2007	Certified
EPA 6020A	Zinc	8/1/2006	7/31/2007	Certified
EPA 7196A	Hexavalent Chromium (Cr-VI)	8/1/2006	7/31/2007	Certified
EPA 7471A	Mercury	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Minerals**				
EPA 9056	Chloride	8/1/2006	7/31/2007	Certified
EPA 9056	Fluoride	8/1/2006	7/31/2007	Certified
EPA 9056	Sulfate	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Miscellaneous**				
EPA 6010B	Silica as SiO2	8/1/2006	7/31/2007	Certified
EPA 9014	Cyanide	8/1/2006	7/31/2007	Certified
EPA 9045C	Soil and Waste pH	8/1/2006	7/31/2007	Certified
EPA 9056	Bromide	8/1/2006	7/31/2007	Certified
EPA 9071A	Hexane Extractable Material (HEM)	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Nutrients**				
EPA 9056	Nitrate-N	8/1/2006	7/31/2007	Certified
EPA 9056	Nitrite-N	8/1/2006	7/31/2007	Certified
EPA 9056	Ortho-phosphate as P	8/1/2006	7/31/2007	Certified

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Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
Discipline/Category: **Chemistry/Oxygenate**				
EPA 8021B	Methyl t-butyl ether (MTBE)	8/1/2006	7/31/2007	Certified
EPA 8260B	Methyl t-butyl ether (MTBE)	11/30/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/PCBs as aroclors**				
EPA 8082	Aroclor 1016	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1221	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1232	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1242	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1248	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1254	8/1/2006	7/31/2007	Certified
EPA 8082	Aroclor 1260	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Pesticides**				
EPA 8081A	4,4'-DDD	8/1/2006	7/31/2007	Certified
EPA 8081A	4,4'-DDE	8/1/2006	7/31/2007	Certified
EPA 8081A	4,4'-DDT	8/1/2006	7/31/2007	Certified
EPA 8081A	Aldrin	8/1/2006	7/31/2007	Certified
EPA 8081A	alpha-BHC	8/1/2006	7/31/2007	Certified
EPA 8081A	alpha-Chlordane	8/1/2006	7/31/2007	Certified
EPA 8081A	beta-BHC	8/1/2006	7/31/2007	Certified
EPA 8081A	delta-BHC	8/1/2006	7/31/2007	Certified
EPA 8081A	Dieldrin	8/1/2006	7/31/2007	Certified
EPA 8081A	Endosulfan I	8/1/2006	7/31/2007	Certified
EPA 8081A	Endosulfan II	8/1/2006	7/31/2007	Certified

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Method	Analyte	Start Date	Date Expires	Status
EPA 8081A	Endosulfan sulfate	8/1/2006	7/31/2007	Certified
EPA 8081A	Endrin	8/1/2006	7/31/2007	Certified
EPA 8081A	Endrin aldehyde	8/1/2006	7/31/2007	Certified
EPA 8081A	Endrin ketone	8/1/2006	7/31/2007	Certified
EPA 8081A	gamma-BHC (Lindane)	8/1/2006	7/31/2007	Certified
EPA 8081A	gamma-Chlordane	8/1/2006	7/31/2007	Certified
EPA 8081A	Heptachlor	8/1/2006	7/31/2007	Certified
EPA 8081A	Heptachlor Epoxide	8/1/2006	7/31/2007	Certified
EPA 8081A	Methoxychlor	8/1/2006	7/31/2007	Certified
EPA 8081A	Toxaphene	8/1/2006	7/31/2007	Certified
EPA 8141A	Azinphos-methyl	8/1/2006	7/31/2007	Certified
EPA 8141A	Chlorpyrifos	8/1/2006	7/31/2007	Certified
EPA 8141A	Demeton-O	8/1/2006	7/31/2007	Certified
EPA 8141A	Demeton-S	8/1/2006	7/31/2007	Certified
EPA 8141A	Diazinon	8/1/2006	7/31/2007	Certified
EPA 8141A	Disulfoton	8/1/2006	7/31/2007	Certified
EPA 8141A	Ethoprop	8/1/2006	7/31/2007	Certified
EPA 8141A	Fenthion	8/1/2006	7/31/2007	Certified
EPA 8141A	Malathion	8/1/2006	7/31/2007	Certified
EPA 8141A	Naled	8/1/2006	7/31/2007	Certified
EPA 8141A	Parathion, methyl	8/1/2006	7/31/2007	Certified
EPA 8141A	Phorate	8/1/2006	7/31/2007	Certified
EPA 8141A	Ronnel	8/1/2006	7/31/2007	Certified

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8141A	Stirophos (Tetrachlorvinphos)	8/1/2006	7/31/2007	Certified
EPA 8151A	MCPP	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Petroleum Hydrocarbons**				
EPA 8015B	Diesel Range Organics	8/1/2006	7/31/2007	Certified
EPA 8015M	Gasoline Range Organics	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Properties**				
EPA 1312	Synthetic precipitation leaching procedure	8/1/2006	7/31/2007	Nevada Approved
Discipline/Category: **Chemistry/Radiochemistry**				
EPA 6020A	Uranium	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Semi-Volatile - BNAs**				
EPA 8270C	2,4,5-Trichlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4,6-Trichlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dichlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dimethylphenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dinitrophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2,4-Dinitrotoluene (2,4-DNT)	8/1/2006	7/31/2007	Certified
EPA 8270C	2,6-Dinitrotoluene (2,6-DNT)	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Chloronaphthalene	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Chlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Methylnaphthalene	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Methylphenol (o-Cresol)	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Nitroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	2-Nitrophenol	8/1/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: ***CO00078*** **Attachment to Certificate Number: CO000782007A Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8270C	3 & 4-Methylphenol (m & p-Cresol)	8/1/2006	7/31/2007	Certified
EPA 8270C	3,3'-Dichlorobenzidine	8/1/2006	7/31/2007	Certified
EPA 8270C	3-Nitroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	4,6-Dinitro-2-methylphenol	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Bromophenyl phenyl ether	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Chloro-3-methylphenol	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Chloroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Chlorophenyl phenyl ether	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Nitroaniline	8/1/2006	7/31/2007	Certified
EPA 8270C	4-Nitrophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	Acenaphthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Acenaphthylene	8/1/2006	7/31/2007	Certified
EPA 8270C	Aniline	8/1/2006	7/31/2007	Certified
EPA 8270C	Anthracene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzidine	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(a)anthracene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(a)pyrene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(b)fluoranthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(g,h,i)perylene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzo(k)fluoranthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzoic acid	8/1/2006	7/31/2007	Certified
EPA 8270C	Benzyl alcohol	8/1/2006	7/31/2007	Certified
EPA 8270C	bis(2-chloroethoxy) methane	8/1/2006	7/31/2007	Certified

Disclaimer: A laboratory that is certified or approved has established that they have the ability to implement a quality control program in accordance with the appropriate Federal or State regulations or statutes. It is the certified laboratory's responsibility to provide the client with their current certified parameter list. Contact ELS to verify certification status. *Not for compliance purposes.

EPA Number: *CO00078* **Attachment to Certificate Number: CO000782007A** **Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8270C	bis(2-chloroethyl) ether	8/1/2006	7/31/2007	Certified
EPA 8270C	bis(2-chloroisopropyl) ether	8/1/2006	7/31/2007	Certified
EPA 8270C	bis(2-ethylhexyl) phthalate (DEHD)	8/1/2006	7/31/2007	Certified
EPA 8270C	Butyl benzyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Carbazole	8/1/2006	7/31/2007	Certified
EPA 8270C	Chrysene	8/1/2006	7/31/2007	Certified
EPA 8270C	Dibenzo(a,h)anthracene	8/1/2006	7/31/2007	Certified
EPA 8270C	Dibenzofuran	8/1/2006	7/31/2007	Certified
EPA 8270C	Diethyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Dimethyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Di-n-butyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Di-n-octyl phthalate	8/1/2006	7/31/2007	Certified
EPA 8270C	Fluoranthene	8/1/2006	7/31/2007	Certified
EPA 8270C	Fluorene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachlorocyclopentadiene	8/1/2006	7/31/2007	Certified
EPA 8270C	Indeno(1,2,3-cd)pyrene	8/1/2006	7/31/2007	Certified
EPA 8270C	Isophorone	8/1/2006	7/31/2007	Certified
EPA 8270C	N-Nitroso-dimethylamine (NDMA)	8/1/2006	7/31/2007	Certified
EPA 8270C	N-Nitroso-di-n-propylamine (NDPA)	8/1/2006	7/31/2007	Certified
EPA 8270C	N-Nitroso-diphenylamine	8/1/2006	7/31/2007	Certified
EPA 8270C	Pentachlorophenol	8/1/2006	7/31/2007	Certified
EPA 8270C	Phenanthrene	8/1/2006	7/31/2007	Certified

EPA Number: ***CO00078*** **Attachment to Certificate Number: CO000782007A Expiration Date: 7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8270C	Phenol	8/1/2006	7/31/2007	Certified
EPA 8270C	Pyrene	8/1/2006	7/31/2007	Certified
EPA 8330	2,4-Dinitrotoluene (2,4-DNT)	8/1/2006	7/31/2007	Certified
EPA 8330	2,6-Dinitrotoluene (2,6-DNT)	8/1/2006	7/31/2007	Certified
EPA 8330	Methyl-2,4,6-trinitrophenylnitramine (Tetyrl)	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Semi-Volatile - NOS**				
EPA 8330	1,3,5-Trinitrobenzene	8/1/2006	7/31/2007	Certified
EPA 8330	1,3-Dinitrobenzene (1,3-DNB)	8/1/2006	7/31/2007	Certified
EPA 8330	2,4,6-Trinitrotoluene (2,4,6-TNT)	8/1/2006	7/31/2007	Certified
EPA 8330	2-Amino-4, 6-dinitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	2-Nitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	3-Nitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	4-Amino-2,6-dinitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	4-Nitrotoluene	8/1/2006	7/31/2007	Certified
EPA 8330	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	8/1/2006	7/31/2007	Certified
EPA 8330	Nitroglycerin	8/1/2006	7/31/2007	Nevada Approved
EPA 8330	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	8/1/2006	7/31/2007	Certified
EPA 8332	Nitroglycerin	8/1/2006	7/31/2007	Nevada Approved
EPA 8332	Pentaerythritol tetranitrate (PETN)	8/1/2006	7/31/2007	Nevada Approved
Discipline/Category: **Chemistry/Trihalomethanes**				
EPA 8260B	Bromodichloromethane	8/1/2006	7/31/2007	Certified
EPA 8260B	Bromoform	8/1/2006	7/31/2007	Certified
EPA 8260B	Chlorodibromomethane	8/1/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8260B	Chloroform	8/1/2006	7/31/2007	Certified
Discipline/Category: **Chemistry/Volatile**				
EPA 8015B	Ethylene glycol	8/1/2006	7/31/2007	Nevada Approved
EPA 8015B	Ethylene glycol monobutyl ether (EGBE) (2-Butoxyethanol)	8/1/2006	7/31/2007	Nevada Approved
EPA 8021B	Benzene	8/1/2006	7/31/2007	Certified
EPA 8021B	Chlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8021B	Ethylbenzene	8/1/2006	7/31/2007	Certified
EPA 8021B	Toluene	8/1/2006	7/31/2007	Certified
EPA 8021B	Total xylenes	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,1,2-Tetrachloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,1-Trichloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,2,2-Tetrachloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1,2-Trichloroethane	11/30/2006	7/31/2007	Certified
EPA 8260B	1,1-Dichloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,1-Dichloroethene (1,1-DCE)	11/30/2006	7/31/2007	Certified
EPA 8260B	1,2,3-Trichloropropane (TCP)	11/30/2006	7/31/2007	Certified
EPA 8260B	1,2,4-Trichlorobenzene	11/30/2006	7/31/2007	Certified
EPA 8260B	1,2-Dibromo-3-chloropropane (DBCP)	11/30/2006	7/31/2007	Certified
EPA 8260B	1,2-Dibromoethane (EDB; Ethylene Dibromide)	11/30/2006	7/31/2007	Certified
EPA 8260B	1,2-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2-Dichloroethane	8/1/2006	7/31/2007	Certified
EPA 8260B	1,2-Dichloropropane	11/30/2006	7/31/2007	Certified
EPA 8260B	1,3-Dichlorobenzene	8/1/2006	7/31/2007	Certified

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8260B	1,4-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	2-Butanone (Methyl ethyl ketone, MEK)	11/30/2006	7/31/2007	Certified
EPA 8260B	2-Chloroethyl vinyl ether	11/30/2006	7/31/2007	Certified
EPA 8260B	2-Hexanone	11/30/2006	7/31/2007	Certified
EPA 8260B	4-Methyl-2-pentanone (MIBK)	8/1/2006	7/31/2007	Certified
EPA 8260B	Acetonitrile	11/30/2006	7/31/2007	Certified
EPA 8260B	Acrolein (Propenal)	11/30/2006	7/31/2007	Certified
EPA 8260B	Acrylonitrile	11/30/2006	7/31/2007	Certified
EPA 8260B	Benzene	8/1/2006	7/31/2007	Certified
EPA 8260B	Bromomethane	11/30/2006	7/31/2007	Certified
EPA 8260B	Carbon disulfide	11/30/2006	7/31/2007	Certified
EPA 8260B	Carbon tetrachloride	8/1/2006	7/31/2007	Certified
EPA 8260B	Chlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	Chloroethane	11/30/2006	7/31/2007	Certified
EPA 8260B	Chloromethane	11/30/2006	7/31/2007	Certified
EPA 8260B	cis-1,2-Dichloroethene	11/30/2006	7/31/2007	Certified
EPA 8260B	cis-1,3-Dichloropropene	11/30/2006	7/31/2007	Certified
EPA 8260B	Dibromomethane	11/30/2006	7/31/2007	Certified
EPA 8260B	Dichlorodifluoromethane	11/30/2006	7/31/2007	Certified
EPA 8260B	Ethylbenzene	8/1/2006	7/31/2007	Certified
EPA 8260B	Isopropylbenzene	11/30/2006	7/31/2007	Certified
EPA 8260B	Methylene chloride (Dichloromethane)	8/1/2006	7/31/2007	Certified
EPA 8260B	Styrene	11/30/2006	7/31/2007	Certified

State of Nevada Department of Conservation and Natural Resources
Division of Environmental Protection Bureau of Water Quality Planning
Laboratory Scope of Accreditation

EPA Number: ***CO00078***

Attachment to Certificate Number: **CO000782007A*** **Expiration Date:** **7/31/2007**

Paragon Analytics
225 Commerce Drive
Fort Collins, CO 80524

Matrix: ***RCRA (soil)***

Method	Analyte	Start Date	Date Expires	Status
EPA 8260B	Tetrachloroethene (Perchloroethene, PCE)	8/1/2006	7/31/2007	Certified
EPA 8260B	Toluene	8/1/2006	7/31/2007	Certified
EPA 8260B	Total xylenes	8/1/2006	7/31/2007	Certified
EPA 8260B	trans-1,2-Dichloroethene	11/30/2006	7/31/2007	Certified
EPA 8260B	trans-1,3-Dichloropropene	11/30/2006	7/31/2007	Certified
EPA 8260B	Trichloroethene	8/1/2006	7/31/2007	Certified
EPA 8260B	Trichlorofluoromethane (Freon 11)	11/30/2006	7/31/2007	Certified
EPA 8260B	Vinyl acetate	11/30/2006	7/31/2007	Certified
EPA 8260B	Vinyl Chloride	11/30/2006	7/31/2007	Certified
EPA 8270C	1,2,4-Trichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	1,2-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	1,3-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	1,4-Dichlorobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachlorobutadiene	8/1/2006	7/31/2007	Certified
EPA 8270C	Hexachloroethane	8/1/2006	7/31/2007	Certified
EPA 8270C	Naphthalene	8/1/2006	7/31/2007	Certified
EPA 8270C	Nitrobenzene	8/1/2006	7/31/2007	Certified
EPA 8270C	Pyridine	8/1/2006	7/31/2007	Certified
EPA 8330	Nitrobenzene	8/1/2006	7/31/2007	Certified

State of Nevada

Department of Conservation and Natural Resources
Division of Environmental Protection

Certifies that

Paragon Analytics

225 Commerce Drive

Fort Collins, CO 80524

Having met the requirements of the
Nevada Administrative Code: NAC 445A

is hereby approved to perform the analyses as indicated on the most recently issued parameter list which must accompany this certificate to be valid. It is the certified laboratories responsibility to provide the client their most current certified parameter list. Contact ELS to verify certification status.

Expiration Date: 7/31/2007

Certificate Number: CO000782007A

Don LaFara

Donald LaFara, Program Manager
Environmental Laboratory Services

Pennsylvania Department of Environmental Protection

P. O. Box 1467
Harrisburg, PA 17105-1467
March 20, 2008

Bureau of Laboratories

Phone: 717-346-7200
Fax: 717-346-8590

Debra Scheib
Paragon Analytics, A Division of DataChem Laboratories, Inc.
225 Commerce Dr
Fort Collins, CO 80524

Re: Lab ID No. 68-03116

Dear Laboratory Director:

Enclosed is your new Certificate of Accreditation to operate as a Pennsylvania Accredited Laboratory. This Certificate of Accreditation expires 3/31/2009 unless suspended or revoked earlier.

Your Laboratory identification number is 68-03116. Please use this number on all correspondence with the PA Department of Environmental Protection (Department).

Your laboratory is accredited to perform only the analyses by the methods listed on the Scope of Accreditation that accompanies the Certificate of Accreditation. The Certificate of Accreditation remains the property of the Department and must be displayed in the laboratory.

Please note this certification must be renewed annually. Renewal applications must be submitted to the Department *no later than 60 days prior to the expiration of the certification.* Failure to submit a renewal application within this time period may result in a lapse of the laboratory's accreditation. Should this occur, the laboratory may not conduct any further analyses for which accreditation is required and, if the laboratory is accredited to perform analyses on drinking water, the laboratory must notify the public water suppliers served by the laboratory of the laboratory's failure to renew its certificate of accreditation. Copies of the renewal application may be found on the Department's web site (www.dep.state.pa.us/dep/deputate/mts/bol).

If you have any questions concerning your certificate, you may contact the Laboratory Accreditation Program at the address, phone number or fax number listed above.

Sincerely,

Aaren S. Alger, Chief
Laboratory Accreditation Program

Enclosure

Laboratory Scope of Accreditation

Attachment to Certificate of Accreditation 001, expiration date March 30, 2009. This listing of accredited analytes should be used only when associated with a valid certificate of accreditation.

State Laboratory ID: 68-03116 **EPA Lab Code: CO00078** **(970) 490-1511**

Paragon Analytics, A Division of DataChem Laboratories, Inc.
225 Commerce Dr
Fort Collins, CO 80524

Program Non-Potable Water

Method	Analyte	Accreditation Type	Primary	Effective Date
DOE Sr-02	Strontium-89 90	NELAP	UT	3/19/2008
DOE U-02	Uranium	NELAP	UT	3/19/2008
EPA 900.0	Gross-alpha	NELAP	UT	3/19/2008
EPA 900.0	Gross-beta	NELAP	UT	3/19/2008
EPA 903.0	Total alpha radium	NELAP	UT	3/19/2008
EPA 903.1	Radium-226	NELAP	UT	3/19/2008
EPA 904.0	Radium-228	NELAP	UT	3/19/2008
EPA 906.0	Tritium	NELAP	UT	3/19/2008

Laboratory Scope of Accreditation

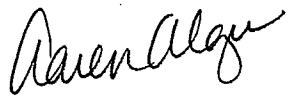
Attachment to Certificate of Accreditation 001, expiration date March 30, 2009. This listing of accredited analytes should be used only when associated with a valid certificate of accreditation.

State Laboratory ID: 68-03116 **EPA Lab Code: CO00078** **(970) 490-1511**

Paragon Analytics, A Division of DataChem Laboratories, Inc.
225 Commerce Dr
Fort Collins, CO 80524

Program Solid and Chemical Materials

Method	Analyte	Accreditation Type	Primary	Effective Date
EPA 9310	Gross-alpha	NELAP	UT	3/19/2008
EPA 9310	Gross-beta	NELAP	UT	3/19/2008
EPA 9315	Total alpha radium	NELAP	UT	3/19/2008
EPA 9320	Radium-228	NELAP	UT	3/19/2008



Laboratory Status Summary

Organization

03116 **(970) 490-1511**
Paragon Analytics, A Division of DataChem Laboratories, Inc.
225 Commerce Dr
Fort Collins, CO 80524

Solid and Chemical Materials Certification

Method Code	Method Ref	Analyte	Status	Date Effective	Type	AA
109	DOE Sr-02	Strontium-89 90	Applied	3/19/2008	NELAP	UT
197	DOE U-02	Uranium	Applied	3/19/2008	NELAP	UT
488	DOE Sr-01	Strontium-89 90	Applied	3/19/2008	NELAP	UT

Non-Potable Water Certification

Method Code	Method Ref	Analyte	Status	Date Effective	Type	AA
488	DOE Sr-01	Strontium-89 90	Applied	3/19/2008	NELAP	UT

COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF ENVIRONMENTAL PROTECTION

OFFICE OF FIELD OPERATIONS

BUREAU OF LABORATORIES

Certifies that

68-03116

PARAGON ANALYTICS, A DIVISION OF DATACHEM LABORATORIES, INC.

225 COMMERCE DR

FORT COLLINS, CO 80524

Having duly met the requirement of
The Act of June 29, 2002 (P.L. 596, No. 90)
dealing with Environmental Laboratory Accreditation
(27 Pa. C.S. §§4101-4113) and the
National Environmental Laboratory Accreditation Conference Standard

is hereby approved as an

Accredited Laboratory

As more fully described in the attached Scope of Accreditation

Expiration Date: **3/30/2009**

Certificate Number: **001**

Certificate not transferable Surrender upon revocation
To Be Conspicuously Displayed at the Laboratory
Not valid unless accompanied by a valid Scope of Accreditation
Shall not be used to imply endorsement by the Commonwealth of Pennsylvania
Customers are urged to verify the laboratory's current accreditation status
PA DEP is a NELAP recognized accrediting authority

Karen S. Alger, Chief
Laboratory Accreditation Program
Bureau of Laboratories

1500-FM-LAB0016 Rev. 10/2007

STATE OF TENNESSEE
DEPARTMENT OF ENVIRONMENT AND CONSERVATION
DIVISION OF WATER SUPPLY
6th Floor, L & C TOWER, 401 Church Street
Nashville, Tennessee 37243-1549

November 27, 2007

Ms. Debra Scheib
Paragon Analytics, Inc.
225 Commerce Drive
Fort Collins, CO 80524

Dear Ms. Scheib,

This is to confirm that the State of Tennessee Drinking Water Laboratory Certification Program has approved Paragon Analytics, Inc. (TN02976) for Drinking Water Laboratory Certification in Radiochemistry by reciprocity with the State of Colorado under the Safe Drinking Water Act.

The certification is through October 31, 2008 unless withdrawn earlier.

Results of future evaluations made by the State of Colorado and/or USEPA such as performance evaluation reports, on-site audits, certifications, or changes in personnel, etc., must be forwarded to this office. Should the State of Colorado withdraw certification of your laboratory, certification by the State of Tennessee shall likewise be revoked.

Please use the identification number TN02976 when submitting analytical data or other correspondence to this office.

If you have any question, please contact Craig LaFever at (615) 532-0181.

Sincerely,

Craig LaFever

Craig LaFever
Certification Officer
Tennessee Division of Water Supply

cc: Jeff Bagwell
Enclosure

Approved Parameters

(TENNESSEE)

Paragon Analytics, Inc. TN02976 EPA ID# CO00078 11/27/2007

Debra Scheib
225 Commerce Drive
Fort Collins, CO 80524

Parameter	EPA Parameter #	Approved Method	Study Type	Date Complete	PT Provider / WS #
Radiological					
Cesium-134 (Radioactive)	4270	EPA - 901.1	Proficiency Test	8/23/2007	ERA / RAD-70
Cesium-137 (Radioactive)	4276	EPA - 901.1	Proficiency Test	8/23/2007	ERA / RAD-70
Cobalt-60 (Radioactive)	4142	EPA - 901.1	Proficiency Test	8/23/2007	ERA / RAD-70
Gross Alpha	4000	EPA - 900.0	Proficiency Test	8/23/2007	ERA / RAD-70
Gross Beta	4100	EPA - 900.0	Proficiency Test	8/23/2007	ERA / RAD-70
Radium-226	4020	EPA - 903.0	Proficiency Test	8/23/2007	ERA / RAD-70
Radium-226	4020	EPA - 903.1	Proficiency Test	8/23/2007	ERA / RAD-70
Radium-228	4030	EPA - 904.0	Proficiency Test	8/23/2007	ERA / RAD-70
Tritium (Radioactive)	4102	EPA - 906.0	Proficiency Test	8/23/2007	ERA / RAD-70
Uranium (Radioactive)	4400	DOE - U-02	Proficiency Test	8/23/2007	ERA / RAD-70

State of Tennessee

Department of Environment & Conservation

Division of Water Supply

Certifies That

Paragon Analytics, Inc.

Having Met the Requirements of the Regulations for the Certification of Laboratories Analyzing Drinking Water is hereby Approved as a

State Certified Laboratory in Radiochemistry

To perform the Analyses as Indicated on the Certified Parameter List For the Public Water Systems of Tennessee

Laboratory ID Number TN02976 - Effective through October 31, 2008

Troy D. Taubert

Laboratory Certification Officer

Division of Water Supply

This certification is subject to performance on E.P.A. Performance Evaluation Samples, laboratory inspections and payment of annual fees

Texas Commission on Environmental Quality

NELAP - Recognized Laboratory Fields of Accreditation

ALS Laboratory Group, Environmental Division (Fort Collins, CO)
225 Commerce Drive
Fort Collins, CO 80524

Certificate T104704241-09A-TX
Issue Date: 11/1/2008
Expiration Date: 10/31/2009

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Matrix: Solid and Chemical Materials

Category / Method: EPA 6010

Analytes:	Code	AA	Analytes:	Code	AA
Aluminum	1000	UT	Antimony	1005	UT
Arsenic	1010	UT	Barium	1015	UT
Beryllium	1020	UT	Boron	1025	UT
Cadmium	1030	UT	Calcium	1035	UT
Chromium	1040	UT	Cobalt	1050	UT
Copper	1055	UT	Iron	1070	UT
Lead	1075	UT	Lithium	1080	UT
Magnesium	1085	UT	Manganese	1090	UT
Molybdenum	1100	UT	Nickel	1105	UT
Potassium	1125	UT	Selenium	1140	UT
Silica	1990	UT	Silver	1150	UT
Sodium	1155	UT	Strontium	1160	UT
Thallium	1165	UT	Tin	1175	UT
Titanium	1180	UT	Vanadium	1185	UT
Zinc	1190	UT			

Category / Method: EPA 6020

Analytes:	Code	AA	Analytes:	Code	AA
Aluminum	1000	UT	Antimony	1005	UT
Arsenic	1010	UT	Cadmium	1030	UT
Copper	1055	UT	Lead	1075	UT
Molybdenum	1100	UT	Selenium	1140	UT
Silver	1150	UT	Thallium	1165	UT
Vanadium	1185	UT			

Category / Method: EPA 7196

Analytes:	Code	AA	Analytes:	Code	AA
Chromium VI	1045	UT			

Category / Method: EPA 7471

Analytes:	Code	AA	Analytes:	Code	AA
Mercury	1095	UT			

Category / Method: EPA 8015

Analytes:	Code	AA	Analytes:	Code	AA
Diesel range organics (DRO)	9369	UT	Gasoline range organics (GRO)	9408	UT

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Matrix: Solid and Chemical Materials

Category / Method: EPA 8021

Analytes:	Code	AA	Analytes:	Code	AA
1 2-Dichlorobenzene	4610	UT	1 3-Dichlorobenzene	4615	UT
1 4-Dichlorobenzene	4620	UT	Benzene	4375	UT
Chlorobenzene	4475	UT	Ethylbenzene	4765	UT
m+p-xylene	5240	UT	Methyl tert-butyl ether (MTBE)	5000	UT
o-Xylene	5250	UT	Toluene	5140	UT
Xylene (total)	5260	UT			

Category / Method: EPA 8081

Analytes:	Code	AA	Analytes:	Code	AA
4 4`-DDD	7355	UT	4 4`-DDE	7360	UT
4 4`-DDT	7365	UT	Aldrin	7025	UT
alpha-BHC (alpha-Hexachlorocyclohexane)	7110	UT	alpha-Chlordane	7240	UT
beta-BHC (beta-Hexachlorocyclohexane)	7115	UT	delta-BHC	7105	UT
Dieldrin	7470	UT	Endosulfan I	7510	UT
Endosulfan II	7515	UT	Endosulfan sulfate	7520	UT
Endrin	7540	UT	Endrin aldehyde	7530	UT
Endrin ketone	7535	UT	gamma-BHC (Lindane gamma-Hexachlorocyclohexane)	7120	UT
Heptachlor	7685	UT	Heptachlor epoxide	7690	UT
Methoxychlor	7810	UT	Toxaphene (Chlorinated camphene)	8250	UT

Category / Method: EPA 8082

Analytes:	Code	AA	Analytes:	Code	AA
Aroclor-1016 (PCB-1016)	8880	UT	Aroclor-1221 (PCB-1221)	8885	UT
Aroclor-1232 (PCB-1232)	8890	UT	Aroclor-1242 (PCB-1242)	8895	UT
Aroclor-1248 (PCB-1248)	8900	UT	Aroclor-1254 (PCB-1254)	8905	UT
Aroclor-1260 (PCB-1260)	8910	UT			

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Matrix: Solid and Chemical Materials

Category / Method: EPA 8141

Analytes:	Code	AA	Analytes:	Code	AA
Azinphos-methyl (Guthion)	7075	UT	Bolstar (Sulprofos)	7125	UT
Chlorpyrifos	7300	UT	Coumaphos	7315	UT
Demeton-o	7395	UT	Demeton-s	7385	UT
Diazinon	7410	UT	Dichlorovos (DDVP Dichlorvos)	8610	UT
Disulfoton	8625	UT	Ethoprop	7570	UT
Fensulfothion	7600	UT	Fenthion	7605	UT
Malathion	7770	UT	Mevinphos	7850	UT
Naled	7905	UT	Parathion methyl	7825	UT
Phorate	7985	UT	Ronnel	8110	UT
Tetrachlorvinphos (Stirophos Gardona)	8200	UT	Tokuthion (Prothiophos)	8245	UT
Trichloronate	8275	UT			

Category / Method: EPA 8151

Analytes:	Code	AA	Analytes:	Code	AA
2 4 5-T	8655	UT	2 4-D	8545	UT
2 4-DB	8560	UT	Dalapon	8555	UT
Dicamba	8595	UT	Dichloroprop (Dichlorprop)	8605	UT
Dinoseb (2-sec-butyl-4 6-dinitrophenol DNBP)	8620	UT	MCPA	7775	UT
MCPP	7780	UT	Silvex (2 4 5-TP)	8650	UT

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Matrix: Solid and Chemical Materials

Category / Method: EPA 8260

Analytes:	Code	AA	Analytes:	Code	AA
1 1 1 2-Tetrachloroethane	5105	UT	1 1 1-Trichloroethane	5160	UT
1 1 2 2-Tetrachloroethane	5110	UT	1 1 2-Trichloroethane	5165	UT
1 1-Dichloroethane	4630	UT	1 1-Dichloroethylene	4640	UT
1 2 3-Trichlorobenzene	5150	UT	1 2 3-Trichloropropane	5180	UT
1 2 4-Trichlorobenzene	5155	UT	1 2 4-Trimethylbenzene	5210	UT
1 2-Dibromo-3-chloropropane (DBCP)	4570	UT	1 2-Dibromoethane (EDB Ethylene dibromide)	4585	UT
1 2-Dichlorobenzene	4610	UT	1 2-Dichloroethane	4635	UT
1 2-Dichloropropane	4655	UT	1 3-Dichlorobenzene	4615	UT
1 3-Dichloropropane	4660	UT	1 4-Dichlorobenzene	4620	UT
1-Chlorohexane	4510	UT	2 2-Dichloropropane	4665	UT
2-Butanone (Methyl ethyl ketone MEK)	4410	UT	2-Chloroethyl vinyl ether	4500	UT
2-Chlorotoluene	4535	UT	2-Hexanone	4860	UT
4-Chlorotoluene	4540	UT	4-Methyl-2-pentanone (MIBK)	4995	UT
Acetone	4315	UT	Acetonitrile	4320	UT
Acrolein (Propenal)	4325	UT	Benzene	4375	UT
Bromobenzene	4385	UT	Bromochloromethane	4390	UT
Bromodichloromethane	4395	UT	Bromoform	4400	UT
Bromomethane	4950	UT	Carbon disulfide	4450	UT
Carbon tetrachloride	4455	UT	Chlorobenzene	4475	UT
Chloroethane	4485	UT	Chloroform	4505	UT
Chloromethane	4960	UT	cis-1 2-Dichloroethylene	4645	UT
cis-1 3-Dichloropropene	4680	UT	Dibromochloromethane	4575	UT
Dibromomethane	4595	UT	Dichlorodifluoromethane	4625	UT
Ethylbenzene	4765	UT	Hexachlorobutadiene	4835	UT
Iodomethane (Methyl iodide)	4870	UT	Isopropylbenzene (cumene)	4900	UT
m+p-xylene	5240	UT	Methyl tert-butyl ether (MTBE)	5000	UT
Methylene chloride	4975	UT	Naphthalene	5005	UT
n-Butylbenzene	4435	UT	n-Propylbenzene	5090	UT
o-Xylene	5250	UT	sec-Butylbenzene	4440	UT
Styrene	5100	UT	tert-Butylbenzene	4445	UT
Tetrachloroethylene (Perchloroethylene)	5115	UT	Toluene	5140	UT
trans-1 2-Dichloroethylene	4700	UT	trans-1 3-Dichloropropylene	4685	UT
Trichloroethene (Trichloroethylene)	5170	UT	Trichlorofluoromethane	5175	UT
Vinyl acetate	5225	UT	Vinyl chloride	5235	UT
Xylene (total)	5260	UT			

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Matrix: Solid and Chemical Materials

Category / Method: EPA 8270

Analytes:	Code	AA	Analytes:	Code	AA
1 2 4-Trichlorobenzene	5155	UT	1 2-Dichlorobenzene	4610	UT
1 3-Dichlorobenzene	4615	UT	1 4-Dichlorobenzene	4620	UT
1-Chloronaphthalene	5790	UT	2 3 4 6-Tetrachlorophenol	6735	UT
2 4 5-Trichlorophenol	6835	UT	2 4 6-Trichlorophenol	6840	UT
2 4-Dichlorophenol	6000	UT	2 4-Dimethylphenol	6130	UT
2 4-Dinitrophenol	6175	UT	2 4-Dinitrotoluene (2 4-DNT)	6185	UT
2 6-Dinitrotoluene (2 6-DNT)	6190	UT	2-Chloronaphthalene	5795	UT
2-Chlorophenol	5800	UT	2-Methyl-4 6-dinitrophenol	6360	UT
2-Methylnaphthalene	6385	UT	2-Methylphenol (o-Cresol)	6400	UT
2-Nitroaniline	6460	UT	2-Nitrophenol	6490	UT
3 3`-Dichlorobenzidine	5945	UT	3-Methylphenol (m-Cresol)	6405	UT
3-Nitroaniline	6465	UT	4-Bromophenyl phenyl ether	5660	UT
4-Chloro-3-methylphenol	5700	UT	4-Chloroaniline	5745	UT
4-Chlorophenyl phenyl ether	5825	UT	4-Methylphenol (p-Cresol)	6410	UT
4-Nitroaniline	6470	UT	4-Nitrophenol	6500	UT
Acenaphthene	5500	UT	Acenaphthylene	5505	UT
Aniline	5545	UT	Anthracene	5555	UT
Benzidine	5595	UT	Benzo(a)anthracene	5575	UT
Benzo(a)pyrene	5580	UT	Benzo(b)fluoranthene	5585	UT
Benzo(g h i)perylene	5590	UT	Benzo(k)fluoranthene	5600	UT
Benzoic acid	5610	UT	Benzyl alcohol	5630	UT
bis(2-Chloroethoxy)methane	5760	UT	bis(2-Chloroethyl) ether	5765	UT
bis(2-Chloroisopropyl) ether	5780	UT	bis(2-Ethylhexyl) phthalate (DEHP)	6255	UT
Butyl benzyl phthalate	5670	UT	Carbazole	5680	UT
Chrysene	5855	UT	Dibenz(a h) anthracene	5895	UT
Dibenzofuran	5905	UT	Diethyl phthalate	6070	UT
Dimethyl phthalate	6135	UT	Di-n-butyl phthalate	5925	UT
Di-n-octyl phthalate	6200	UT	Fluoranthene	6265	UT
Fluorene	6270	UT	Hexachlorobenzene	6275	UT
Hexachlorobutadiene	4835	UT	Hexachlorocyclopentadiene	6285	UT
Hexachloroethane	4840	UT	Indeno(1,2,3-c,d)pyrene	6315	UT
Isophorone	6320	UT	Naphthalene	5005	UT
Nitrobenzene	5015	UT	n-Nitrosodimethylamine	6530	UT
n-Nitrosodi-n-propylamine	6545	UT	n-Nitrosodiphenylamine	6535	UT
Pentachlorophenol	6605	UT	Phenanthrene	6615	UT

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Fort Collins, CO 80524

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Matrix: Solid and Chemical Materials

Category / Method: EPA 8270

Phenol	6625	UT	Pyrene	6665	UT
Pyridine	5095	UT			

Category / Method: EPA 9014

Analytes:	Code	AA	Analytes:	Code	AA
Amenable cyanide	1510	UT	Cyanide, Total	1635	UT

Category / Method: EPA 9045

Analytes:	Code	AA	Analytes:	Code	AA
pH	1900	UT			

Category / Method: EPA 9056

Analytes:	Code	AA	Analytes:	Code	AA
Bromide	1540	UT	Chloride	1575	UT
Fluoride	1730	UT	Nitrate as N	1810	UT
Nitrite as N	1840	UT	Orthophosphate as P	1870	UT
Sulfate	2000	UT			

Category / Method: EPA 9071

Analytes:	Code	AA	Analytes:	Code	AA
n-Hexane Extractable Material	10219	UT			

Category / Method: EPA 9095

Analytes:	Code	AA	Analytes:	Code	AA
Paint Filter Test	10312	UT			

Category / Method: EPA 9310

Analytes:	Code	AA	Analytes:	Code	AA
Gross-alpha	2830	UT	Gross-beta	2840	UT

Matrix: Non-Potable Water

Category / Method: EPA 1010

Analytes:	Code	AA	Analytes:	Code	AA
Ignitability	1780	UT			

Category / Method: EPA 120.1

Analytes:	Code	AA	Analytes:	Code	AA
Conductivity	1610	UT			

Category / Method: EPA 150.1

Analytes:	Code	AA	Analytes:	Code	AA
pH	1900	UT			

Category / Method: EPA 160.1

Analytes:	Code	AA	Analytes:	Code	AA
Residue-filterable (TDS)	1955	UT			

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Matrix: Non-Potable Water

Category / Method: EPA 160.2

Analytes:	Code	AA	Analytes:	Code	AA
Residue-nonfilterable (TSS)	1960	UT			

Category / Method: EPA 160.3

Analytes:	Code	AA	Analytes:	Code	AA
Residue-total	1950	UT			

Category / Method: EPA 1664

Analytes:	Code	AA	Analytes:	Code	AA
n-Hexane Extractable Material	10219	UT	Silica Gel Treated n-Hexane Extractable Material	10220	UT

Category / Method: EPA 200.7

Analytes:	Code	AA	Analytes:	Code	AA
Aluminum	1000	UT	Antimony	1005	UT
Arsenic	1010	UT	Barium	1015	UT
Beryllium	1020	UT	Boron	1025	UT
Cadmium	1030	UT	Calcium	1035	UT
Chromium	1040	UT	Cobalt	1050	UT
Copper	1055	UT	Iron	1070	UT
Lead	1075	UT	Lithium	1080	UT
Magnesium	1085	UT	Manganese	1090	UT
Molybdenum	1100	UT	Nickel	1105	UT
Potassium	1125	UT	Selenium	1140	UT
Silica-dissolved	1995	UT	Silver	1150	UT
Sodium	1155	UT	Strontium	1160	UT
Thallium	1165	UT	Tin	1175	UT
Titanium	1180	UT	Vanadium	1185	UT
Zinc	1190	UT			

Category / Method: EPA 200.8

Analytes:	Code	AA	Analytes:	Code	AA
Aluminum	1000	UT	Antimony	1005	UT
Arsenic	1010	UT	Cadmium	1030	UT
Copper	1055	UT	Lead	1075	UT
Molybdenum	1100	UT	Selenium	1140	UT
Silver	1150	UT	Thallium	1165	UT
Uranium	3035	UT	Vanadium	1185	UT

Category / Method: EPA 245.1

Analytes:	Code	AA	Analytes:	Code	AA
Mercury	1095	UT			

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Matrix: Non-Potable Water

Category / Method: EPA 300.0

Analytes:	Code	AA	Analytes:	Code	AA
Bromide	1540	UT	Chloride	1575	UT
Fluoride	1730	UT	Nitrate as N	1810	UT
Nitrite as N	1840	UT	Orthophosphate as P	1870	UT
Sulfate	2000	UT			

Category / Method: EPA 310.1

Analytes:	Code	AA	Analytes:	Code	AA
Alkalinity as CaCO3	1505	UT			

Category / Method: EPA 325.3

Analytes:	Code	AA	Analytes:	Code	AA
Chloride	1575	UT			

Category / Method: EPA 335.1

Analytes:	Code	AA	Analytes:	Code	AA
Amenable cyanide	1510	UT			

Category / Method: EPA 335.2

Analytes:	Code	AA	Analytes:	Code	AA
Cyanide, Total	1635	UT			

Category / Method: EPA 340.2

Analytes:	Code	AA	Analytes:	Code	AA
Fluoride	1730	UT			

Category / Method: EPA 350.1

Analytes:	Code	AA	Analytes:	Code	AA
Ammonia as N	1515	UT			

Category / Method: EPA 353.2

Analytes:	Code	AA	Analytes:	Code	AA
Nitrate-nitrite	1820	UT			

Category / Method: EPA 354.1

Analytes:	Code	AA	Analytes:	Code	AA
Nitrite as N	1840	UT			

Category / Method: EPA 365.2

Analytes:	Code	AA	Analytes:	Code	AA
Orthophosphate as P	1870	UT	Phosphorus total	1910	UT

Category / Method: EPA 376.1

Analytes:	Code	AA	Analytes:	Code	AA
Sulfide	2005	UT			

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Matrix: Non-Potable Water

Category / Method: EPA 415.1

Analytes:	Code	AA	Analytes:	Code	AA
Total organic carbon	2040	UT			

Category / Method: EPA 6010

Analytes:	Code	AA	Analytes:	Code	AA
Aluminum	1000	UT	Antimony	1005	UT
Arsenic	1010	UT	Barium	1015	UT
Beryllium	1020	UT	Boron	1025	UT
Cadmium	1030	UT	Calcium	1035	UT
Chromium	1040	UT	Cobalt	1050	UT
Copper	1055	UT	Iron	1070	UT
Lead	1075	UT	Lithium	1080	UT
Magnesium	1085	UT	Manganese	1090	UT
Molybdenum	1100	UT	Nickel	1105	UT
Potassium	1125	UT	Selenium	1140	UT
Silica-dissolved	1995	UT	Silver	1150	UT
Sodium	1155	UT	Strontium	1160	UT
Thallium	1165	UT	Tin	1175	UT
Titanium	1180	UT	Vanadium	1185	UT
Zinc	1190	UT			

Category / Method: EPA 6020

Analytes:	Code	AA	Analytes:	Code	AA
Aluminum	1000	UT	Antimony	1005	UT
Arsenic	1010	UT	Cadmium	1030	UT
Copper	1055	UT	Lead	1075	UT
Molybdenum	1100	UT	Selenium	1140	UT
Silver	1150	UT	Thallium	1165	UT
Vanadium	1185	UT			

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Matrix: Non-Potable Water

Category / Method: EPA 608

Analytes:	Code	AA	Analytes:	Code	AA
4 4`-DDD	7355	UT	4 4`-DDE	7360	UT
4 4`-DDT	7365	UT	Aldrin	7025	UT
alpha-BHC (alpha-Hexachlorocyclohexane)	7110	UT	Aroclor-1016 (PCB-1016)	8880	UT
Aroclor-1221 (PCB-1221)	8885	UT	Aroclor-1232 (PCB-1232)	8890	UT
Aroclor-1242 (PCB-1242)	8895	UT	Aroclor-1248 (PCB-1248)	8900	UT
Aroclor-1254 (PCB-1254)	8905	UT	Aroclor-1260 (PCB-1260)	8910	UT
beta-BHC (beta-Hexachlorocyclohexane)	7115	UT	Chlordane, Technical	7250	UT
delta-BHC	7105	UT	Dieldrin	7470	UT
Endosulfan I	7510	UT	Endosulfan II	7515	UT
Endosulfan sulfate	7520	UT	Endrin	7540	UT
Endrin aldehyde	7530	UT	Endrin ketone	7535	UT
gamma-BHC (Lindane gamma-Hexachlorocyclohexane)	7120	UT	Heptachlor	7685	UT
Heptachlor epoxide	7690	UT	Methoxychlor	7810	UT
Toxaphene (Chlorinated camphene)	8250	UT			

Category / Method: EPA 615

Analytes:	Code	AA	Analytes:	Code	AA
2 4 5-T	8655	UT	2 4-D	8545	UT
2 4-DB	8560	UT	Dalapon	8555	UT
Dicamba	8595	UT	Dichloroprop (Dichlorprop)	8605	UT
Dinoseb (2-sec-butyl-4 6-dinitrophenol DNBP)	8620	UT	MCPA	7775	UT
MCPP	7780	UT	Silvex (2 4 5-TP)	8650	UT

Texas Commission on Environmental Quality

NELAP - Recognized Laboratory Fields of Accreditation

ALS Laboratory Group, Environmental Division (Fort Collins, CO)
225 Commerce Drive
Fort Collins, CO 80524

Certificate T104704241-09A-TX
Issue Date: 11/1/2008
Expiration Date: 10/31/2009

These fields of accreditation supercede all previous fields. The Texas Commission on Environmental Quality urges customers to verify the laboratory's current accreditation status for particular methods and analyses.

Matrix: Non-Potable Water

Category / Method: EPA 624

Analytes:	Code	AA	Analytes:	Code	AA
1 1 1-Trichloroethane	5160	UT	1 1 2 2-Tetrachloroethane	5110	UT
1 1 2-Trichloroethane	5165	UT	1 1-Dichloroethane	4630	UT
1 1-Dichloroethylene	4640	UT	1 2-Dibromoethane (EDB Ethylene dibromide)	4585	UT
1 2-Dichlorobenzene	4610	UT	1 2-Dichloroethane	4635	UT
1 2-Dichloropropane	4655	UT	1 3-Dichlorobenzene	4615	UT
1 4-Dichlorobenzene	4620	UT	2-Chloroethyl vinyl ether	4500	UT
Acrolein (Propenal)	4325	UT	Acrylonitrile	4340	UT
Benzene	4375	UT	Bromodichloromethane	4395	UT
Bromoform	4400	UT	Bromomethane	4950	UT
Carbon tetrachloride	4455	UT	Chlorobenzene	4475	UT
Chloroethane	4485	UT	Chloroform	4505	UT
Chloromethane	4960	UT	cis-1 3-Dichloropropene	4680	UT
Dibromochloromethane	4575	UT	Ethylbenzene	4765	UT
Methylene chloride	4975	UT	Tetrachloroethylene (Perchloroethylene)	5115	UT
Toluene	5140	UT	trans-1 2-Dichloroethylene	4700	UT
trans-1 3-Dichloropropylene	4685	UT	Trichloroethene (Trichloroethylene)	5170	UT
Trichlorofluoromethane	5175	UT	Vinyl chloride	5235	UT
Xylene (total)	5260	UT			

Texas Commission on Environmental Quality

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225 Commerce Drive
Fort Collins, CO 80524

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Matrix: Non-Potable Water

Category / Method: EPA 625

Analytes:	Code	AA	Analytes:	Code	AA
1 2 4-Trichlorobenzene	5155	UT	1 2-Dichlorobenzene	4610	UT
1 3-Dichlorobenzene	4615	UT	1 4-Dichlorobenzene	4620	UT
2 4 5-Trichlorophenol	6835	UT	2 4 6-Trichlorophenol	6840	UT
2 4-Dichlorophenol	6000	UT	2 4-Dimethylphenol	6130	UT
2 4-Dinitrophenol	6175	UT	2 4-Dinitrotoluene (2 4-DNT)	6185	UT
2 6-Dinitrotoluene (2 6-DNT)	6190	UT	2-Chloronaphthalene	5795	UT
2-Chlorophenol	5800	UT	2-Methyl-4 6-dinitrophenol	6360	UT
2-Methylphenol (o-Cresol)	6400	UT	2-Nitrophenol	6490	UT
3 3`-Dichlorobenzidine	5945	UT	4-Bromophenyl phenyl ether	5660	UT
4-Chloro-3-methylphenol	5700	UT	4-Chlorophenyl phenyl ether	5825	UT
4-Methylphenol (p-Cresol)	6410	UT	4-Nitrophenol	6500	UT
Acenaphthene	5500	UT	Acenaphthylene	5505	UT
Anthracene	5555	UT	Benzidine	5595	UT
Benzo(a)anthracene	5575	UT	Benzo(a)pyrene	5580	UT
Benzo(b)fluoranthene	5585	UT	Benzo(g h i)perylene	5590	UT
Benzo(k)fluoranthene	5600	UT	bis(2-Chloroethoxy)methane	5760	UT
bis(2-Chloroethyl) ether	5765	UT	bis(2-Chloroisopropyl) ether	5780	UT
bis(2-Ethylhexyl) phthalate (DEHP)	6255	UT	Butyl benzyl phthalate	5670	UT
Chrysene	5855	UT	Dibenz(a h) anthracene	5895	UT
Diethyl phthalate	6070	UT	Dimethyl phthalate	6135	UT
Di-n-butyl phthalate	5925	UT	Di-n-octyl phthalate	6200	UT
Fluoranthene	6265	UT	Fluorene	6270	UT
Hexachlorobenzene	6275	UT	Hexachlorobutadiene	4835	UT
Hexachlorocyclopentadiene	6285	UT	Hexachloroethane	4840	UT
Indeno(1,2,3-c,d)pyrene	6315	UT	Isophorone	6320	UT
Naphthalene	5005	UT	Nitrobenzene	5015	UT
n-Nitrosodimethylamine	6530	UT	n-Nitrosodi-n-propylamine	6545	UT
n-Nitrosodiphenylamine	6535	UT	Pentachlorophenol	6605	UT
Phenanthrene	6615	UT	Phenol	6625	UT
Pyrene	6665	UT			

Category / Method: EPA 7470

Analytes:	Code	AA	Analytes:	Code	AA
Mercury	1095	UT			

Texas Commission on Environmental Quality

NELAP - Recognized Laboratory Fields of Accreditation

ALS Laboratory Group, Environmental Division (Fort Collins, CO)
225 Commerce Drive
Fort Collins, CO 80524

Certificate T104704241-09A-TX
Issue Date: 11/1/2008
Expiration Date: 10/31/2009

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Matrix: Non-Potable Water

Category / Method: EPA 8011

Analytes:	Code	AA	Analytes:	Code	AA
1 2-Dibromo-3-chloropropane (DBCP)	4570	UT	1 2-Dibromoethane (EDB Ethylene dibromide)	4585	UT

Category / Method: EPA 8015

Analytes:	Code	AA	Analytes:	Code	AA
Diesel range organics (DRO)	9369	UT	Gasoline range organics (GRO)	9408	UT

Category / Method: EPA 8021

Analytes:	Code	AA	Analytes:	Code	AA
1 2-Dichlorobenzene	4610	UT	1 3-Dichlorobenzene	4615	UT
1 4-Dichlorobenzene	4620	UT	Benzene	4375	UT
Chlorobenzene	4475	UT	Ethylbenzene	4765	UT
Methyl tert-butyl ether (MTBE)	5000	UT	o-Xylene	5250	UT
Toluene	5140	UT	Xylene (total)	5260	UT

Category / Method: EPA 8081

Analytes:	Code	AA	Analytes:	Code	AA
4 4`-DDD	7355	UT	4 4`-DDE	7360	UT
4 4`-DDT	7365	UT	Aldrin	7025	UT
alpha-BHC (alpha-Hexachlorocyclohexane)	7110	UT	alpha-Chlordane	7240	UT
beta-BHC (beta-Hexachlorocyclohexane)	7115	UT	Dieldrin	7470	UT
Endosulfan I	7510	UT	Endosulfan II	7515	UT
Endosulfan sulfate	7520	UT	Endrin	7540	UT
Endrin aldehyde	7530	UT	Endrin ketone	7535	UT
gamma-BHC (Lindane gamma-Hexachlorocyclohexane)	7120	UT	Heptachlor	7685	UT
Heptachlor epoxide	7690	UT	Methoxychlor	7810	UT
Toxaphene (Chlorinated camphene)	8250	UT			

Category / Method: EPA 8082

Analytes:	Code	AA	Analytes:	Code	AA
Aroclor-1016 (PCB-1016)	8880	UT	Aroclor-1221 (PCB-1221)	8885	UT
Aroclor-1232 (PCB-1232)	8890	UT	Aroclor-1242 (PCB-1242)	8895	UT
Aroclor-1248 (PCB-1248)	8900	UT	Aroclor-1254 (PCB-1254)	8905	UT
Aroclor-1260 (PCB-1260)	8910	UT			

Texas Commission on Environmental Quality

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Fort Collins, CO 80524

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Matrix: Non-Potable Water

Category / Method: EPA 8141

Analytes:	Code	AA	Analytes:	Code	AA
Azinphos-methyl (Guthion)	7075	UT	Bolstar (Sulprofos)	7125	UT
Chlorpyrifos	7300	UT	Coumaphos	7315	UT
Demeton-o	7395	UT	Demeton-s	7385	UT
Diazinon	7410	UT	Dichlorovos (DDVP Dichlorvos)	8610	UT
Disulfoton	8625	UT	Ethoprop	7570	UT
Fensulfothion	7600	UT	Fenthion	7605	UT
Malathion	7770	UT	Mevinphos	7850	UT
Naled	7905	UT	Parathion methyl	7825	UT
Phorate	7985	UT	Ronnel	8110	UT
Tetrachlorvinphos (Stirophos Gardona)	8200	UT	Tokuthion (Prothiophos)	8245	UT
Trichloronate	8275	UT			

Category / Method: EPA 8151

Analytes:	Code	AA	Analytes:	Code	AA
2 4 5-T	8655	UT	2 4-D	8545	UT
2 4-DB	8560	UT	Dalapon	8555	UT
Dicamba	8595	UT	Dichloroprop (Dichlorprop)	8605	UT
Dinoseb (2-sec-butyl-4 6-dinitrophenol DNBP)	8620	UT	MCPA	7775	UT
MCPP	7780	UT	Silvex (2 4 5-TP)	8650	UT

Texas Commission on Environmental Quality

NELAP - Recognized Laboratory Fields of Accreditation

ALS Laboratory Group, Environmental Division (Fort Collins, CO)
225 Commerce Drive
Fort Collins, CO 80524

Certificate T104704241-09A-TX
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Expiration Date: 10/31/2009

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Matrix: Non-Potable Water

Category / Method: EPA 8260

Analytes:	Code	AA	Analytes:	Code	AA
1 1 1 2-Tetrachloroethane	5105	UT	1 1 1-Trichloroethane	5160	UT
1 1 2 2-Tetrachloroethane	5110	UT	1 1 2-Trichloroethane	5165	UT
1 1-Dichloroethane	4630	UT	1 1-Dichloroethylene	4640	UT
1 1-Dichloropropene	4670	UT	1 2 3-Trichlorobenzene	5150	UT
1 2 3-Trichloropropane	5180	UT	1 2 4-Trichlorobenzene	5155	UT
1 2 4-Trimethylbenzene	5210	UT	1 2-Dibromo-3-chloropropane (DBCP)	4570	UT
1 2-Dibromoethane (EDB Ethylene dibromide)	4585	UT	1 2-Dichlorobenzene	4610	UT
1 2-Dichloroethane	4635	UT	1 2-Dichloropropane	4655	UT
1 3 5-Trimethylbenzene	5215	UT	1 3-Dichlorobenzene	4615	UT
1 3-Dichloropropane	4660	UT	1 4-Dichlorobenzene	4620	UT
1-Chlorohexane	4510	UT	2 2-Dichloropropane	4665	UT
2-Butanone (Methyl ethyl ketone MEK)	4410	UT	2-Chloroethyl vinyl ether	4500	UT
2-Chlorotoluene	4535	UT	2-Hexanone	4860	UT
4-Chlorotoluene	4540	UT	4-Methyl-2-pentanone (MIBK)	4995	UT
Acetone	4315	UT	Acetonitrile	4320	UT
Acrolein (Propenal)	4325	UT	Acrylonitrile	4340	UT
Benzene	4375	UT	Bromobenzene	4385	UT
Bromochloromethane	4390	UT	Bromodichloromethane	4395	UT
Bromoform	4400	UT	Bromomethane	4950	UT
Carbon disulfide	4450	UT	Carbon tetrachloride	4455	UT
Chlorobenzene	4475	UT	Chloroethane	4485	UT
Chloroform	4505	UT	Chloromethane	4960	UT
cis-1 2-Dichloroethylene	4645	UT	cis-1 3-Dichloropropene	4680	UT
Dibromochloromethane	4575	UT	Dibromomethane	4595	UT
Dichlorodifluoromethane	4625	UT	Ethylbenzene	4765	UT
Hexachlorobutadiene	4835	UT	Iodomethane (Methyl iodide)	4870	UT
Isopropylbenzene (cumene)	4900	UT	m+p-xylene	5240	UT
Methyl tert-butyl ether (MTBE)	5000	UT	Methylene chloride	4975	UT
Naphthalene	5005	UT	n-Butylbenzene	4435	UT
n-Propylbenzene	5090	UT	o-Xylene	5250	UT
sec-Butylbenzene	4440	UT	Styrene	5100	UT
tert-Butylbenzene	4445	UT	Tetrachloroethylene (Perchloroethylene)	5115	UT
Toluene	5140	UT	trans-1 2-Dichloroethylene	4700	UT
trans-1 3-Dichloropropylene	4685	UT	Trichloroethene (Trichloroethylene)	5170	UT
Trichlorofluoromethane	5175	UT	Vinyl acetate	5225	UT

Texas Commission on Environmental Quality

NELAP - Recognized Laboratory Fields of Accreditation

ALS Laboratory Group, Environmental Division (Fort Collins, CO)
225 Commerce Drive
Fort Collins, CO 80524

Certificate T104704241-09A-TX
Issue Date: 11/1/2008
Expiration Date: 10/31/2009

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Matrix: Non-Potable Water

Category / Method: EPA 8260

Vinyl chloride	5235	UT	Xylene (total)	5260	UT

Texas Commission on Environmental Quality

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225 Commerce Drive
Fort Collins, CO 80524

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Issue Date: 11/1/2008
Expiration Date: 10/31/2009

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Matrix: Non-Potable Water

Category / Method: EPA 8270

Analytes:	Code	AA	Analytes:	Code	AA
1 2 4-Trichlorobenzene	5155	UT	1 2-Dichlorobenzene	4610	UT
1 3-Dichlorobenzene	4615	UT	1 4-Dichlorobenzene	4620	UT
1-Chloronaphthalene	5790	UT	2 3 4 6-Tetrachlorophenol	6735	UT
2 4 5-Trichlorophenol	6835	UT	2 4 6-Trichlorophenol	6840	UT
2 4-Dimethylphenol	6130	UT	2 4-Dinitrophenol	6175	UT
2 4-Dinitrotoluene (2 4-DNT)	6185	UT	2 6-Dinitrotoluene (2 6-DNT)	6190	UT
2-Chloronaphthalene	5795	UT	2-Chlorophenol	5800	UT
2-Methyl-4 6-dinitrophenol	6360	UT	2-Methylnaphthalene	6385	UT
2-Methylphenol (o-Cresol)	6400	UT	2-Nitroaniline	6460	UT
2-Nitrophenol	6490	UT	3 3`-Dichlorobenzidine	5945	UT
3-Methylphenol (m-Cresol)	6405	UT	3-Nitroaniline	6465	UT
4-Bromophenyl phenyl ether	5660	UT	4-Chloro-3-methylphenol	5700	UT
4-Chloroaniline	5745	UT	4-Chlorophenyl phenyl ether	5825	UT
4-Methylphenol (p-Cresol)	6410	UT	4-Nitroaniline	6470	UT
4-Nitrophenol	6500	UT	Acenaphthene	5500	UT
Acenaphthylene	5505	UT	Aniline	5545	UT
Anthracene	5555	UT	Benzidine	5595	UT
Benzo(a)anthracene	5575	UT	Benzo(b)fluoranthene	5585	UT
Benzo(e)pyrene	5605	UT	Benzo(g h i)perylene	5590	UT
Benzo(k)fluoranthene	5600	UT	Benzoic acid	5610	UT
Benzyl alcohol	5630	UT	bis(2-Chloroethoxy)methane	5760	UT
bis(2-Chloroethyl) ether	5765	UT	bis(2-Chloroisopropyl) ether	5780	UT
bis(2-Ethylhexyl) phthalate (DEHP)	6255	UT	Butyl benzyl phthalate	5670	UT
Carbazole	5680	UT	Chrysene	5855	UT
Dibenz(a h) anthracene	5895	UT	Dibenzofuran	5905	UT
Diethyl phthalate	6070	UT	Dimethyl phthalate	6135	UT
Di-n-butyl phthalate	5925	UT	Di-n-octyl phthalate	6200	UT
Fluoranthene	6265	UT	Fluorene	6270	UT
Hexachlorobenzene	6275	UT	Hexachlorobutadiene	4835	UT
Hexachlorocyclopentadiene	6285	UT	Hexachloroethane	4840	UT
Indeno(1,2,3-c,d)pyrene	6315	UT	Isophorone	6320	UT
Naphthalene	5005	UT	Nitrobenzene	5015	UT
n-Nitrosodiethylamine	6525	UT	n-Nitrosodi-n-propylamine	6545	UT
n-Nitrosodiphenylamine	6535	UT	Pentachlorophenol	6605	UT
Phenanthrene	6615	UT	Phenol	6625	UT

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Matrix: Non-Potable Water

Category / Method: EPA 8270

Pyrene	6665	UT	Pyridine	5095	UT

Category / Method: EPA 900

Analytes:	Code	AA	Analytes:	Code	AA
Gross-alpha	2830	UT	Gross-beta	2840	UT

Category / Method: EPA 9014

Analytes:	Code	AA	Analytes:	Code	AA
Amenable cyanide	1510	UT	Cyanide, Total	1635	UT

Category / Method: EPA 903

Analytes:	Code	AA	Analytes:	Code	AA
Total radium	2975	UT			

Category / Method: EPA 903.1

Analytes:	Code	AA	Analytes:	Code	AA
Radium-226	2965	UT			

Category / Method: EPA 9040

Analytes:	Code	AA	Analytes:	Code	AA
pH	1900	UT			

Category / Method: EPA 9050

Analytes:	Code	AA	Analytes:	Code	AA
Conductivity	1610	UT			

Category / Method: EPA 9056

Analytes:	Code	AA	Analytes:	Code	AA
Bromide	1540	UT	Chloride	1575	UT
Fluoride	1730	UT	Nitrate as N	1810	UT
Nitrite as N	1840	UT	Orthophosphate as P	1870	UT
Sulfate	2000	UT			

Category / Method: EPA 9060

Analytes:	Code	AA	Analytes:	Code	AA
Total organic carbon	2040	UT			

Category / Method: EPA 9214

Analytes:	Code	AA	Analytes:	Code	AA
Fluoride	1730	UT			

Category / Method: SM 2340 B

Analytes:	Code	AA	Analytes:	Code	AA
Total hardness as CaCO3	1755	UT			

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Matrix: Non-Potable Water

Category / Method: SM 4500-NH3 H

Analytes:	Code	AA	Analytes:	Code	AA
Ammonia as N	1515	UT			

Category / Method: SM 4500-P E

Analytes:	Code	AA	Analytes:	Code	AA
Phosphorus total	1910	UT			

Category / Method: SM 5310C

Analytes:	Code	AA	Analytes:	Code	AA
Total organic carbon	2040	UT			

From: "Deb Scheib" <dscheib@paragonlabs.com>
To: "(TX) Jamison, Frank" <fjamison@tceq.state.tx.us>
Date: 11/19/2008 5:31 PM
Subject: Notification of Paragon Acquisition / Name Change
Attachments: Acquisition Announcement.pdf

Frank -

Please accept this e-mail as official notification that effective 11/1/08, DataChem (of which Paragon is a part of) was purchased by ALS Laboratory Group (owned overall by Campbell Brothers, Ltd., Australia). Please see the acquisition announcement on letterhead attached. Paragon was able to bring extensive environmental and radiochemistry capabilities to ALS; in addition to the Environmental Division, ALS has Mineral, Coal, Tribology, Food/Pharma, and Electronics/Consumer Divisions. I am confident that ALS Paragon will be able to accomplish great things together.

Please note that Datachem was purchased as an intact entity - there have been no changes to equipment or staffing, including key personnel.

We'll be known as ALS Paragon for awhile, transitioning fully to ALS Environmental Division (Fort Collins, CO) by March 31st. To that end, please re-issue our current certification as ALS Laboratory Group, Environmental Division (Fort Collins, CO), at your convenience. Additionally, I would appreciate your referencing us as 'formerly Paragon Analytics, a Division of DataChem Laboratories, Inc.' in the cover letter.

Please don't hesitate to let me know if you have any questions or concerns.

Best Regards,

Deb

PARAGON ANALYTICS
A Division of DataChem Laboratories, Inc.

ALS Laboratory Group
ANALYTICAL CHEMISTRY & TESTING SERVICES

November 1, 2008

We are pleased and excited to announce that Paragon (a division of DataChem Laboratories, Inc.) has been acquired by the ALS Laboratory Group, North America, based in Houston, Texas. Paragon is now part of the global ALS Laboratory Group, offering a greater range of analytical chemistry all around the world.

Paragon is a recognized quality leader and is one of the largest providers of environmental, industrial hygiene, and radiochemistry testing services in the U.S. Paragon has clients throughout the U.S. and enjoys a nationwide reputation for producing quality and legally defensible data.

We want to assure Paragon's clients that senior management, technical managers, project managers, and our highly trained chemists and scientists will remain with the company. We are committed to the continued success and geographic expansion of our business; which has developed into one of the most successful environmental, industrial hygiene, and radiochemistry laboratories consistently delivering the highest level of performance. We will continue to honor all pricing and service arrangements you have with Paragon. As a group, we will be going forward with ALS Laboratory Group to combine the best aspects of both companies into a stronger network of laboratories that will continue to excel as your preferred laboratory partner. We will continue to provide you a high level of service and legally defensible data.

With this union, Paragon joins a most impressive global network of environmental laboratories which now includes 51 locations spread around the globe. These countries include Canada, Mexico, Chile, Peru, Australia, China, Indonesia, Malaysia, Singapore, Taiwan, Sweden, Czech Republic, Denmark, Norway, and the U.S.; all providing clients with superior analytical and technical support for local and international projects. The ALS Laboratory Group is a diverse, global company with 117 laboratories operating in 35 countries staffed by over 6,000 employees. In addition to environmental services, the ALS Laboratory Group offers a broad range of sophisticated state-of-the-art services to four main market segments including: mining and mineral exploration, equipment maintenance through used lubricant analysis, commodity analysis and certification, and environmental monitoring. The ALS Laboratory Group is part of a long established Australian public company, Campbell Brothers Limited which has operated service-oriented businesses for over 130 years.

If you have any questions, please do not hesitate to contact the following:

Ken Campbell	Laboratory Director and Vice President—Ft. Collins, CO	(970) 490-1511	kcampbell@paragonlabs.com
Ken Olson	DataChem President and CEO	(801) 266-7700	olsonk@datachem.com

We look forward to continuing to work with you.

Regards,
Ken R. Olson, President and CEO—DataChem Laboratories, Inc.

www.datachem.com
www.alsglobal.com

Right solutions....
....Right partner

DataChem Laboratories, Inc.
Part of the ALS Laboratory Group
225 Commerce Drive Ft. Collins, Colorado 80524
Phone (970) 490 1511 Fax (970) 490 1522 www.paragonlabs.com www.alsenviro.com
A Campbell Brothers Limited Company

Texas Commission on Environmental Quality

NELAP-Recognized Laboratory Accreditation is hereby awarded to

ALS LABORATORY GROUP, ENVIRONMENTAL DIVISION (FORT COLLINS, CO)
225 COMMERCE DRIVE
FORT COLLINS, CO 80524

in accordance with Texas Water Code Chapter 5, Subchapter R, Title 30 Texas Administrative Code Chapter 25, and the National Environmental Laboratory Accreditation Program.

The laboratory's scope of accreditation includes the fields of accreditation that accompany this certificate. Continued accreditation depends upon successful ongoing participation in the program. The Texas Commission on Environmental Quality urges customers to verify the laboratory's current accreditation status for particular methods and analyses.

Certificate Number: T104704241-09A-TX
Effective Date: 11/1/2008
Expiration Date: 10/31/2009

Executive Director
Texas Commission on Environmental Quality

State of Utah
JON HUNTSMAN Jr.
Governor
GARY HERBERT
Lieutenant Governor

Utah Department of Health
David N. Sundwall, MD
Executive Director

Epidemiology and Laboratory Services
Patrick F. Luedtke, MD, MPH.
Director of Public Health Laboratories

Bureau of Laboratory Improvement
David B Mendenhall, MPA, MT (ASCP)
Bureau Director

NELAP
Recognized

7/9/2008

Paragon Analytics
Ken Campbell
225 Commerce Drive
Fort Collins CO 80524

ID # ATL2
EPA ID: CO00078

Director,

On the basis of your most recent assessment, Proficiency Testing results and continuing compliance with the ELCP requirements, the laboratory listed is certified for environmental monitoring under the Safe Drinking Water Act and authorized to perform the following methods, for the analytes and matrix listed:

Drinking Water

Inorganics and Metals

120.1 [1982]	Conductivity
150.1 [1982]	pH
160.1 [1971]	Residue, Filterable
200.7 [1994]	Aluminum
200.7 [1994]	Antimony
200.7 [1994]	Arsenic
200.7 [1994]	Barium
200.7 [1994]	Beryllium
200.7 [1994]	Boron
200.7 [1994]	Cadmium
200.7 [1994]	Calcium
200.7 [1994]	Chromium
200.7 [1994]	Cobalt
200.7 [1994]	Iron
200.7 [1994]	Lithium
200.7 [1994]	Magnesium
200.7 [1994]	Manganese
200.7 [1994]	Molybdenum
200.7 [1994]	Nickel
200.7 [1994]	Potassium
200.7 [1994]	Selenium
200.7 [1994]	Silica
200.7 [1994]	Silver
200.7 [1994]	Sodium
200.7 [1994]	Strontium
200.7 [1994]	Thallium
200.7 [1994]	Tin
200.7 [1994]	Titanium
200.7 [1994]	Vanadium

The expiration for the laboratory's certification is 6/30/2009. The Utah Environmental Laboratory Certification Program (ELCP) encourages clients and data users to verify the most current certification letter for the authorized method. For further assistance please call 801-584-8469.

Inorganics and Metals

200.7 [1994]	Zinc
200.8 [1994]	Aluminum
200.8 [1994]	Antimony
200.8 [1994]	Arsenic
200.8 [1994]	Cadmium
200.8 [1994]	Selenium
200.8 [1994]	Silver
200.8 [1994]	Thallium
200.8 [1994]	Uranium
200.8 [1994]	Vanadium
200.8 [1994]	Molybdenum
2320 B [20th ED	Alkalinity - Titration Method [20th ED]
2340 B [20th ED	Hardness by Calculation (CaCO3) [20th ED]
245.1 [1994]	Mercury
2510 B [20th ED	Conductivity by Laboratory Method [20th ED]
2540 B [20th ED	Total Solids [20th ED]
2540 C [20th ED	Total Dissolved Solids [20th ED]
2540 D [20th ED	Total Suspended Solids [20th ED]
300.0	Bromide
300.0	Chloride
300.0	Fluoride
300.0	Ortho-Phosphate
310.1 [1978]	Alkalinity
314.0 [1999]	Perchlorate
331.0	Perchlorate
4500 (H+) B [20t	pH [20th ED]
5310 C [20th ED	TOC by Persulfate-Ultraviolet Oxidation Method [20th ED]

Nitrate

300.0	Nitrate

Nitrite

300.0	Nitrite

Pb/Cu

200.7 [1994]	Copper
200.7 [1994]	Lead
200.8 [1994]	Copper
200.8 [1994]	Lead

Radionuclides

4.5.2.3	Gamma Emitters Gamma Ray Spectrometry Technique
900.0	Gross Alpha & Beta Radioactivity in Drinking Water Evaporation Technique
900.0	Gross Alpha
900.0	Gross Beta
901.1	Gamma Emitting Radionuclidies in Drinking Water
903.0	Alpha-Emitting Radium Isotopes in Drinking Water
903.0	Radium 226
903.0	Total Radium
903.1	Radium 226 in Drinking Water Radon Emanation Technique
904.0	Radium 228 in Drinking Water Radiochemical Technique
906.0	Tritium in Drinking Water Liquid Scintillation Technique
ASTM D5811-95	Strontium 90
D-3972-90	Uranium Alpha Spectrometry Technique
SR-01	Strontium 89/90 Radiochemical Technique
SR-02	Strontium 89/90 Radiochemical Technique
U 02	Uranium Alpha Spectrometry Technique

Sulfates

300.0	Sulfate

The effective date of this certificate letter is: 7/1/2008.

The analytes by method which a laboratory is authorized to perform at any given time will be those indicated in the most recent certificate letter. The most recent certification letter supersedes all previous certification or authorization letters. It is the certified laboratory's responsibility to review this letter for discrepancies. The certified laboratory must document any discrepancies in this letter and send notice to this bureau within 15 days of receipt. This certificate letter will be recalled in the event your laboratory's certification is revoked.

Respectfully,

Barbara R. Jepson for Luedtke

Patrick F. Luedtke, MD, MPH.
Director of Public Health Laboratories
Deputy Director of Epidemiology and Laboratory Services

Utah Department of Health

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Patrick F. Luedtke, MD, MPH.
Director of Public Health Laboratories

Bureau of Laboratory Improvement
David B Mendenhall, MPA, MT (ASCP)
Bureau Director

NELAP
Recognized

7/9/2008

Paragon Analytics
Ken Campbell
225 Commerce Drive
Fort Collins CO 80524

ID # ATL2
EPA ID: CO00078

Director,

On the basis of your most recent assessment, Proficiency Testing results and continuing compliance with the ELCP requirements, the laboratory listed is certified for environmental monitoring under the Clean Water Act and authorized to perform the following methods, for the analytes and matrix listed:

Non-Potable Water

Inorganics and Metals

120.1 [1982]	Conductance (Specific Conductance, umhos at 25-C)
150.1 [1982]	pH (Electometric)
160.1 [1971]	Residue, Filterable (Gravimetric, Dried at 180-C)
160.2 [1971]	Residue, Non-Filterable (Gravimetric, Dried at 103-105-C)
160.3 [1971]	Residue, Total (Gravimetric, Dried at 103-105-C)
1664 A [1999]	Oil & Grease and Total Petroleum Hydrocarbons
200.7 [1994]	Aluminum
200.7 [1994]	Antimony
200.7 [1994]	Arsenic
200.7 [1994]	Barium
200.7 [1994]	Beryllium
200.7 [1994]	Boron
200.7 [1994]	Cadmium
200.7 [1994]	Calcium
200.7 [1994]	Chromium, Total
200.7 [1994]	Cobalt
200.7 [1994]	Copper
200.7 [1994]	Iron
200.7 [1994]	Lead
200.7 [1994]	Lithium
200.7 [1994]	Magnesium
200.7 [1994]	Manganese
200.7 [1994]	Molybdenum
200.7 [1994]	Nickel
200.7 [1994]	Potassium
200.7 [1994]	Selenium
200.7 [1994]	Silica
200.7 [1994]	Silver
200.7 [1994]	Sodium
200.7 [1994]	Strontium

The expiration for the laboratory's certification is 6/30/2009. The Utah Environmental Laboratory Certification Program (ELCP) encourages clients and data users to verify the most current certification letter for the authorized method. For further assistance please call 801-584-8469.

Inorganics and Metals

200.7 [1994]	Thallium
200.7 [1994]	Tin
200.7 [1994]	Titanium
200.7 [1994]	Vanadium
200.7 [1994]	Zinc
200.7 [1994]	Hardness
200.8 [1994]	Aluminum
200.8 [1994]	Antimony
200.8 [1994]	Arsenic
200.8 [1994]	Cadmium
200.8 [1994]	Copper
200.8 [1994]	Lead
200.8 [1994]	Molybdenum
200.8 [1994]	Selenium
200.8 [1994]	Silver
200.8 [1994]	Thallium
200.8 [1994]	Uranium
200.8 [1994]	Vanadium
2320 B [20th ED	Alkalinity (Titration) [SM 20th ED]
2340 B [20th ED	Hardness (Calculation) [SM 20th ED]
245.1 [1994]	Mercury
2510 B [20th ED	Conductivity (Laboratory) [SM 20th ED]
2540 B [20th ED	Total Solids Dried at 103-105-C [SM 20th ED]
2540 C [20th ED	Total Dissolved Solids Dried at 180-C [SM 20th ED]
2540 D [20th ED	Total Suspended Solids Dried at 103-105-C [SM 20th ED]
300.0 [1993]	Bromide
300.0 [1993]	Chloride
300.0 [1993]	Fluoride
300.0 [1993]	Nitrate
300.0 [1993]	Nitrite
300.0 [1993]	ortho-Phosphate
300.0 [1993]	Sulfate
310.1 [1978]	Alkalinity
335.1 [1974]	Cyanides, Amenable To Chlorination
335.2 [1980]	Cyanide, Total
340.2 [1974]	Fluoride
350.1 [1993]	Nitrogen, Ammonia
3500 (Cr) B [20t	Chromium VI (Colorimetric) [SM 20th ED]
3500 (Cr) D [19t	Chromium VI (Colorimetric) [SM 19th ED]
353.2 [1993]	Nitrogen, Nitrate-Nitrite
354.1 [1971]	Nitrogen, Nitrite
365.2 [1971]	Phosphorous, Total
365.2 [1971]	Ortho-Phosphate
376.1 [1978]	Sulfide
415.1 [1974]	Organic Carbon, Total
4500 (CN-) C [20	Total Cyanide after Distillation [SM 20th ED]
4500 (CN-) E [20	Cyanide (Colorimetric) [SM 20th ED]
4500 (CN-) G [2	Cyanides Amenable to Chlorination after Distillation [SM 20th ED]
4500 (F-) C [20th	Fluoride (Ion-Selective Electrode) [SM 20th ED]
4500 (H+) B [20t	pH (Electrometric) [SM 20th ED]
4500 (NH3) H [2	Nitrogen (Ammonia) (Phenate, Automated) [SM 20th ED]
4500 (NO2-) B [2	Nitrogen (Nitrite, Colorimetric) [SM 20th ED]
4500 (P) E [20th	Phosphorus, Total (Ascorbic Acid) [SM 20th ED]
4500 (P) E [20th	Ortho-Phosphate (Ascorbic Acid) [SM 20th ED]

Inorganics and Metals

4500 (S2-) F [20t	Sulfide (Calculation of Un-ionized Hydrogen Sulfide) [SM 20th ED]
4500-NH3 H [18t	Nitrogen, Ammonia [18th ED] (Automated Phenate Method)
5310 C [20th ED	Total Organic Carbon (Persulfate-Ultraviolet Oxidation) [SM 20th ED]
6850	Perchlorate

Organics

608	Organochlorine Pesticides and Polychlorinated Biphenyls
608	Aldrin
608	alpha-BHC
608	beta-BHC
608	delta-BHC
608	gamma-BHC (Lindane)
608	Chlordane
608	Chlordane (Technical)
608	4,4'-DDD
608	4,4'-DDE
608	4,4'-DDT
608	Dieldrin
608	Endosulfan I
608	Endosulfan II
608	Endosulfan Sulfate
608	Endrin
608	Endrin Aldehyde
608	Endrin Ketone
608	Heptachlor
608	Heptachlor Epoxide
608	Methoxychlor
608	Toxaphene
608	Aroclor 1016
608	Aroclor 1221
608	Aroclor 1232
608	Aroclor 1242
608	Aroclor 1248
608	Aroclor 1254
608	Aroclor 1260
615	Chlorinated Herbicides in Industrial and Municipal Wastewater
615	2,4-D
615	Dalapon
615	2,4-DB
615	Dicamba
615	Dichlorprop
615	Dinoseb
615	MCPA
615	MCPP
615	2,4,5-T
615	2,4,5-TP (Silvex)
624	Purgeables
624	Acrolein
624	Acrylonitrile
624	Benzene
624	Bromodichloromethane
624	Bromoform
624	Bromomethane
624	Carbon Tetrachloride
624	Chlorobenzene

Organics

624	Chloroethane
624	2-Chloroethylvinyl Ether
624	Chloroform
624	Chloromethane
624	Dibromochloromethane
624	1,2-Dibromo-3-chloropropane (DBCP)
624	1,2-Dibromoethane (EDB)
624	Dibromomethane
624	1,2-Dichlorobenzene
624	1,3-Dichlorobenzene
624	1,4-Dichlorobenzene
624	1,1-Dichloroethane
624	1,2-Dichloroethane
624	1,1-Dichloroethene
624	trans-1,2-Dichloroethene
624	1,2-Dichloropropane
624	cis-1,3-Dichloropropene
624	trans-1,3-Dichloropropene
624	Ethylbenzene
624	Dichloromethane (DCM, Methylene chloride)
624	1,1,1,2-Tetrachloroethane
624	1,1,2,2-Tetrachloroethane
624	Tetrachloroethylene
624	Toluene
624	1,1,1-Trichloroethane
624	1,1,2-Trichloroethane
624	Trichloroethene
624	Trichlorofluoromethane
624	Vinyl Chloride
624	Xylenes, total
625	Base/Neutrals and Acids
625	Acenaphthene
625	Acenaphthylene
625	Anthracene
625	Aniline
625	Benzidine
625	Benzo(a)anthracene
625	Benzo(b)fluoranthene
625	Benzo(k)fluoranthene
625	Benzo(g,h,i)perylene
625	Benzo(a)pyrene
625	Benzyl alcohol
625	Benzyl Butyl Phthalate
625	bis(2-Chloroethyl)ether
625	bis(2-Chloroethoxy)methane
625	bis(2-Ethylhexyl)phthalate
625	bis(2-Chloroisopropyl)ether
625	4-Bromophenyl Phenyl Ether
625	4-Chloroaniline
625	2-Chloronaphthalene
625	4-Chlorophenyl Phenyl Ether
625	Chrysene
625	Dibenz(a,h)anthracene
625	Dibenzofuran

Organics	
625	Di-n-butylphthalate
625	1,2-Dichlorobenzene
625	1,3-Dichlorobenzene
625	1,4-Dichlorobenzene
625	3,3'-Dichlorobenzidine
625	Diethyl phthalate
625	Dimethyl phthalate
625	2,4-Dinitrotoluene
625	2,6-Dinitrotoluene
625	Di-n-octylphthalate
625	Fluoranthene
625	Fluorene
625	Hexachlorobenzene
625	Hexachlorobutadiene
625	Hexachlorocyclopentadiene
625	Hexachloroethane
625	Indeno(1,2,3-cd)pyrene
625	Isophorone
625	2-Methylnaphthalene
625	2-Methylphenol
625	3-Methylphenol
625	Naphthalene
625	m-Nitroaniline
625	o-Nitroaniline
625	p-Nitroaniline
625	Nitrobenzene
625	N-Nitrosodimethylamine
625	N-Nitrosodi-n-propylamine
625	N-Nitrosodiphenylamine
625	Phenanthrene
625	Pyrene
625	1,2,4-Trichlorobenzene
625	4-Chloro-3-methylphenol
625	2-Chlorophenol
625	2,4-Dichlorophenol
625	2,4-Dimethylphenol
625	2,4-Dinitrophenol
625	2-Methyl- 4,6-dinitrophenol
625	2-Nitrophenol
625	4-Nitrophenol
625	Pentachlorophenol
625	Phenol
625	2,4,5-Trichlorophenol
625	2,4,6-Trichlorophenol
625	Carbazole
Radiological	
7500 (3H) B	Tritium
7500 (Ra) C	Radium by Emanation
900.0	Gross Alpha
900.0	Gross Beta
901.1	Photon Emitters
903.0	Radium
903.0	radium-226
903.1	radium-226

The expiration for the laboratory's certification is 6/30/2009. The Utah Environmental Laboratory Certification Program (ELCP) encourages clients and data users to verify the most current certification letter for the authorized method. For further assistance please call 801-584-8469.

Radiological

904.0	radium-228
906	Tritium
Sr 02	strontium-90
U 02	uranium

The effective date of this certificate letter is: 7/1/2008.

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Respectfully,

Barbara R. Jepson for Dr. Luedtke

Patrick F. Luedtke, MD, MPH.
Director of Public Health Laboratories
Deputy Director of Epidemiology and Laboratory Services

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Bureau Director

NELAP
Recognized

7/9/2008

Paragon Analytics
Ken Campbell
225 Commerce Drive
Fort Collins CO 80524

ID # ATL2
EPA ID: CO00078

Director,

On the basis of your most recent assessment, Proficiency Testing results and continuing compliance with the ELCP requirements, the laboratory listed is certified for environmental monitoring under the Resource Conservation and Recovery Act and authorized to perform the following methods, for the analytes and matrix listed:

Characteristics

	Solid	Non-Potable Water	
1010 A	☐	☑	Ignitability
1311	☑	☐	Toxicity Characteristic Leaching Procedure Metals
1311	☑	☐	Toxicity Characteristic Leaching Procedure Semi-Volatiles
1311	☑	☐	Toxicity Characteristic Leaching Procedure Volatiles
1312	☑	☐	Synthetic Precipitation Leaching Procedure (TCLP Approval)
Sec 7.3.3	☑	☐	Reactive Cyanide
Sec 7.3.4	☑	☐	Reactive Sulfide
Sec 8.3	☑	☐	Reactivity

Inorganics

	Solid	Non-Potable Water	
1664 A [199	☐	☑	Oil & Grease
6850	☑	☑	Perchlorate
9010 B	☑	☑	Cyanide Distillation Procedure
9013	☑	☐	Cyanide Extraction Procedure for Solids and Oils
9014	☑	☑	Cyanide
9040 B	☐	☑	pH
9045 C	☑	☐	Soil and Waste pH
9050 A	☐	☑	Specific Conductance
9056 [1996]	☑	☑	Bromide
9056 [1996]	☑	☑	Chloride
9056 [1996]	☑	☑	Fluoride
9056 [1996]	☑	☑	Nitrate
9056 [1996]	☑	☑	Nitrite
9056 [1996]	☑	☑	Ortho Phosphate
9056 [1996]	☑	☑	Sulfates

The expiration for the laboratory's certification is 6/30/2009. The Utah Environmental Laboratory Certification Program (ELCP) encourages clients and data users to verify the most current certification letter for the authorized method. For further assistance please call 801-584-8469.

Inorganics

	Solid	Non-Potable Water	
9060	☐	☑	Total Organic Carbon
9071 B [199	☑	☐	Oil and Grease Extraction Method for Sludge and Sediment Samples
9095 A	☑	☐	Paint Filter Liquids Test
9214	☐	☑	Fluoride

Metal Digestion

	Solid	Non-Potable Water	
3005 A	☐	☑	Acid Digestion Total Recoverable or Dissolved Metals
3010 A	☐	☑	Acid Digestion for Total Metals
3050 B	☑	☐	Acid Digestion of Sediments, Sludges and Soils
3060 A	☑	☐	Alkaline Digestion for Hexavalent Chromium

Metals

	Solid	Non-Potable Water	
6010 B	☑	☑	Aluminum
6010 B	☑	☑	Antimony
6010 B	☑	☑	Arsenic
6010 B	☑	☑	Barium
6010 B	☑	☑	Beryllium
6010 B	☑	☑	Boron
6010 B	☑	☑	Cadmium
6010 B	☑	☑	Calcium
6010 B	☑	☑	Chromium
6010 B	☑	☑	Cobalt
6010 B	☑	☑	Copper
6010 B	☑	☑	Iron
6010 B	☑	☑	Lead
6010 B	☑	☑	Lithium
6010 B	☑	☑	Magnesium
6010 B	☑	☑	Manganese
6010 B	☑	☑	Molybdenum
6010 B	☑	☑	Nickel
6010 B	☑	☑	Potassium
6010 B	☑	☑	Selenium
6010 B	☑	☑	Silica
6010 B	☑	☑	Silicon
6010 B	☑	☑	Silver
6010 B	☑	☑	Sodium
6010 B	☑	☑	Strontium
6010 B	☑	☑	Thallium
6010 B	☑	☑	Tin
6010 B	☑	☑	Titanium
6010 B	☑	☑	Vanadium
6010 B	☑	☑	Zinc
6020 A	☑	☑	Aluminum
6020 A	☑	☑	Antimony
6020 A	☑	☑	Arsenic
6020 A	☑	☑	Cadmium
6020 A	☑	☑	Copper

Metals

	Solid	Non-Potable Water	
6020 A	☑	☑	Lead
6020 A	☑	☑	Molybdenum
6020 A	☑	☑	Selenium
6020 A	☑	☑	Silver
6020 A	☑	☑	Thallium
6020 A	☑	☑	Uranium
6020 A	☑	☑	Vanadium
7196 A	☑	☑	Chromium, Hexavalent (Chromium, VI)
7470 A	☐	☑	Mercury
7471 A	☑	☐	Mercury

Organic Cleanup

	Solid	Non-Potable Water	
3620 B	☑	☑	Florisil Cleanup
3630 C	☑	☑	Silica Gel Cleanup
3640 A	☑	☑	Gel Permeation Cleanup
3660 A	☑	☑	Sulfur Cleanup

Organic Extraction

	Solid	Non-Potable Water	
3510 C	☐	☑	Separatory Funnel Liquid-Liquid Extractions
3520 C	☐	☑	Continuous Liquid-Liquid Extraction
3540 C	☑	☐	Soxhlet Extraction
3580 A	☑	☐	Waste Dilution

Organic Instrumentation

	Solid	Non-Potable Water	
8011	☐	☑	1,2-Dibromo-3-chloropropane (DBCP, Dibromochloropropane)
8011	☐	☑	1,2-Dibromoethane (EDB, Ethylene dibromide)
8015 B	☑	☑	Diesel Range Organics (DROs)
8015 B	☑	☑	Gasoline Range Organics (GROs)
8015 B	☑	☑	Nonhalogenated Organics Using GC/FID
8021 B	☑	☑	1,2-Dichlorobenzene
8021 B	☑	☑	1,3-Dichlorobenzene
8021 B	☑	☑	1,4-Dichlorobenzene
8021 B	☑	☑	Aromatic and Halogenated Volatiles
8021 B	☑	☑	Benzene
8021 B	☑	☑	Chlorobenzene
8021 B	☑	☑	Ethylbenzene
8021 B	☑	☑	meta-Xylene
8021 B	☑	☑	Methyl-t-Butyl Ether (MTBE)
8021 B	☑	☑	ortho-Xylene
8021 B	☑	☑	para-Xylene
8021 B	☑	☑	Toluene
8021 B	☑	☑	Xylenes, Total
8081 A	☑	☑	4,4'-DDD
8081 A	☑	☑	4,4'-DDE
8081 A	☑	☑	4,4'-DDT
8081 A	☑	☑	Aldrin

Organic Instrumentation

	Solid	Non-Potable Water	
8081 A	☑	☑	alpha-BHC(alpha-hexachlorocyclohexane)
8081 A	☑	☑	alpha-Chlordane
8081 A	☑	☑	beta-BHC(beta-hexachlorocyclohexane)
8081 A	☑	☑	Chlordane (technical)
8081 A	☑	☑	Chlordane, total
8081 A	☑	☑	delta-BHC(delta-hexachlorocyclohexane)
8081 A	☑	☑	Dieldrin
8081 A	☑	☑	Endosulfan I
8081 A	☑	☑	Endosulfan II
8081 A	☑	☑	Endosulfan sulfate
8081 A	☑	☑	Endrin
8081 A	☑	☑	Endrin Aldehyde
8081 A	☑	☑	Endrin Ketone
8081 A	☑	☑	gamma-BHC (Lindane, gamma-hexachlorocyclohexane)
8081 A	☑	☑	gamma-Chlordane
8081 A	☑	☑	Heptachlor
8081 A	☑	☑	Heptachlor Epoxide
8081 A	☑	☑	Methoxychlor
8081 A	☑	☑	Organochlorine Pesticides
8081 A	☑	☑	Toxaphene [Chlorinated camphene]
8082	☑	☑	Aroclor-1016 [PCB-1016]
8082	☑	☑	Aroclor-1221 PCB-1221]
8082	☑	☑	Aroclor-1232 [PCB-1232]
8082	☑	☑	Aroclor-1242 [PCB-1242]
8082	☑	☑	Aroclor-1248 [PCB-1248]
8082	☑	☑	Aroclor-1254 [PCB-1254]
8082	☑	☑	Aroclor-1260 [PCB-1260]
8082	☑	☑	PCBs
8141 A	☑	☑	Azinphos methyl (Guthion)
8141 A	☑	☑	Bolstar (Sulprofos)
8141 A	☑	☑	Chlorpyrifos
8141 A	☑	☑	Coumaphos
8141 A	☑	☑	Demeton-o
8141 A	☑	☑	Demeton-s
8141 A	☑	☑	Diazinon
8141 A	☑	☑	Dichlorovos [DDVP]
8141 A	☑	☑	Disulfoton
8141 A	☑	☑	Ethoprop
8141 A	☑	☑	Fensulfothion
8141 A	☑	☑	Fenthion
8141 A	☑	☑	Malathion
8141 A	☑	☑	Merphos
8141 A	☑	☑	Mevinphos
8141 A	☑	☑	Naled
8141 A	☑	☑	Organophosphorus Compounds
8141 A	☑	☑	Parathion, methyl
8141 A	☑	☑	Phorate
8141 A	☑	☑	Ronnel
8141 A	☑	☑	Tetrachlorvinphos [Stirophos, Gardona]
8141 A	☑	☑	Tokuthion [Prothiophos]
8141 A	☑	☑	Trichloronate

Organic Instrumentation

	Solid	Non-Potable Water	
8151 A	☑	☑	2,4,5-T
8151 A	☑	☑	2,4,5-TP (Silvex)
8151 A	☑	☑	2,4-D
8151 A	☑	☑	2,4-DB
8151 A	☑	☑	Chlorinated Herbicides
8151 A	☑	☑	Dalapon
8151 A	☑	☑	Dicamba
8151 A	☑	☑	Dichlorprop(Dichloroprop)
8151 A	☑	☑	Dinoseb (DNBP, 2-sec-butyl-4,6-dinitrophenol)
8151 A	☑	☑	MCPA
8151 A	☑	☑	MCPP
8260 B	☑	☑	1,1,1,2-Tetrachloroethane
8260 B	☑	☑	1,1,1-Trichloroethane
8260 B	☑	☑	1,1,2,2-Tetrachloroethane
8260 B	☑	☑	1,1,2-Trichloroethane
8260 B	☑	☑	1,1-Dichloroethane
8260 B	☑	☑	1,1-Dichloroethylene (-ethene)
8260 B	☑	☑	1,1-Dichloropropene
8260 B	☑	☑	1,2,3-Trichlorobenzene
8260 B	☑	☑	1,2,3-Trichloropropane
8260 B	☑	☑	1,2,4-Trichlorobenzene
8260 B	☑	☑	1,2,4-Trimethylbenzene
8260 B	☑	☑	1,2-Dibromo-3-chloropropane (DBCP, Dibromochloropropane)
8260 B	☑	☑	1,2-Dibromoethane (EDB, Ethylene dibromide)
8260 B	☑	☑	1,2-Dichlorobenzene
8260 B	☑	☑	1,2-Dichloroethane
8260 B	☑	☑	1,2-Dichloropropane
8260 B	☑	☑	1,3,5-Trimethylbenzene
8260 B	☑	☑	1,3-Dichlorobenzene
8260 B	☑	☑	1,3-Dichloropropane
8260 B	☑	☑	1,4-Dichlorobenzene
8260 B	☑	☑	1,4-Dioxane (1,3-Diethyleneoxide)
8260 B	☑	☑	1-Chlorohexane
8260 B	☑	☑	2,2-Dichloropropane
8260 B	☑	☑	2-Chloroethyl Vinyl Ether
8260 B	☑	☑	2-Chlorotoluene
8260 B	☑	☑	2-Hexanone
8260 B	☑	☑	4-Chlorotoluene
8260 B	☑	☑	4-Methyl-2-pentanone (MIBK, Isopropylacetone, Hexone)
8260 B	☑	☑	Acetone
8260 B	☑	☑	Acetonitrile
8260 B	☑	☑	Acrolein (Propenal)
8260 B	☑	☑	Acrylonitrile
8260 B	☑	☑	Benzene
8260 B	☑	☑	Bromobenzene
8260 B	☑	☑	Bromochloromethane
8260 B	☑	☑	Bromodichloromethane
8260 B	☑	☑	Bromoform
8260 B	☑	☑	Carbon Disulfide
8260 B	☑	☑	Carbon Tetrachloride
8260 B	☑	☑	Chlorobenzene

Organic Instrumentation

	Solid	Non-Potable Water	
8260 B	☑	☑	Chlorodibromomethane [Dibromochloromethane]
8260 B	☑	☑	Chloroethane
8260 B	☑	☑	Chloroform
8260 B	☑	☑	cis-1,2-Dichloroethene (-ethylene)
8260 B	☑	☑	cis-1,3-dichloropropene
8260 B	☑	☑	Dibromomethane
8260 B	☑	☑	Dichlorodifluoromethane
8260 B	☑	☑	Dichloromethane (DCM, Methylene chloride)
8260 B	☑	☑	Ethanol
8260 B	☑	☑	Ethylbenzene
8260 B	☑	☑	Hexachlorobutadiene
8260 B	☑	☑	Iodomethane (Methyl iodide)
8260 B	☑	☑	Isopropylbenzene
8260 B	☑	☑	meta-Xylene
8260 B	☑	☑	Methyl bromide [Bromomethane]
8260 B	☑	☑	Methyl chloride [Chloromethane]
8260 B	☑	☑	Methyl Ethyl Ketone (MEK, 2-Butanone)
8260 B	☑	☑	Methyl-t-Butyl Ether (MTBE)
8260 B	☑	☑	Naphthalene
8260 B	☑	☑	n-Butylbenzene
8260 B	☑	☑	n-Propylbenzene
8260 B	☑	☑	ortho-Xylene
8260 B	☑	☑	para-Xylene
8260 B	☑	☑	p-Isopropyltoluene
8260 B	☑	☑	sec-Butylbenzene
8260 B	☑	☑	Styrene
8260 B	☑	☑	tert-Butylbenzene
8260 B	☑	☑	Tetrachloroethylene (Perchloroethylene -ethene)
8260 B	☑	☑	Toluene
8260 B	☑	☑	trans-1,2-Dichloroethylene (-ethene)
8260 B	☑	☑	trans-1,3-Dichloropropylene (-propene)
8260 B	☑	☑	Trichloroethene (Trichloroethylene)
8260 B	☑	☑	Trichlorofluoromethane
8260 B	☑	☑	Vinyl Acetate
8260 B	☑	☑	Vinyl Chloride
8260 B	☑	☑	Volatile Organic Compounds
8260 B	☑	☑	Xylenes, Total
8270 D	☑	☑	1,2,4-Trichlorobenzene
8270 D	☑	☑	1,2-Dichlorobenzene
8270 D	☑	☑	1,3-Dichlorobenzene
8270 D	☑	☑	1,4-Dichlorobenzene
8270 D	☑	☑	2,3,4,6-Tetrachlorophenol
8270 D	☑	☑	2,4,5-Trichlorophenol
8270 D	☑	☑	2,4,6-Trichlorophenol
8270 D	☑	☑	2,4-Dichlorophenol
8270 D	☑	☑	2,4-Dimethylphenol
8270 D	☑	☑	2,4-Dinitrophenol
8270 D	☑	☑	2,4-Dinitrotoluene (2,4-DNT)
8270 D	☑	☑	2,6-Dinitrotoluene (2,6-DNT)
8270 D	☑	☑	2-Chloronaphthalene
8270 D	☑	☑	2-Methyl-4,6-dinitrophenol (4,6-Dinitro-2-methylphenol)

Organic Instrumentation

	Solid	Non-Potable Water	
8270 D	☑	☑	2-Methylnaphthalene
8270 D	☑	☑	2-Methylphenol (o-cresol, 2-Hydroxytoluene)
8270 D	☑	☑	2-Nitroaniline
8270 D	☑	☑	2-Nitrophenol
8270 D	☑	☑	3,3'-Dichlorobenzidine
8270 D	☑	☑	3-Methylphenol (m-cresol, 3-Hydroxytoluene)
8270 D	☑	☑	3-Nitroaniline
8270 D	☑	☑	4-Bromophenyl Phenyl Ether
8270 D	☑	☑	4-Chloro-3-methylphenol
8270 D	☑	☑	4-Chloroaniline
8270 D	☑	☑	4-Chlorophenyl Phenyl Ether
8270 D	☑	☐	4-Methylphenol (p-cresol, 4-Hydroxytoluene)
8270 D	☑	☑	4-Nitroaniline
8270 D	☑	☑	4-Nitrophenol
8270 D	☑	☑	Acenaphthene
8270 D	☑	☑	Acenaphthylene
8270 D	☑	☑	Aniline
8270 D	☑	☑	Anthracene
8270 D	☑	☑	Benzo(a)anthracene
8270 D	☑	☑	Benzo(a)pyrene
8270 D	☑	☑	Benzo(b)fluoranthene
8270 D	☑	☑	Benzo(g,h,i)perylene
8270 D	☑	☑	Benzo(k)fluoranthene
8270 D	☑	☑	Benzoic Acid
8270 D	☑	☑	Benzyl alcohol
8270 D	☑	☑	bis(2-chloroethoxy)methane
8270 D	☑	☑	bis(2-Chloroethyl)ether
8270 D	☑	☑	bis(2-chloroisopropyl)ether
8270 D	☑	☑	bis(2-Ethylhexyl) phthalate (DEHP)
8270 D	☑	☑	Butyl Benzyl Phthalate
8270 D	☑	☑	Chrysene
8270 D	☑	☑	Dibenzo(a,h)anthracene
8270 D	☑	☑	Dibenzofuran
8270 D	☑	☑	Diethyl Phthalate
8270 D	☑	☑	Dimethyl Phthalate
8270 D	☑	☑	Di-n-butyl phthalate
8270 D	☑	☑	Di-n-octyl Phthalate
8270 D	☑	☑	Fluoranthene
8270 D	☑	☑	Fluorene
8270 D	☑	☑	Hexachlorobenzene
8270 D	☑	☑	Hexachlorobutadiene
8270 D	☑	☑	Hexachlorocyclopentadiene
8270 D	☑	☑	Hexachloroethane
8270 D	☑	☑	Indeno(1,2,3-cd)pyrene
8270 D	☑	☑	Isophorone
8270 D	☑	☑	Naphthalene
8270 D	☑	☑	Nitrobenzene
8270 D	☑	☑	n-Nitrosodimethylamine
8270 D	☑	☑	n-Nitroso-di-n-Propylamine
8270 D	☑	☑	n-Nitrosodiphenylamine
8270 D	☑	☑	Pentachlorophenol

Organic Instrumentation

	Solid	Non-Potable Water	
8270 D	☑	☑	Phenanthrene
8270 D	☑	☑	Phenol
8270 D	☑	☑	Pyrene
8270 D	☑	☑	Semivolatile Organic Compounds
8330	☑	☑	1,3,5-Trinitrobenzene (1,3,5-TNB)
8330	☑	☑	1,3-Dinitrobenzene (1,3-DNB)
8330	☑	☑	2,4,6-Trinitrotoluene (2,4,6-TNT)
8330	☑	☑	2,4-Dinitrotoluene (2,4-DNT)
8330	☑	☑	2,6-Dinitrotoluene (2,6-DNT)
8330	☑	☑	2-Amino-4,6-Dinitrotoluene (2-Am-DNT)
8330	☑	☑	2-Nitrotoluene (2-NT)
8330	☑	☑	3-Nitrotoluene (3-NT)
8330	☑	☑	4-Amino-2,6-Dinitrotoluene (4-Am-DNT)
8330	☑	☑	4-Nitrotoluene (4-NT)
8330	☑	☑	Hexahydro-1, 3, 5-tritro-1, 3, 5-triazine (RDX)
8330	☑	☑	Methyl-2,4,6-Trinitrophenylnitramine (TETRYL)
8330	☑	☑	Nitroaromatics and Nitramines
8330	☑	☑	Nitrobenzene
8330	☑	☑	Nitroglycerin
8330	☑	☑	Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine (HMX)
8330	☑	☑	Pentaerythrite tetranitrate (PETN)
8332	☑	☑	Nitroglycerine
8332	☑	☑	Nitroglycerine By HPLC

Radiochemistry

	Solid	Non-Potable Water	
9310	☑	☑	Gross Alpha and Gross Beta
9315	☑	☑	Alpha Emit Radium Isotope
9320	☑	☑	Radium 228

Volatile Organic Preparation

	Solid	Non-Potable Water	
5030 C	☐	☑	Purge-and-Trap for Aqueous Samples
5035A	☑	☐	Purge-and-Trap and Extraction for Volatile Organics

The effective date of this certificate letter is: 7/1/2008.

The analytes by method which a laboratory is authorized to perform at any given time will be those indicated in the most recent certificate letter. The most recent certification letter supersedes all previous certification or authorization letters. It is the certified laboratory's responsibility to review this letter for discrepancies. The certified laboratory must document any discrepancies in this letter and send notice to this bureau within 15 days of receipt. This certificate letter will be recalled in the event your laboratory's certification is revoked.

Respectfully,

Barbara R. Jepson for Dr. Luedtke

Patrick F. Luedtke, MD, MPH.

Director of Public Health Laboratories
Deputy Director of Epidemiology and Laboratory Services

State of Utah
JON HUNTSMAN Jr.
Governor
GARY HERBERT
Lieutenant Governor

Utah Department of Health
David N. Sundwall, MD
Executive Director

Epidemiology and Laboratory Services
Patrick F. Luedtke, MD, MPH.
Director of Public Health Laboratories

Bureau of Laboratory Improvement
David B Mendenhall, MPA, MT (ASCP)
Bureau Director

NELAP
Recognized

STATE OF UTAH
DEPARTMENT OF HEALTH

ENVIRONMENTAL LABORATORY CERTIFICATION PROGRAM

CERTIFICATION

is hereby granted to

Paragon Analytics

225 Commerce Drive
Fort Collins CO 80524

Scope of accreditiation is limited to the
State of Utah Accredited Fields of Accreditiation
Which accompanies this Certificate

Continued accredited status depends on successful
Ongoing particitpation in the program

EPA Number: CO00078
Expiration Date: 6/30/2009

Barbara R. Jepson for Dr. Luedtke
Patrick F. Luedtke, MD, MPH.
Director of Public Health Laboratories
Deputy Director of Epidemiology and Laboratory Services

State of Utah
JON HUNTSMAN Jr.
Governor
~~GARY HERBERT~~
Lieutenant Governor

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Bureau of Laboratory Improvement
David B Mendenhall, MPA, MT (ASCP)
Bureau Director

NELAP Recognized

7/9/2008

Paragon Analytics
Ken Campbell
225 Commerce Drive
Fort Collins CO 80524

ID # ATL2
EPA ID: CO00078

The following parameters have been requested but certification was not granted or was removed due to PT compliance factors, or for other reasons:

Clean Water Act

Method	Analyte
625	4-Methylphenol

Last PT study was over 13 months ago.

RCRA

Method	Solid	NP Water	Analyte
8270 D	☐	☑	4-Methylphenol (p-cresol, 4-Hydroxytoluene)

Last PT study was over 13 months ago.

Safe Drinking Water Act

Method	Analyte

If your laboratory feels that there is an error with these parameters which have not been included on your certificate, please contact your assessor within 15 days of receipt of this letter.

EPA Number: CO00078
Expiration Date: 6/30/2009
The effective date of this certificate letter is: 7/1/2008.

Utah Department of Health
46 North Medical Drive • Salt Lake City, UT 84113-1105 • phone (801) 584-8469 • fax (801) 584-8501
www.health.utah.gov/els/labimp/

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
PO Box 488 • Manchester, WA 98353-0488 • (360) 895-6144

November 20, 2008

Ms. Debra Scheib
ALS Lab Group, Environmental Division (Fort Collins)
225 Commerce Drive
Fort Collins, CO80524-1416

Dear Ms. Scheib:

Per your request a new Certificate and Scope of Accreditation have been issued and are enclosed to reflect the ownership change for your laboratory, formerly Paragon Analytics, a Division of DataChem Laboratories, Inc. We wish you success in your new situation.

If you have any further comments or questions please feel free to contact Lee Fearon in our office at (360) 895-6146 or at his e-mail address of lfea461@ecy.wa.gov.

Sincerely,

Stewart M. Lombard
Lab Accreditation Unit Supervisor

Enclosures: 1. Certificate
2. Scope of Accreditation

Scope of Accreditation

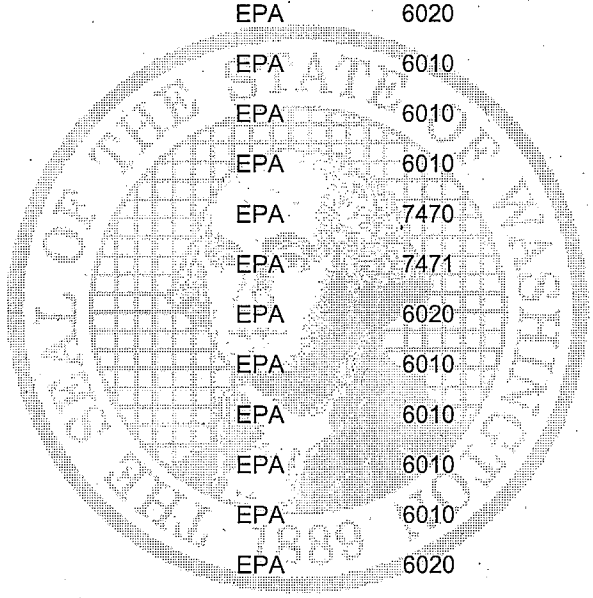
ALS Lab Group, Environmental Division (Fort Collins)

Fort Collins, CO

is accredited by the State of Washington Department of Ecology to perform analyses for the parameters listed below using the analytical methods indicated. This Scope of Accreditation may apply to any of the following matrix types: non-potable water, drinking water, solid and chemical materials, and air and emissions. Accreditation for all parameters is final unless indicated otherwise in a note. Accreditation is for the latest version of a method unless otherwise specified in a note. EPA refers to the U.S. Environmental Protection Agency. SM refers to American Public Health Association's publication, Standard Methods for the Examination of Water and Wastewater, 18th, 19th or 20th Edition, unless otherwise noted. ASTM stands for the American Society for Testing and Materials. PSEP stands for Puget Sound Estuary Program. Other references are detailed in the notes section.

Matrix Type/Parameter Name	Reference	Method Number	Notes
Non-potable Water			
Alpha, Gross	EPA	900.0	1
Beta, Gross	EPA	900.0	1
Gamma Emitting Isotopes	EPA	901.1	1
Radium 226	EPA	903.0	1
Radium 226	EPA	903.1	1
Radium 228	EPA	904.0	1
Strontium 89/90	DOE	Sr-02	1,3
Tritium	EPA	906.0	1
Uranium	DOE	U-02	1
Solid and Chemical Materials			
Chromium, Hexavalent	EPA	7196	1
Aluminum	EPA	6020	1
Aluminum	EPA	6010	1
Antimony	EPA	6010	1
Antimony	EPA	6020	1
Arsenic	EPA	6010	1
Arsenic	EPA	6020	1
Barium	EPA	6010	1
Beryllium	EPA	6010	1

Matrix Type/Parameter Name	Reference	Method Number	Notes
Boron	EPA	6010	1
Cadmium	EPA	6020	1
Cadmium	EPA	6010	1
Calcium	EPA	6010	1
Chromium	EPA	6010	1
Cobalt	EPA	6010	1
Copper	EPA	6020	1
Copper	EPA	6010	1
Iron	EPA	6010	1
Lead	EPA	6010	1
Lead	EPA	6020	1
Lithium	EPA	6010	1
Magnesium	EPA	6010	1
Manganese	EPA	6010	1
Mercury, Liquid Waste	EPA	7470	1
Mercury, Solid Waste	EPA	7471	1
Molybdenum	EPA	6020	1
Molybdenum	EPA	6010	1
Nickel	EPA	6010	1
Potassium	EPA	6010	1
Selenium	EPA	6010	1
Selenium	EPA	6020	1
Silica	EPA	6010	1
Silver	EPA	6020	1
Silver	EPA	6010	1
Sodium	EPA	6010	1
Strontium	EPA	6010	1
Thallium	EPA	6020	1
Thallium	EPA	6010	1
Tin	EPA	6010	1



Matrix Type/Parameter Name	Reference	Method Number	Notes
Titanium	EPA	6010	1
Uranium	EPA	6020 Mod	1
Vanadium	EPA	6010	1
Vanadium	EPA	6020	1
Zinc	EPA	6010	1
Organochlorine Pesticides	EPA	8081	1
Polychlorinated Biphenyls	EPA	8082	1
BNA Extr (Semivolatile) Organics	EPA	8270	1, 2
Volatile Organic Compounds	EPA	8260	1
Alpha, Gross	EPA	9310	1
Beta, Gross	EPA	9310	1
Radium 228	EPA	9320	1
Radium Alpha Emiting Isotopes	EPA	9315	1

Accredited Parameter Note Detail

(1) Accreditation based in part on recognition of Utah NELAP accreditation. (2) Method has been modified to use lower concentrations of surrogate compounds than specified in the method. (3) Only Sr 90 is determined.

S M Lombard — November 20, 2008

Authentication Signature — Date

Stewart M. Lombard, Lab Accreditation Unit Supervisor

The State of Washington Department of Ecology

This is to certify that

ALS Lab Group, Environmental Division (Fort Collins)
Fort Collins, CO

has complied with provisions set forth in Chapter 173-50 WAC and is hereby recognized by the Department of Ecology as an ACCREDITED LABORATORY for the analytical parameters listed on the accompanying Scope of Accreditation. This certificate is effective February 3, 2008, and shall expire February 2, 2009.

Witnessed under my hand on November 20, 2008.

Stewart M. Lombard

Stewart M. Lombard
Lab Accreditation Unit Supervisor

Laboratory ID
C1280

Radioactive Materials License

STATE OF COLORADO

Bill Ritter, Jr., Governor
James B. Martin, Executive Director

Dedicated to protecting and improving the health and environment of the people of Colorado

4300 Cherry Creek Dr. S.
Denver, Colorado 80246-1530
Phone (303) 692-2000
TDD Line (303) 691-7700
Located in Glendale, Colorado

http://www.cdphe.state.co.us

Laboratory Services Division
8100 Lowry Blvd.
Denver, Colorado 80230-6928
(303) 692-3090

Colorado Department
of Public Health
and Environment

SEP 1 2 2007

Paragon Analytics, Inc.
225 Commerce Drive
Fort Collins, CO 80524

Attention: Charles Orchard, Radiation Safety Officer

Enclosed is Radioactive Materials License Number Colo. 847-02, Amendment No. 12. Please review this document thoroughly. This amendment incorporates changes requested in the renewal application dated May 21, 2007.

Please note that the Radiation Management Program may be contacted during business hours at (303) 692-3423 and that our 24-hour emergency phone number is (303) 877-9757. This Department must be notified in the event that your company has an emergency or accident involving radioactive materials in Colorado.

If you have any questions regarding your license or this letter, please contact Tom Pentecost of this Division at (303) 692-3458.

Steve Tarlton, Unit Leader
Radiation Management Unit
Hazardous Materials and Waste Management Division

Enclosures: Radioactive Materials License

State of Colorado
Department of Public Health and Environment

RADIOACTIVE MATERIALS LICENSE

Pursuant to the *Colorado Radiation Control Act*, Title 25, Article 11, *Colorado Revised Statutes*, and the State of Colorado *Rules and Regulations Pertaining to Radiation Control* (the Regulations) and in reliance on statements and representations heretofore made by the licensee designated below; a license is hereby issued authorizing such licensee to transfer, receive, possess and use the radioactive material(s) designated below; and to use such radioactive material(s) for the purpose(s) and at the place(s) designated below. This license is subject to all applicable rules, regulations, and orders now or hereafter in effect of the Colorado Department of Public Health and Environment and to any conditions specified below.

---

1. **Licensee: Paragon Analytics a Division of DataChem Laboratories**
   dba: Paragon Analytics

2. Address: 225 Commerce Drive, Fort Collins, Colorado 80524

3. Colorado License Number 847-02, Amendment Number: 12

4. Expiration date: June 30, 2012

5. Reference Number: Fee Category: 3.M

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6. Radioactive materials (element and mass no.)	7. Chemical and/or physical form	8. Maximum quantity licensee may possess at any one time
A. Hydrogen-3	A. Any	A. 1.85 GBq (50 mCi)
B. Any radioactive material with atomic numbers 3-83	B. Any	B. 370 MBq (10 mCi)
C. Any radioactive material with atomic number 84-100	C. Any	C. 370 MBq (10 mCi)
D. Source Material	D. Any	D. 37 MBq (1 mCi)
E. Any radioactive material with atomic numbers 3-98	E Sealed Sources	E. 187 MBq (5 mCi) total, no single source to exceed 1.48 MBq (40 μCi)

RADIOACTIVE MATERIALS LICENSE

CONDITIONS

9. Radioactive material authorized in Items 6.A. through 6.D. may be received in the form of environmental samples (such as soil, water, vegetation, milk, and building debris, etc.) for radiochemical analysis. Radioactive material authorized in Items 6.A. through 6.D. may also be received and used as reference standards in the analytical procedures.

10. Radioactive materials authorized in Item 6.E. is limited to commercially distributed radioactive standards and/or calibration sources to be used for the calibration and checks of analytical equipment.

11. Radioactive material may be used and stored only at 225 Commerce Drive, Fort Collins, Colorado, 80524.

12. The licensee shall comply with the provisions of the State of Colorado *Rules and Regulations Pertaining to Radiation Control*, Part 4, "Standards for Protection Against Radiation", and Part 10, "Notices, Instructions and Reports to Workers: Inspections".

13. Radioactive material shall be used by, or under the supervision of Steven Workman, Lance Steere, Charles Orchard, Renee Gallegos, or Rebecca Schwab.

14. The designated Radiation Safety Officer is Charles Orchard.

15. Radioactive material authorized by Item 6 of this license shall be stored and used in a manner that will preclude possession or use by unauthorized personnel.

16. Each sealed source containing radioactive material authorized in Item 6 shall be tested for leakage and/or contamination in accordance with RH 4.16 of the State of Colorado *Rules and Regulations Pertaining to Radiation Control* at intervals not to exceed six months.

17. The licensee shall not transfer possession and/or control of radioactive material or products containing radioactive material as a contaminant except by transfer of waste to an authorized recipient; by transfer to a specifically licensed recipient; or as provided otherwise by specific condition of this license pursuant to the requirements of Section 3.22 of the Regulations.

18. Wipe tests for contamination must be completed weekly when radioactive materials are used.

19. The analysis of the wipes must be capable of detecting 20 disintegrations per minute (DPM) of alpha emitting radioactive material and 200 DPM of beta/gamma emitting radioactive material on the test sample.

RADIOACTIVE MATERIALS LICENSE

20. If an area survey or wipe test detects the presence of radioactive materials in excess of the limits specified below, then the area and/or affected equipment shall be decontaminated until:

    A. the removable contamination is not greater than: 20 DPM (alpha) per 100 cm2 and 200 DPM (beta/gamma) per 100 cm2.

    B. the average fixed contamination is not greater than: 100 DPM (alpha) per 100 cm2 and 1000 DPM (beta/gamma) per 100 cm2.

    C. the maximum fixed contamination is not greater than 300 DPM (alpha) per 100 cm2 and 3000 DPM (beta/gamma) per 100 cm2.

21. The licensee shall maintain records of surveys and wipe tests for contamination, waste disposal, and the analysis of liquid process wastes disposed of via the sewer.

22. The licensee shall maintain in effect a decommissioning financial warranty acceptable to the Department in accordance with the requirements of Part 3, Section 3.9.5 of the Regulations.

23. The State of Colorado *Rules and Regulations Pertaining to Radiation Control* shall govern the licensee's statements in applications or letters, unless the licensee's statements are more restrictive than the regulations. Except as specifically provided otherwise by this license, the licensee shall possess and use radioactive material described in Item 6 of this license in accordance with statements, representations, and procedures contained in:

    A. the application and attachments dated May 21, 2007; and

    B. the license correspondence and attachments received June 7, 2007; August 23, 2007; and

    C. the Irrevocable Standby Letter of Credit Number NZS535426, dated January 14, 2005, in the amount of $250,000.00, issued by Wells Fargo Bank, N.A., Trade Services Division, Northern California, One Front Street 21st Floor, San Francisco, California 94111.

FOR THE COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVIRONMENT

Date: 9/12/07 By: _____

Comments:

- Paragon Analytics is also a listed radiochemistry laboratory with the State of Indiana (Phillip Zillinger 317-921-5571)

- The certifications and licenses depicted herein represent the suite of certifications that Paragon maintains. In some cases, expired certificates are shown to indicate that re-application has been submitted, and receipt of updated certification is pending.

APPENDIX F
OFF-SITE LABORATORY STANDARD OPERATING PROCEDURES

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Paragon Analytics

SOP Table of Contents

SOP	Scheduled Date for Review	Title	Notes	Author
001-049 SAFETY/WASTE				
001 R7	11/15/2010	Treatment of Quarantined Soils, Aqueous Extracts, and Solid Residues and Cleaning Containers Used To Store Quarantined Sample Materials	re-released w/o revision 3/9/09	CRO
002 R7	8/15/2009	Laboratory Fume Hood Velocity Monitoring	re-released w/o revision 10/2/07	CRO
003 R5	9/15/2009	Management of Nonradioactive Hazardous Waste		CRO
008 R8	1/15/2011	Initial Receipt of Radioactive Samples and External Radiation Exposure Rate and Removeable Radioactive Material Contamination Survey of Incoming Radioactive Material Packages	re-released w/o revision 3/9/09	CRO
009 R7	1/15/2011	Incoming Radioactive Material Packages That Exceed Removable Radioactive Material Contamination Limits	re-released w/o revision 3/9/09; upon next rev., combine with 008?	CRO
010 R4	7/15/2010	Survey of Laboratory Areas for Radioactive Contamination	re-released w/o revision 7/20/08	CRO
012 R6	7/15/2010	Contamination Surveys using Portable Survey Meters (Electra, Micro Roentgen)	CONTAINS OPERATOR AID! re-released w/o revision 7/20/08	CRO
015 R6	9/15/2009	Disposal of Radioactive Waste		CRO
016 R6	8/15/2009	Electron Capture Detector Leak Tests		JFN
017 R5	1/15/2011	Effluent Monitoring and Release	re-released w/o revision 3/9/09	CRO
024 R3	8/15/2010	Disposal of Short Lived Radionuclides by Decay in Storage	re-released w/o revision 3/9/09	CRO
026 R2	8/15/2010	Radioactive Materials Inventory Control Using LIMS	re-released w/o revision 3/9/09	CRO
027 R1	11/15/2010	Packaging Samples for Return to Client	re-released w/o revision 3/9/09	CRO
029 R2	7/15/2009	Calibration and Use of the Berthold LB 1043 AS Hand and Foot Monitors		CRO
030 R1	11/15/2009	Operation of the Rampactor Compactor	re-released w/o revision 2/29/08	CRO
050-099 DATA REPORTING				
052 R8	9/15/2008	Data Package Review Procedures for Stable Chemistry Methods		EXK
069 R8	9/15/2010	Managing and Archiving Client Workorders and Records, and Retrieving Archived Information	re-released without revision 3/12/09	DAS

This pdf is updated periodically. Trust the individual SOP postings as more updated information. 3/14/09 DAS

SOP	Scheduled Date for Review	Title	Notes	Author
100-199 ADMINISTRATION				
103 R7	8/15/2009	Qualification and Use of Subcontract Laboratories		DAS
127 R9	2/15/2010	Procurement of Supplies and Materials, Including Radioactive Materials, and Evaluation of Purchased Items Received		DAS
132 R6	1/15/2011	Building Security	re-released w/o revision 3/9/09	CRO
143 R4	10/15/2009	New Employee Quality Assurance Orientation and Training	Add HS overview next revision	DAS
200-299 SAMPLE CONTROL				
202 R10	12/15/2010	Login and Distribution of Samples and Workorders	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed); re-published to the lab 12/24/08	CRO
205 R8	11/15/2011	Preparation of Bottle Orders, Shipping Sample Kits, and Maintaining Inventory of Bottles, Preservatives, and Labels	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed); re-released w/o revision 3/9/09	CRO
210 R6	11/15/2011	Use and Calibration Verification of Infrared Temperature Guns	re-released w/o revision 3/9/09	CRO
300-399 GENERAL CHEMISTRY				
300 R13	3/15/2010	Standards, Solvents, Acids, Bases and Reagents Management in the Laboratory	re-released with amendments 9/11/08	DAS
303 R10	10/15/2009	Control, Format and Review of Laboratory Logbooks	re-released with amendments 1/29/08	DAS
305 R10	1/15/2011	Balance Calibration, Verification and Utilization	re-released w/o revision 3/12/09	DAS
306 R4	8/15/2010	The Use of Significant Figures and Rules For Rounding Numbers	re-released w/o revision 3/12/09	DAS
317 R10	1/15/2011	Removing and Returning Equipment From Service	re-released w/o revision 3/12/09	DAS
318 R6	8/15/2010	Chain-of-Custody	re-released with amendments 9/11/08	DAS
319 R8	1/15/2011	Generation and Monitoring of Deionized (DI) Water	re-released w/o revision 3/12/09	DAS
320 R8	2/15/2011	Monitoring and Recording of Oven Temperatures	re-released w/o revision 3/12/09	DAS
321 R5	9/15/2010	Calibration Verification of Pipettes and Pippettors	re-released w/o revision 3/12/09	DAS
326 R7	2/15/2011	Monitoring and Recording Refrigerator and Freezer Temperatures	re-released w/o revision 3/12/09	DAS

This pdf is updated periodically. Trust the individual SOP postings as more updated information. 3/14/09 DAS

SOP	Scheduled Date for Review	Title	Notes	Author
329 R6	1/15/2010	Method Demonstration Procedures: Instrument Detection Limit (IDL) and Method Detection Limit (MDL) Studies; Demonstration of Capability (DOC)	contol limits removed from SOP, title changed	DAS
334 R7	3/15/2010	Glassware Cleaning Procedures and Maintenance of Glassware Used in The Organics and Inorganics Departments	NOTE-SOP CONTAINS OPERATOR AID (REPLACE!)	DAS
336 R0	12/15/2009	Representative Laboratory Subsampling	Formerly SOP 721, now labwide. Inquire about additional Appendices w/each annual review.	DAS
400-499 GC/HPLC and FUELS				
402 R12	7/15/2008	Determination of Organochlorine Pesticides by Gas Chromatography - Methods SW8081A and EPA 608		JFN
404 R15	8/15/2009	Analysis of Nitroaromatics and Nitroamines (Explosives Residues) by HPLC -- Method SW8330		JFN
406 R14	6/15/2010	Extractable Petroleum Hydrocarbons Analysis by Gas Chromatography (TEPH, DRO)	Note change in Title.	JFN
407 R8	7/15/2008	Organophosphorus Compounds by Gas Chromatography - Methods SW8141A and EPA 614		JFN
408 R11	8/15/2009	Analysis of Nitroglycerin and/or PETN by HPLC -- Method SW8332		JFN
409 R5	8/15/2008	Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography -- Methods SW8082 and EPA 608		JFN
424 R12	5/15/2008	Determination of Aromatic Volatile Organics by Gas Chromatography - Method SW8021B		JFN
425 R12	5/15/2008	Analysis of Total Volatile Petroleum Hydrocarbon (TVPH) Gasoline Range Organics (GRO) by Gas Chromatography -- Methods SW8015B and CAL-LUFT		JFN
434 R8	8/15/2009	Analysis of Chlorinated Herbicides by Gas Chromatography - Methods SW 8151A, EPA 615 and EPA 515.1	re-released w/o revision 3/9/09	JFN
438 R10	6/15/2009	Microextraction and Analysis of EDB and DBCP in Water by Gas Chromatography - Methods EPA 504.1 and SW8011		JFN
439 R5	9/15/2010	Analysis of Nitroguanidine by HPLC -- Methods CRREL 89-35 and SW8000B	re-released w/o revision 3/9/09	JFN
444 R1	6/15/2011	Extraction and Determination of Glycols by Gas Chromatography -- Method SW8015B	re-released without revision 3/9/09	JFN
446 R1	11/15/2008	Analysis of Crystal Violet in Water by HPLC		JFN
448 R1	5/15/2010	Determination of Perchlorate in Liquids and Solids using High Performance Liquid Chromatography, Electrospray Ionization Tandem Mass Spectrometry (LC/MS/MS)	Effective 12/31/08; not signed until 1/5/09; published to lab 1/13/09	LSJ
500-599 GCMS				
506 R15	4/15/2010	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Capillary Column Technique - Methods SW8270D and EPA 625	re-released with amendment 1/3/08	JFN
511 R8	4/15/2010	Volatiles Reagent Water Preparation and Blank Analysis	re-released with amendment 12/27/07	JFN
512 R10	4/15/2010	Refrigerator Blank Preparation and Analysis	re-released with amendment	JFN
525 R12	4/15/2009	Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry -- Methods SW8260B and EPA 624		JFN

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600-699 EXTRACTIONS

SOP	Scheduled Date for Review	Title	Notes	Author
603 R11	10/15/2010	Extraction of Hydrocarbons From Soil and Water Samples	Note change in Title	JFN
604 R8	11/15/2009	Silica Gel Cleanup -- Method SW3630C		JFN
607 R9	8/15/2009	Extract Concentration Using Kuderna-Danish Apparatus	Contains Steam Generator Operator's AidNOTE-SOP CONTAINS OPERATOR AID! (replace as needed)	JFN
608 R12	9/15/2009	Method for Toxicity Characteristic Leaching Procedure (TCLP) Extraction of Wastes for the Analysis of Volatile Organic Compounds by Zero Headspace Extraction (ZHE) - Method SW1311	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
609 R12	9/15/2009	Method for Toxicity Characteristic Leaching Procedure (TCLP) of Wastes and Soils For The Analysis of Metals and Semivolatile Organics - Method SW1311	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
617 R13	3/15/2010	Continuous Liquid/Liquid Extraction (CLE) -- Method SW3520C	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed);	JFN
622 R6	2/15/2011	Waste Dilution Extraction -- Method SW3580A	re-released without revision 3/9/09	JFN
625 R11	3/15/2010	Soxhlet Extraction -- Method SW3540C	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed);	JFN
626 R9	9/15/2010	Separatory Funnel Liquid-Liquid Extraction -- Method SW3510C	re-released w/o revision 3/9/09	JFN
629 R10	8/15/2009	Determination of Ignitability by The Pensky-Martens Closed-Cup Tester -- Method SW1010A		JFN
634 R6	10/15/2010	Sulfur Cleanup -- Method SW3660B	re-released w/o revision 3/9/09	JFN
637 R9	8/15/2009	Concentration and Solvent Exchange by The Nitrogen Blowdown Technique	Re-issued/amended 12/26/07 (Navy Findings), traininng conducted	JFN
640 R7	4/15/2011	Extraction and Gravimetric Determination of Hexane Extractable Material in Solids -- Method SW9071B	re-released without revision 3/9/09	JFN
641 R8	2/15/2011	Gel Permeation Chromatography (GPC) Cleanup -- Method SW3640A	re-released w/o revision 3/9/09	JFN
642 R8	6/15/2009	Gravimetric Determination of Percent Moisture For Solid Matrices		JFN
648 R7	11/15/2009	Florisil Cleanup -- Method SW3620B		JFN
651 R9	5/15/2011	Sulfuric Acid Cleanup -- Method SW3665A	re-released without revision 3/9/09	JFN
658 R7	1/15/2010	Paint Filter Liquids Test -- Method SW9095A	re-released w/o revision 11/9/07	JFN
663 R7	2/15/2011	Monitoring TCLP Tumbler Revolutions and Room Temperature		DAS

SOP	Scheduled Date for Review	Title	Notes	Author
664 R8	11/16/2010	Extraction and Derivatization of Samples For Herbicide Analysis by Gas Chromatography -- Methods SW8151A, EPA 615 and EPA 515.1	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed); re-released w/o revision 3/14/09	JFN
665 R7	11/15/2009	Extraction of Explosives from Water and Soil -- Methods SW8330 and SW8332		JFN
666 R6	9/15/2009	Waste Extraction Test (Cal-WET) For The Analysis of Metals and Semivolatile Organic Compounds		JFN
668 R4	9/15/2009	Synthetic Precipitation Leaching Procedure (SPLP) For The Analysis of Metals and Semivolatile Organics -- Method SW1312	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
669 R4	9/15/2009	Method for Synthetic Precipitation Leaching Procedure (SPLP) Extraction of Samples For The Analysis of Volatile Organic Compounds by Zero Headspace Extraction (ZHE) -- Method SW1312	iteration (a) published to lab 11/17/08, iteration (b) published to lab 3/4/08	JFN
670 R12	11/15/2009	Analysis of Total Organic Carbon By Methods EPA 415.1, SW9060, and SM5310 C		JFN
671 R6	4/15/2010	Determination of n-Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry For Aqueous Samples -- Methods EPA 1664 and SW9070A	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed);	JFN
672 R3	4/15/2010	Extraction and Gravimetric Determination of Lipids in Tissues	NOTE-SOP CONTAINS OPERATOR AID! (replace as needed);	JFN
673 R2	6/15/2009	Extraction of Polychlorinated Biphenyl Wipes Using Ultrasonic Bath Agitation		JFN
700-799 RADIOCHEMISTRY				
700 R10	5/15/2009	Preparation of Environmental And Drinking Water Samples For Tritium Analysis -- Method EPA 906.0		RXG
701 R0	4/15/2009	DRAFT: Determination of Ra-226 by Alpha Spectrometry using Astatine 217 Tracer	New	RXG
702 R19	6/15/2009	Preparation of Gross Alpha and Gross Beta in Environmental Matrices -- EPA Method 900.0 and SW-846 Method 9310		RXG
703 R8	7/15/2010	Sample Prescreening		RXG
704 R9	6/15/2009	Analysis of Tritium and Other Beta-Emitting Nuclides by Liquid Scintillation Counting -- Method EPA 906.0		RXG
707 R10	8/15/2009	Radiostrontium in Water, Soil, Filters, Vegetation and Hazardous Waste Samples		RXG
708 R8	7/15/2010	Determination of Minimum Detectable Concentrations for Radioanalytical Methods		RXG
709 R6	8/15/2011	Verification and Validation of Radioanalytical Software	re-released without revision 3/13/09	RXG
711 R7	6/15/2009	Preparation of Water and Solid Samples for the Analysis of Polonium-210 -- EML Procedure Po-01	re-released with amendment 9/27/07	RXG
712 R14	8/15/2009	Determination of Total Alpha-Emitting Radium Isotopes in Drinking Water -- EPA Method 903.0 and SW9315		RXG
713 R10	7/15/2010	Analysis of Gamma Emitting Radionuclides by Gamma Spectrometry -- Method EPA 901.1		RXG
714 R11	8/15/2009	Analysis of Alpha Emitting Radionuclides by Alpha Spectrometry		RXG
715 R15	7/15/2011	Review of Radioanalytical Data	re-released w/o revision 3/13/09	RXG

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SOP	Scheduled Date for Review	Title	Notes	Author
724 R10	6/15/2009	Analysis of Alpha and Beta Emitting Radionuclides by Gas Flow Proportional Counter -- EPA Method 900.0		RXG
726 R6	6/15/2009	Determination of Lead -210 in Soils, Sediments, and Waters	re-released with amendment 11/30/07	RXG
733 R7	4/15/2009	Checking the pH of Aqueous Samples in the Radiochemistry Department		RXG
739 R9	4/15/2009	Preparation of Samples for Analysis by Gamma Spectroscopy		RXG
746 R8	7/15/2009	Determination of Radium-228 According to EPA Method 904.0 or SW846 Method 9320, With Modifications	re-released with amendment 9/27/07	RXG
748 R4	4/15/2009	Preparation of Water and Solid Samples For The Analysis of Fe-55 by Eichrom Method FEW01		RXG
751 R2	4/15/2009	Actinides -- Americium/Curium Separation -- Purification by TRU and TEVA Spec Column		RXG
753 R3	7/15/2011	Determination of Radioactive Iodine in Environmental Samples -- EPA Method 902.0	re-released w/o revision 3/13/09	RXG
754 R5	4/15/2009	Preparation of Solid Samples For Tritium Analysis by Microwave Oven		RXG
755 R9	7/15/2010	Determination of Technetium-99 in Solid and Water/Aqueous Samples	Editorial changes only; no technical revisions.	RXG
758 R2	5/15/2008	Determination of Promethium-147 in Water		RXG
760 R6	7/15/2010	Preparation of Solid Samples by Potassium Pyrosulfate Fusion		RXG
765 R4	6/15/2009	Separation and Analysis of Neptunium-237 in Environmental Matrices	re-released with amendment 9/27/07	RXG
766 R6	7/15/2010	Witnessing the Addition of Carriers, Tracers and Standards in Radiochemistry Samples	re-released w/o revision 7/17/08	RXG
767 R7	4/15/2009	Sample Preparation: Filter Leaching		RXG
772 R4	4/15/2009	Preparation of Water and Soil Samples for the Analysis of Carbon-14 Using Potassium Permanganate -- EPA EERF Method C-01		RXG
773 R10	4/15/2009	Total Dissolution of Solids for the Radiochemical Determination of Actinides and Other Non-Volatile Radionuclides		RXG
774 R1	7/15/2010	Nickel 59, 63 in Water and Soil Samples Using Eichrom Nickel Resin		RXG
776 R11	7/15/2009	Preparation of Water Samples for Actinides		RXG
777 R9	5/15/2009	Actinides - Thorium and Plutonium Sequential Separation by Anion Exchange		RXG
778 R12	8/15/2008	Actinides - Uranium, Plutonium, and Americium/Curium (Partial) Sequential Separation by Ion Exchange		RXG
780 R8	7/15/2010	Actinides - Americium/Curium Separation -- Purification by Methanolic Anion Exchange and TEVA Spec Column	Only clerical corrections/updates made, no technical revisions	RXG
783 R8	8/15/2009	Radium-226 in Aqueous and Soil Matrices -- Radon Emanation Technique--Method EPA 903.1		RXG
784 R0	8/15/2009	Radium-228 Determination for SDWA Compliance Analysis -- Method 904.0	re-released with amendment 9/27/07	RXG
785 R4	7/15/2010	Total Activity in Environmental Matrices		RXG
786 R5	8/15/2009	Gross Alpha in Water by Coprecipitation Method -- SM7110C		RXG
791 R3	5/15/2009	Preparation of Silica Gel Samples For Tritium Analysis		RXG

SOP	Scheduled Date for Review	Title	Notes	Author
792 R0	5/15/2009	Preparation of Ra226 for Analysis by Alpha Spectrometry	was DRAFT, formally published 9/8/07	RXG
799 R3	6/15/2008	Determination of Radon-222 in Water Samples by Liquid Scintillation Counting - SM 7500-Rn B and ASTM D5072-92		RXG
800-899 METALS				
806 R13	7/15/2009	Digestion of Waters, Soils and Wastes for Metals Analysis -- Methods SW3005A, SW3010A, SW3050B, EPA 200.2 and CLP SOW ILMO3.0 and ILMO4.0		RTF
807 R11	7/15/2010	Determination of Metals by Inductively Coupled Plasma Emission Spectroscopy - Method EPA 200.7 (Trace ICAP)	re-released w/o revision 3/9/09	RTF
812 R14	7/15/2009	Preparation and Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy -- Methods SW7470A, SW7471A, EPA 245.1, ILMO3.0, ILMO4.0		RTF
827 R6	7/15/2011	Determination of Elements by Inductively Coupled Plasma Mass Spectrometry -- Methods EPA 200.8 AND SW6020A	re-released with amendment 3/9/09	REM
834 R7	7/15/2009	Determination of Metals by Inductively Coupled Plasma Emission Spectroscopy -- Method SW6010B (Trace ICAP)		RTF
900-999 QUALITY ASSURANCE				
901 R7	1/15/2011	Verifying Weights	re-released with amendments 3/12/09	DAS
923 R8	2/15/2009	Verification of Thermometers		DAS
926 R8	6/15/2011	Review, Revision, Distribution and Archiving of Controlled Documents	re-released with amendments 3/9/09	DAS
928 R8	3/15/2010	Non-Conformances and Corrective Actions		DAS
937 R7	6/15/2010	Internal Audits	re-released with amendment 3/9/09	DAS
939 R3	8/15/2009	Manual Re-Integration Policy and Procedures		JFN
1100-1199 WET CHEMISTRY				
1100 R10	1/15/2009	Determination of Total Suspended Solids (TSS or Total Non-Filterable Residue) -- Methods EPA 160.2 and SM2540D		EAL
1101 R10	1/15/2009	Total Solids, Total Dissolved Solids (TDS or Total Filterable Residue), and Total Fixed and Volatile Solids -- Methods EPA 160.3, EPA 160.1, and EPA 160.4 and Methods SM2540B, SM2540C and SM2540E		EAL
1104 R6	4/15/2010	Potentiometric Determnation of (Simple) Fluoride in Water and Soil Using an Ion Selective Electrode -- Methods EPA 340.2, SW9214 and SM4500-F~C		EAL
1106 R7	4/15/2010	Bicarbonate, Carbonate, Hydroxide, and Total Alkalinity by Titration -- Methods EPA 310.1 and SM2320B		EAL
1110 R12	1/15/2009	Determination of Total and Amenable Cyanide (Distillation) - - Methods SW9010B, SW9013, SW9014, EPA 335.1, EPA 335.2 and CLP Inorganic SOW (ILMO4.0); Determination of Weak and Dissociable Cyanide -- Method SM4500-CN I		EAL
1112 R5	1/15/2009	Determination of Reactive Cyanide and Sulfide -- EPA Method SW-846, Chapter 7	re-released without revision 1/19/07	EAL
1113 R11	4/15/2011	Determination of Inorganic Anions by Ion Chromatography -- Methods EPA 300.0 and SW9056	re-released with amendment 10/22/08	EAL

SOP	Scheduled Date for Review	Title	Notes	Author
1117 R3	4/15/2009	Total Organic Carbon in Soil by Rapid Dicromate Oxidation -- MSA Walkley-Black Method	re-released w/o revision 8/15/07	EAL
1119 R6	2/15/2010	Determination of Total Phosphorus and Ortho-Phosphate in Water -- Methods EPA 365.2 and SM4500-P B(5) and E		EAL
1120 R5	5/15/2009	Determination of Total Sulfides in Water -- Methods EPA 376.1 and SM4500-S2F		EAL
1121 R6	3/15/2010	Determination of Hexavalent Chromium in Solid Matrices Using Alkaline Digestion (Method SW3060A) and Analysis by Method SW7196A		EAL
1122 R6	3/15/2010	Determination of Hexavalent Chromium by Methods SW7196A and SM3500-Cr-B		EAL
1125 R4	4/15/2010	Determination of Perchlorate in Water Using Ion Chromatography -- Methods EPA 314.0 and SW9058	re-released w/o revision 7/20/08; (include maintenance next update)	EAL
1126 R16	4/15/2009	Determination of pH by Electrometric Meaurement -- Methods EPA 150.1, SW9040B, SW9045C and SM4500-H+ B		EAL
1127 R7	4/15/2010	Determination of Nitrogen as Nitrate Plus Nitrite, Nitrite, and Nitrate in Environmental Water and Soil Samples Using a Colorimetric, Automated, Cadmium Reduction Procedure -- Methods EPA 353.2, SM4500-NO3-I, and Quikchem Method 10-107-04-1-C		EAL
1128 R9	1/15/2010	Determination of Specific Conductance -- EPA Methods 120.1, SW9050A, and SM2510B		EAL
1129 R6	1/15/2010	Determination of Ammonia Using An Automated Phenolate Procedure -- Methods EPA 350.1, SM4500 NH3-NH, and Quikchem Method 10-107-06-1-C		EAL
1130 R5	5/15/2010	Determination of Nitrogen, Nitrite (as NO2-N) in Water And Soil by Colorimetric Spectrophotometric Determination -- EPA Method 354.1 and SM4500-NO2 -B		EAL
1132 R3	1/15/2011	Sediment Load	re-release w/o revision 3/9/09	EAL
1133 R3	1/15/2011	Acidity by Titration - Methods EPA 350.1 and SM2310B	re-released w/o revision 3/9/09	EAL
1400-1499 INFORMATIONS SYSTEMS MANAGEMENT				
1400 R6	1/15/2011	Process Software Validation	re-released w/o revision 3/9/09	MSR
1401 R5	1/15/2011	Computer and LIMS Backup and Restoration Protocols	re-released w/o revision 3/9/09	GRB
1402 R6	1/15/2011	Laboratory Information Management System (LIMS) Version Control	Review LIMS Change Management for update as well.	MSR
MISC- ANNUAL DOCUMENTS/REFRESHERS				
CHP R12	9/16/2009	Chemical Hygiene Plan (CHP)	re-released w/o revision 3/9/09	CRO
ECP R6	9/16/2009	Emergency and Contingency Plan (ECP)	re-released w/o revision 3/9/09	CRO
FORM159	1/8/2010	Annual IS and LIMS Policy Training	Year 2009; effective 1/8/09	DAS
FORM162	1/8/2010	Annual Ethical Behavior Policy Training	Year 2009; effective 1/8/09	DAS
FORM166	1/8/2010	Annual Waste, Abuse and Fraud Reporting Notification	Year 2009; effective 1/8/09	DAS

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SOP	Scheduled Date for Review	Title	Notes	Author
LQAP R12	7/15/2009	Laboratory Quality Assurance Plan (LQAP)		DAS
RESPP R	9/15/2009	Respiratory Protection Plan (RESPP)	Was DRAFT; published to the lab 1/24/08; re-released w/o revision 3/9/09	CRO
RPP R5	9/15/2009	Radiation Protection Plan (RPP)	re-published to lab 8/20/08	CRO
WMP R7	9/15/2009	Waste Management Plan (WMP)		CRO

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 001 REVISION 7

TITLE: TREATMENT OF QUARANTINED SOILS, AQUEOUS EXTRACTS, AND SOLID RESIDUES AND CLEANING CONTAINERS USED TO STORE QUARANTINED SAMPLE MATERIALS

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/2/07

QUALITY ASSURANCE MANAGER _____ DATE 2/2/07

LABORATORY MANAGER _____ DATE 2-2-07

HISTORY: Rev0, 4/15/92; Rev1, PCN #218, 4/13/94; Rev2, PCN #476, 5/26/95; Rev3, 3/15/99; Rev4, 2/11/02; Rev5, 4/7/03; Rev6, 2/13/04 and 11/10/05 (re-released w/o revision); Rev7, 2/2/07.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used to destroy possible biological infestation (e.g., fire ants, nematodes, etc.), in soils obtained from geographic areas, domestic or foreign, designated as 'Quarantined', by the United States Department of Agriculture (USDA) Animal and Plant Health Inspection Service (APHIS). The treatment protocols described herein apply also to the aqueous extracts, including TCLP extracts, and solid residues derived from 'APHIS QUARANTINE' soils. Procedures for cleaning the containers in which these potentially contaminated materials are stored are also discussed. **Note that APHIS QUARANTINE does NOT apply to solvent extracts or acid digestates because the solvent or acid treatment of the sample aliquot is sufficient to kill any biological infestation that may be present.**

2. SUMMARY

Disposal of APHIS QUARANTINE soils and derivatives, without treatment, is permitted so long as the APHIS QUARANTINE materials are disposed in a waste stream that is incinerated at an approved facility at temperatures above 110°C. However, it is best to treat prior to disposal.

Adding bleach to the APHIS QUARANTINE materials is one means by which potential biological infestation may be destroyed. APHIS QUARANTINE soils or solid sample residues may also be treated by heating at a specified minimum temperature for a prescribed period of time. Aqueous (including TCLP) extracts of APHIS QUARANTINE soils may also be treated by boiling rapidly for one full minute.

The specific means used to treat APHIS QUARANTINE materials is at the discretion of Paragon's Waste Manager. After suitable treatment, the materials are handled as non-

quarantined laboratory waste, and are disposed in accordance with Paragon SOPs 003 and 015.

3. RESPONSIBILITIES

3.1 Information about APHIS QUARANTINE soil samples is disseminated to laboratory staff via project special handling instructions created by the Sample Control Manager. APHIS QUARANTINE soils, and the aqueous extracts (including TCLP) and solid residues derived from them, are distinguished by an 'APHIS QUARANTINE' label. The Sample Control Manager is responsible for creating 'APHIS QUARANTINE' labels so that they are available to laboratory staff.

3.2 The Paragon Project Manager is responsible for working with the Sample Control Manager to identify samples that are APHIS QUARANTINE, and for assuring that appropriate information and labeling materials are provided to laboratory staff.

3.3 As discussed in SOP 202, upon receipt, Sample Receiving personnel apply an 'APHIS QUARANTINE' label to all APHIS QUARANTINE soil sample containers received. Additional 'APHIS QUARANTINE' labels are distributed to laboratory staff along with the samples, when they are delivered to the individual laboratory areas.

Laboratory staff are responsible for applying the APHIS QUARANTINE labels to applicable aqueous (including TCLP) extracts, and solid residues.

3.4 Paragon's Waste Manager is responsible for adequately training staff per the treatment procedures described in this SOP.

3.5 It is the responsibility of the Technician to perform these procedures according to this SOP and to inform the Health & Safety Manager and Waste Compliance Officer of any problems that may occur during the performance of these procedures.

4. APPARATUS AND MATERIALS

4.1 beakers, Pyrex™, 1L or sufficient size

4.2 spatula or disposable "tongue depressors"

4.3 squirt bottle

4.4 hot plate(s)

4.5 oven, capable of maintaining 110-130°C or greater

4.6 baking containers (e.g., large aluminum pan)

4.7 scrub brush

5. REAGENTS

5.1 tap water

5.2 laboratory soap

5.3 bleach, common household

6. PROCEDURES

6.1 BOILING AQUEOUS EXTRACTS OF APHIS QUARANTINE SOILS

6.1.1 Shake the container to loosen any solids that may be present, and dump the container's contents into a Pyrex™ beaker large enough to contain the materials and sufficient tap water to allow a full boil without boiling over. Use a spatula or other suitable implement to loosen any solids that remain in the container and add them to the Pyrex™ beaker.

6.1.2 Use a squirt bottle filled with tap water to rinse the container, its lid, and the spatula. Collect the rinsate in the same Pyrex™ beaker.

6.1.3 Fill the beaker to approximately three-quarters full with tap water, and place it on a hot plate located in a fume hood. Bring the contents to a full boil.

6.1.4 Allow the contents to boil rapidly for at least one full minute.

6.1.5 Carefully remove the beaker from the hotplate. Allow the contents to cool to nearly room temperature.

6.1.6 Discard the liquid contents of the beaker as aqueous laboratory waste. Transfer any residual solid material to a baking container, and treat as described in Section 6.2.

6.1.7 Clean the beaker in a normal manner (SOP 334).

6.2 HEAT TREATMENT FOR APHIS QUARANTINE SOILS AND SOLID RESIDUES

6.2.1 Use a spatula or other suitable implement to spread the quarantined soil or solid residues on the bottom of a suitable baking container (e.g., aluminum pan). Do not allow the thickness of the solid materials to exceed approximately two inches. Use the spatula to scrape away as much solid material as possible that is clinging to the inside of the container, add the scraped-off material to the baking container. Use the edge of the baking container to scrape off any solid material remaining on the spatula.

NOTE: Solid samples in heat resistant containers may be heat-treated in the original sample container.

6.2.2 Place the baking container(s) in an oven set to maintain 110-120°C. Allow sufficient time for the solid materials to equilibrate to oven temperature and continue to bake for at least 16 hours.

Alternately, the solid materials may be equilibrated to 130°C or greater and baked for two hours.

6.2.3 Carefully remove the baking containers from the oven and allow them to cool to nearly room temperature.

6.2.4 Discard the solids and aluminum baking containers as contaminated soils and solids waste.

6.3 BLEACH TREATMENT OF APHIS QUARANTINE SOILS AND SOLID RESIDUES

6.3.1 Place solid materials in a bath of bleach solution. Make sure that the materials are totally submerged, let them soak for at least 1 hour.

6.3.2 Remove the solid materials from the bleach bath, and dispose of them in the appropriate waste stream.

6.3.3 Dispose of the bleach bath solution via an appropriate waste stream.

6.4 TREATMENT OF APHIS QUARANTINED MATERIALS CONTAINERS

6.4.1 Fill empty containers with bleach solution. Let soak for a period of at least 1hour. Empty and wash as described below.

6.4.2 Fill the sink to about three-quarters full with hot, soapy water.

6.4.3 Place the APHIS QUARANTINE materials containers in the sink and allow them to soak. Remove the APHIS QUARANTINE and any other labels from the containers and discard them as sanitary waste.

6.4.4 Thoroughly scrub the containers with a brush.

6.4.5 After scrubbing and cleaning with hot soapy water, rinse thoroughly with tap water.

6.4.6 Dispose of the cleaned containers as sanitary waste.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

7.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel are trained in the use and location of these items.

7.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), and when handling materials or equipment potentially contaminated with chemicals, or within a laboratory area.

7.1.3 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) are labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

7.1.4 Food and drink are prohibited in all lab areas.

7.2 WASTE DISPOSAL

7.2.1 Dispose of treated APHIS QUARANTINE soils, solid residues, and aqueous extracts per the standard waste handling procedures found in SOPs 003 and 015.

7.2.2 Containers used to store quarantined materials, and cleaned as described in this SOP, shall be disposed of as sanitary waste.

8. REFERENCES

8.1 Code of Federal Regulations, Title 7, Chapter 330, October 2002.

8.2 US Department of Agriculture, Animal and Plant Health Inspection Service (APHIS), Plant Protection and Quarantine Programs Compliance Agreement.

DOCUMENT REVISION HISTORY

2/2/07: Revamped Sections 1, 2. Updated RESPONSIBILITIES, Section 3. Added bleach to REAGENTS, and bleach option to SUMMARY and PROCEDURES. Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 002 REVISION 6

TITLE: LABORATORY FUME HOOD VELOCITY MONITORING

FORMS: 016 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/7/06

QUALITY ASSURANCE MANAGER _____ DATE 9/7/06

LABORATORY MANAGER _____ DATE 9-7-06

HISTORY: NEW, 7/14/94; Rev1, PCN #032, 8/12/96; Rev2, 3/15/99; Rev3, 2/11/02; Rev4, 3/06/03; Rev5, 2/9/04; Rev6, 7/25/04, 7/24/06; Rev7, 9/7/06.

Re-released w/o revision 10/2/07 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures used to verify that the face velocity of laboratory exhaust fume hoods is within normal and acceptable operating parameters.

2. SUMMARY

The face velocity of the laboratory exhaust hoods shall be checked on a monthly basis to ensure that the face velocity for each hood is within the operating range specified for that hood. The face velocity will be checked using an air velocity-measuring device. The results of the measurement shall be indicated on a label affixed to the hood indicating the date checked, rated face velocity, sash position to give the rated face velocity, and due date for the next face velocity check.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician performing this procedure to:

- follow the SOP explicitly.
- complete the associated Test Log and return it to the Health and Safety Manager.
- tag-out (SOP 317) any hood that fails to meet the minimum acceptance criteria.
- notify the Health & Safety Manager when a fume hood fails to meet the minimum acceptance criteria.

3.2 It is the responsibility of the Health and Safety Manager to investigate any hood that fails to meet the minimum acceptance criteria and effect any repairs necessary before returning the fume hood to normal service.

3.3 In the event that professional services, such as plumbers or HVAC technicians, are required to effect the repairs, the Health and Safety Manager is responsible for

requesting those services from the Facilities Manager. The Facilities Manager is responsible for procuring professional services.

4. APPARATUS AND MATERIALS

4.1 Alnor Model RVA Anemometer or equivalent.

4.2 Avery® #5160 labels or equivalent.

5. PROCEDURE

5.1 FACE VELOCITY MEASUREMENTS

The face velocity shall be determined by taking a face velocity measurement in feet per minute averaged over the entire surface area of the hood's opening.

5.1.1 During the measurement the technician should always stand to the side of the anemometer, with the instrument at arm's length, so that the measured airflow is not blocked by the person performing the measurement.

5.1.2 The sash shall be positioned at the level indicating the rated face velocity.

5.1.3 The Alnor model RVA is placed at the top left corner of the hood opening, with the center of the instrument six inches away from the top and left side of the opening (see Figure 1).

5.1.4 The Alnor Model RVA's anemometer is allowed to spool up until a constant readout is achieved prior to measurement.

5.1.5 After the Alnor Model RVA has spooled up, depress and hold the test button.

5.1.6 Slowly (approx. 3-4 inches per second) move the anemometer to the right until the center of the instrument is approximately six inches from the right side of the hood opening. Slowly move the anemometer down six inches and move to the left, as shown in Figure 1.

5.1.7 Continue to move the anemometer along the path shown in Figure 1 until the center of the instrument is within six inches of the bottom of the hood opening.

5.1.8 Complete the last pass of the hood opening.

5.1.9 Release the test button and record the reading. This reading is the average face velocity over the entire hood surface.

5.2 ANALYSIS OF FACE VELOCITY MEASUREMENTS

5.2.1 The average face velocities and date of test for each hood shall be recorded in the Monthly Fume Hood Face Velocity Test Log (see attached example).

5.2.2 If the minimum target velocity is not achieved, corrective action must be taken, as described in the next Section.

5.2.3 The sash location that meets the face velocity requirement must be marked with an approved label, such as the one shown in Figure 2. These labels may be printed on Avery 5160® labels from the template located at i:\oprnts\safety\hoodlbl.doc. Any equivalent label with the same information is acceptable.

5.3 CORRECTIVE ACTION FOR NONCONFORMING MEASUREMENTS

5.3.1 If the fume hood velocity check fails to meet the minimum acceptance criteria, the hood sash height may be adjusted to achieve the target velocity.

5.3.1.1 Measure the sash height, in any units.

5.3.1.2 Multiply this number by the measured face velocity, determined in Step 5.1.9.

5.3.1.3 Divide the result by the desired face velocity. The result is the desired sash height, in the same units used to measure the sash height in Step 5.3.1.1.

5.3.1.4 Move the hood sash to the desired height.

5.3.1.5 IN NO CASE WILL THE APPROVED SASH HEIGHT BE LESS THAN TWELVE INCHES FROM THE BOTTOM OF THE HOOD OPENING.

5.3.1.6 Go to Step 5.1.3 and repeat the velocity measurement.

5.3.1.7 If the new measurement is acceptable, record it in the Test Log and note in the comments field that the sash height was adjusted.

5.3.1.8 If the new measurement is still unacceptable, the hood must be tagged out of service (SOP 317) and the Health and Safety Manager must be notified as described in the next Step.

5.3.2 Any exhaust fume hood exhibiting an average face velocity measurement that is below the minimum face velocity required for that hood shall be taken out of service and tagged (SOP 317). The Health and Safety Manager must be notified immediately.

5.3.3 After corrective action is taken (i.e., repairs), the face velocity of the hood shall be measured and shall meet the minimum acceptance criteria before being placed back into service. A notation describing the corrective action will be made in the Test Log of the month the hood is returned to service.

6. SAFETY AND HAZARDS

6.1 The technician performing this procedure must be observant of any hazardous operations that are being undertaken in the hood at the time of the measurement. If the hood is currently in use for a task that may pose any undue risk to the technician, the test should be delayed until it is safe to perform the test. In no case shall the test be delayed past the expiration date of the current calibration without taking the hood out of service.

6.2 As the technician may be working in non-routine or unfamiliar locations to perform this task, he or she must be familiar with the location of the nearest safety shower and eyewash station before beginning measurements in any hood being used for hazardous operations.

6.3 Gloves, safety glasses, and a lab coat shall be worn during fume hood face velocity measurements.

7. REFERENCE

Industrial Ventilation, 23rd Ed., ACGIH, Cincinnati, OH, 1998.

8. FIGURES AND ATTACHMENTS

8.1 Figure 1 is attached and shows the proper technique for taking an average hood velocity.

8.2 Figure 2 is attached and shows a proper hood sash calibration label.

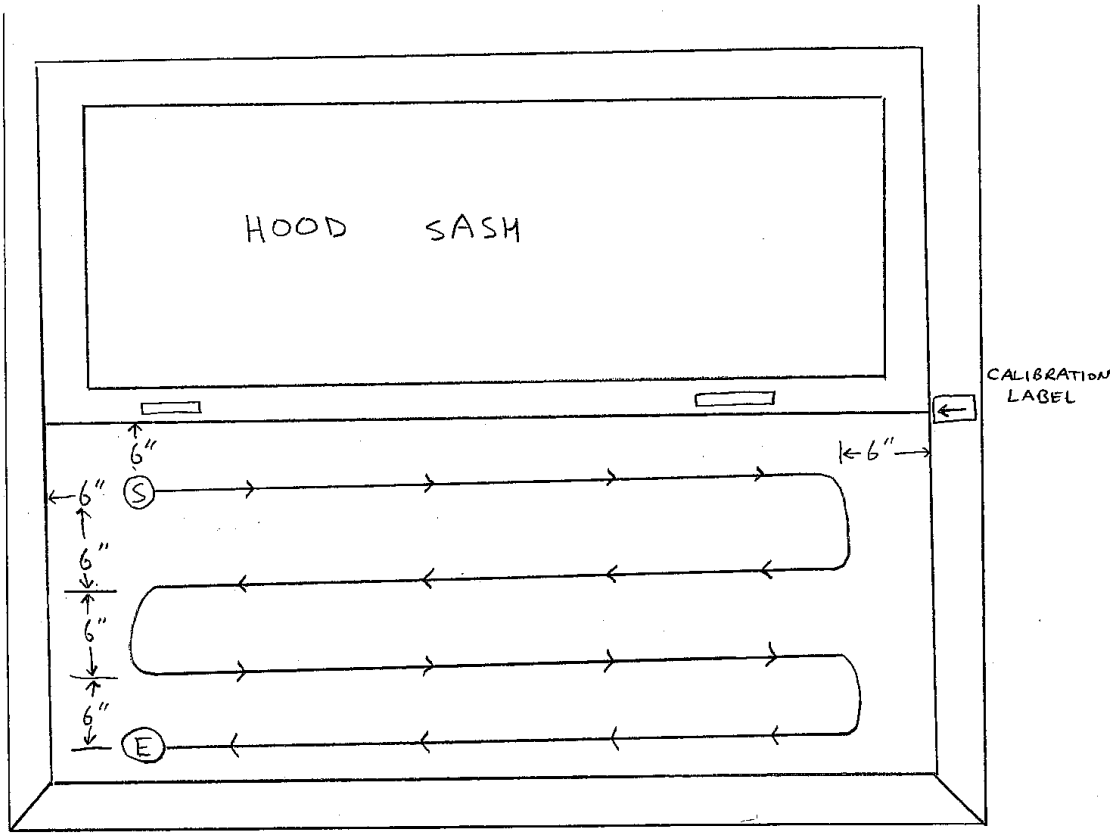
8.3 A scanned copy of the Monthly Fume Hood Face Velocity Test Log is attached and can also be found at i:\oprtns\safety\hoodckl.xls.

DOCUMENT REVSION HISTORY

7/24/06: Rev6 re-released w/o revision.

9/7/06: Form attachment updated. DOCUMENT REVISION HISTORY section added.

FIG. 1



(S) = START

(E) = END

FIG. 2

Date: _____ Inspector: _____
Fume Hood # _____ Location: _____
Next Airflow Check Due In One Month.
← _____ FPM Sash Location

PARAGON ANALYTICS
Monthly Fume Hood Face Velocity Test Log

CONTROL CRITERIA
Lower Limit = Minimum Target Velocity listed below.
Upper Limit = 125 fpm, or as approved by H&S Manager

CORRECTIVE ACTION:
1) If a simple sash adjustment is required to meet acceptance criteria, adjust the sash, re-measure the face velocity, place the calibration mark at the new sash height location, and make a note in the comment section below.
2) Otherwise, tag the hood "OUT OF SERVICE", per SOP 317, and note in the comment section below.
3) Report "OUT OF SERVICE" hood to the Health and Safety Manager.
4) After corrective action, and before returning the hood to service, make note in the comment section below describing repairs.

Inspection Date	Hood #	Hood Location	Minimum Target Velocity (fpm)	Maximum Velocity (fpm)	Measured Velocity (fpm)	Comments	Initials
	1	Sample Receiving	80	125			
	3	Prescreen	80	125			
	4	Prescreen	80	125			
	6	Actinides	80	125			
	7	Actinides	80	125			
	8	Actinides	80	125			
	9	Actinides	80	125			
	10	Actinides	80	125			
	11	Actinides	80	125			
	12	Waste Lab	80	125			
	13	Waste Lab	80	125			
	14	Waste Lab	80	125			
	15	Waste Lab	80	125			
	16	Low Level	80	125			
	17	Low Level	80	125			
	18	Grinding Lab	80	125			
	19	Grinding Lab	80	125			
	20	Wet Chem	80	125			
	21	Wet Chem	80	125			
	22	Wet Chem	80	125			
	23	Wet Chem	80	125			
	24	Ra/Sr	80	125			
	25	Ra/Sr	80	125			
	26	Ra/Sr	80	125			
	27	Ra/Sr	80	125			

Form 016r3.xls (9/7/06)

PARAGON ANALYTICS
Monthly Fume Hood Face Velocity Test Log

CONTROL CRITERIA
Lower Limit = Minimum Target Velocity listed below.
Upper Limit = 125 fpm, or as approved by H&S Manager

CORRECTIVE ACTION:
1) If a simple sash adjustment is required to meet acceptance criteria, adjust the sash, re-measure the face velocity, place the calibration mark at the new sash height location, and make a note in the comment section below.
2) Otherwise, tag the hood "OUT OF SERVICE", per SOP 317, and note in the comment section below.
3) Report "OUT OF SERVICE" hood to the Health and Safety Manager.
4) After corrective action, and before returning the hood to service, make note in the comment section below describing repairs.

Inspection Date	Hood #	Hood Location	Minimum Target Velocity (fpm)	Maximum Velocity (fpm)	Measured Velocity (fpm)	Comments	Initials
	28	Ra/Sr	80	125			
	29	Ra/Sr	80	125			
	32	Micro Precip	80	125			
	33	RAM Standard	80	125			
	34	Metals	80	125			
	35	Metals	80	125			
	36	Metals	80	125			
	37	Metals	80	125			
	38	Organic Standards	80	125			
	40	Extractions	80	125			
	41	Extractions	80	125			
	42	Extractions	80	125			
	43	Extractions	80	125			
	46	HPLC	80	125			
	47	Fuels	80	125			
	52	GC-Voa upstairs	80	125			
	53	New Waste lab	80	125			
	TR 1-2	Tank Room	80	125			
	TR 2-3	Tank Room	80	125			
	TR 3-4	Tank Room	80	125			

Form 016r3.xls (9/7/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 003 REVISION 5

TITLE: MANAGEMENT OF NONRADIOACTIVE HAZARDOUS WASTE

FORMS: 783 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/7/07

QUALITY ASSURANCE MANAGER _____ DATE 11/7/07

LABORATORY MANAGER _____ DATE 11-7-07

HISTORY: New, 7/14/94;; Rev1, PCN #241, 2/3/00; Rev2, 4/3/02; Rev3, 8/9/02; Rev4, 9/22/03, 7/20/05 (re-released without revision); Rev5, 11/7/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the management of hazardous waste throughout the analytical chemistry laboratories. This SOP shall be used to provide the laboratory staff with guidelines for managing the hazardous waste aspects of all waste generated in the laboratory, including hazardous waste, mixed hazardous/radioactive wastes, and polychlorinated biphenyl (PCB) wastes, which are regulated under the Toxic Substances Control Act (TSCA).

Procedures for dealing with the radioactive aspects of wastes are dealt with in SOP 015 – Disposal of Radioactive Waste. The hazardous waste management requirements for mixed wastes are identical to nonradioactive hazardous wastes, although disposal options may be limited. TSCA PCB wastes may be a TSCA only waste, with no RCRA hazardous components, or the TSCA PCB waste may have RCRA hazardous components.

Paragon is a large quantity generator of hazardous waste and must comply with Environmental Protection Agency (EPA) regulations found in the Resource, Conservation and Recovery Act (RCRA). Paragon must also comply with Colorado State Department of Public Health and the Environment (CDPHE) waste regulations.

It should be noted that not all aspects of the regulations are discussed in this SOP. The State and Federal regulations are the basis for the information contained herein. The State and Federal regulations will be adhered to during all waste handling and disposal operations.

2. SUMMARY

This SOP covers hazardous waste characterization, waste accumulation containers, Satellite Accumulation Area (SAA) management, 90-Day Accumulation Area management, waste streams unique to Paragon, waste disposal requirements, and safety and training requirements for personnel who dispose of hazardous waste. Special

requirements for mixed hazardous/radioactive waste and TSCA PCB waste management are also discussed.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who perform this procedure to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. HAZARDOUS WASTE CHARACTERIZATION

4.1 REFERENCE INFORMATION
40 CFR 261.3, 6CCR 1007-3, Section 261, Subpart C and Section 268.7
40 CFR 262.11, 6CCR 1007-3, Section 262.11 and Section 262.40(c)

4.2 GENERAL INFORMATION
Paragon is a large quantity generator and must identify all hazardous waste generated at the facility by one or all of the following methods: analysis, process knowledge, or other determinations.

A hazardous waste is a solid, liquid, or contained gaseous material that is no longer used or serves the purpose for which it was produced, and could pose a danger to human health or the environment.

Laboratory materials and sample remainders to be discarded are considered solid wastes. Most of these solid wastes are classified as hazardous waste based upon the presence of characteristic, or listed hazards as defined by RCRA. These RCRA hazards are determined by chemical analyses or process knowledge. Their presence will make the material being discarded a hazardous waste that requires special handling and disposal.

A waste determination is performed by gathering information about each process and the chemicals involved. It is then determined if the chemicals and/or the process classifies the waste as hazardous and subject to RCRA requirements.

NOTE: Additional tests may be needed to completely characterize the waste.

4.3 CHARACTERISTIC HAZARDOUS WASTE
40 CFR 261.10, 6CCR 1007-3, Section 261, Subpart C

Characteristic hazardous wastes are solid wastes that are hazardous to human health and/or the environment because of their physical or chemical character. The EPA identifies four physical/chemical properties or hazardous characteristics that determine a solid waste as a “Characteristic Hazardous Waste”: :ignitability,

corrosivity, reactivity, and toxicity. The presence of any one of these hazards is sufficient to make the material a hazardous waste. The characteristic hazards may be determined via analytical tests. Knowledge about the material itself, or the process that created the material may also provide sufficient information to classify a waste as hazardous.

NOTE: Additional tests may be needed to completely characterize the waste.

4.3.1 Ignitability Hazards (D001)
40 CFR 261.21(a)

A solid waste is hazardous due to ignitability if a representative sample of the waste falls into any of the following categories:

- A liquid (other than an aqueous solution containing <24% alcohol by volume) with a flash point <140°F (60°C). The lower the flash point, the more dangerous the material. 40 CFR 261.21(a)(1).
- A nonliquid that can burn under standard temperature (68°F) and pressure (1 atm) through friction, moisture absorption, or spontaneous chemical changes, and burns vigorously and persistently once ignited. 40 CFR 261.21(a)(2).
- An ignitable compressed gas as defined in 49 CFR 173.300.
- An oxidizer as defined by the United States Department of Transportation (DOT) 49 CFR 173.151. 40 CFR 261.21 (a)(4).

4.3.2 Corrosivity Hazards (D002)
40 CFR 261.22

A solid waste is hazardous due to corrosivity if it has either of the following properties:

- Any aqueous waste with a pH ≤2.0 or ≥12.5.
- A liquid waste that corrodes steel at a rate of 6.35mm (0.25 inches) per year.

4.3.3 Reactivity Hazards (D003)
40 CFR 261.23

A solid waste is hazardous due to reactivity if it exhibits any of the following properties:

- Unstable and readily undergoes violent change without detonating.

- Reacts violently with water.
- Forms potential explosive mixtures with water.
- Produces toxic gases, vapors, or fumes in sufficient quantities to present a danger to human health or the environment when mixed with water.
- It is a cyanide or sulfide bearing waste which when exposed to pH conditions between 2 and 12.5, generates toxic gases, vapors, or fumes in sufficient quantities to present a danger to human health or the environment.

  Waste material that contains cyanides or sulfides in concentrations greater than 50ppm is considered a hazardous waste. CDPHE states a waste meets the definition of reactive if it contains a releasable sulfide concentration of 500 mg H_2S/Kg or a releasable cyanide concentration of 250mg HCN/Kg.
- Is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.
- Is a forbidden explosive or a Class A or Class B explosive as defined in 49 CFR 173.51, 173.53 and 173.88.

4.3.4 Toxicity Hazards (D004 through D043)
40 CFR 261.24

A solid waste exhibits toxicity characteristics if the extract from a representative sample of the waste contains any of the contaminants at a concentration greater than or equal to the applicable regulatory level during a leaching test called the Toxic Characteristic Leaching Procedure (TCLP).

4.4 LISTED WASTES
40 CFR 261.11(a)(3), 261.30 - 261.33, 6CCR 1007-3, Section 261, Subpart D

Listed Wastes are those waste streams or chemicals that EPA knows from experience present a threat to human health or the environment regardless of their concentration when disposed. A waste is considered a Listed Waste if it meets the description in one of the four lists of waste contained in 40 CFR Section 261 Subpart D. The four lists of hazardous waste are F-, K-, P-, and U. Paragon will generally only produce F, U and sometimes P listed waste. General definitions for the listed wastes are as follows:

- F listed hazardous wastes are from non-specific sources.
- K listed hazardous wastes are from specific sources.

- P listed wastes posses "extremely hazardous properties" that make them lethal in very small quantities and are identified as acutely hazardous waste.
- U listed wastes meet the criteria of 40 CFR 261.11(a)(3), which identifies various factors that could render a waste toxic.

P and U listed wastes are any commercial chemical product, or manufacturing chemical intermediate, having the generic name listed in paragraph (e) or (f) in 40 CFR 261.33. Commercial chemical product or manufacturing chemical intimidates refer to a chemical substance which is manufactured or formulated for commercial or manufacturing use. The chemical in question must also be the sole active ingredient in the product to qualify as a U or P listed waste. Mixtures of Chemicals contained on the P or U list in items such as standards for volatile analysis, may not be considered a P or U listed waste. This is because these chemicals are in small amounts and are not the sole active ingredient. The main ingredient is the solvent. Questions regarding waste classifications should be referred to the Waste Disposal Coordinator.

Also, P and U listed waste are off-specification or discarded commercial chemical products, any residue remaining in a container that held commercial chemical products, or any residue or contaminated media resulting from the cleanup of a spill of a commercial chemical product in the P or U listing.

5. WASTE HANDLING REQUIREMENTS

After a waste has been classified as a Hazardous Waste, EPA requires these wastes to be handled according to RCRA and CDPHE regulations. Included in these regulations are requirements for Satellite Accumulation Areas (SAA) and 90-Day Accumulation Areas used for waste collection. The regulations have requirements for the waste container types, labeling of containers, waste quantities, and inspections of these areas.

5.1 SATELLITE ACCUMULATION AREA (SAA) MANAGEMENT
40 CFR 262.34 (c), 6CCR 1007-3, Section 262.34(c)

A Satellite Accumulation Area (SAA) as defined by EPA is a small accumulation site where Hazardous Wastes are accumulated in close proximity to the point of generation prior to transfer to the 90-Day Accumulation Area. RCRA and the CDPHE have specific requirements for the management of Satellite Accumulation Areas. The requirements include designated areas as Satellite Accumulation Areas, container type, container labeling, container maintenance, limitations on waste quantities in the SAA, and weekly inspections.

5.1.1 Defining Satellite Accumulation Areas
6CCR 1007-3, Section 262.34(c)

The SAAs at Paragon are unique to each lab's function. An SAA must be at or near the location where the waste is generated. Each lab generating waste will have an area or areas designated as an SAA(s) defined by a sign and/or an area marked with tape. The locations of all SAAs shall be designated in the Emergency & Contingency Plan.

The satellite accumulation waste containers are stored only in designated SAAs. The waste containers cannot be left outside the SAA such as on a bench, in another SAA, or in another lab. The only location to which waste from an SAA may be moved is to a 90-Day Accumulation Area.

All SAAs must be accessible at all times and must be free and clear of debris.

5.1.2 Satellite Accumulation Container Types
40 CFR 265.172, 6CCR 1007-3, Section 265, Subpart I

Specific types of containers are required for use as Satellite Accumulation Containers. UN Specification Hazardous Materials containers fulfill all the requirements for Satellite Accumulation Containers. Other types of containers may be used in SAAs if the container is compatible with the waste stream. The Waste Management Staff must approve all SAA containers used in the lab.

Containers holding ignitable or reactive waste must be located at least 50 feet (15 meters) from the facility's property line and away from any source of possible ignition.

5.1.3 Labeling Requirements For Satellite Accumulation Area Containers
40 CFR 262.34(a)(3), 6CCR 1007-3, Sections 262.34(d)(4), 262.34(a)(3), & 262.34(c)

Regulations require that all Satellite Waste Accumulation Containers be labeled at a minimum with the phrase "Hazardous Waste" and the identity of the waste (e.g., Hazardous Waste, Aqueous Laboratory Waste). A preprinted Uniform Hazardous Waste label may be used.

Start dates are not required for containers in SAAs until the 55-gallon limit is obtained. Once the 55-gallon limit is reached the container must be dated immediately (within a few minutes).

5.1.4 Satellite Accumulation Container Maintenance
40 CFR 265.171 and 265.173

All containers must be kept in a clean condition. Any spills of waste materials onto the container are required to be cleaned up immediately. If waste containers are in secondary containment, the secondary containment must be free and clear of all liquids and debris.

The condition of the containers is required to be managed such that the containers are in good condition at all times. The container must be replaced if it becomes damaged (e.g., distended, cracked, or dented). If a container has been damaged, request a new container from waste management staff immediately. Transfer the material from the damaged container into the new container and apply the proper labels.

PAR laboratory staff are required to ensure that all containers of hazardous waste are closed at all times when not in use. The definition for "in use" is when a staff member is in direct control and in the presence of the container during waste transfer operations.

Container labels must be visible during storage. Replace any worn, mutilated, or defaced labeling on the containers. Contact the waste management staff if labels or assistance is needed.

There are "In Process Waste" containers used throughout some of the labs. These containers are not regulated as SAA containers until they leave the process from which they were generated. "In Process Waste" containers that are not attached to and instrument shall be emptied into the appropriate SAA container at the end of work every day.

Instrument effluent "In Process Waste" containers that are attached to an instrument are not required to be emptied until the container is full. Once the container is full and removed from the instrument, it must then be placed in an assigned SAA or disposed into a drum in the 90-Day Accumulation Area as appropriate.

NOTE: Instrument effluent may not be a RCRA hazardous waste. Waste determinations should be performed to verify if RCRA hazardous waste regulations are applicable to the effluent.

5.1.5 Quantity of Wastes Allowed in Satellite Accumulation Area
40 CFR 262.34(c), 6CCR 1007-3, Section 262.34(c)

Wastes may be accumulated in an SAA in total quantities of no more than 55 gallons. A SAA may have more than one waste stream but the total of all waste streams cannot exceed 55 gallons. Each laboratory has a limited number of containers for waste. Paragon's policy is to

limit the number of containers so that the total volume is less than 55 gallons per SAA. The procurement of more carboys for the purpose of storing waste is not allowed without consent of the waste management staff.

Any waste streams that have accumulated 55 gallons or more must be dated within a few minutes of becoming full as stated in Section 1. The full container must be removed from the SAA to the 90-Day Accumulation Area as required in Section 1. PAR laboratory staff are responsible to ensure that no more than 55 gallons is accumulated in any Satellite Accumulation Area.

Once a process has been discontinued, the waste generated from that process must be removed from the SAA and disposed into a 90-Day Accumulation Area. If the waste from the discontinued process is the only waste accumulated in the SAA, then the SAA must be closed.

5.1.6 Waste Accumulation Time Limits
40 CFR 262.34(c)(2), 6CCR 1007-3, Section 262.34(c)

When the 55-gallon limit has been reached in the SAA, the container(s) must be removed from the SAA immediately. CDPHE interprets "immediately" to mean within 24 hours. PAR staff must notify waste management personnel immediately when their SAA has reached the 55-gallon limit.

NOTE: Colorado has adopted the 24-hour regulation that is more stringent than the EPA RCRA regulations.

5.1.7 Weekly Inspections of the Satellite Accumulation Area
40 CFR 265.174

Weekly inspections of the SAA are required by the State of Colorado Hazardous waste regulations and by RCRA. This inspection must cover container condition, container labeling, and container closure condition. Waste management staff shall use the lab specific SAA Weekly Inspection forms to document the weekly inspections. The Weekly Inspection forms (Form 783) are bound into logbooks located near the SAAs.

5.2 90-DAY ACCUMULATION AREA MANAGEMENT
40 CFR 262.34(b)

The 90-Day Accumulation Area is the designated area where wastes are stored in drums upon leaving the Satellite Accumulation Area. Also, waste can be directly

disposed into assigned drums in the 90-Day Accumulation Area, instead of in an SAA, with permission from the waste management staff.

The 90-Day Accumulation Area must be clean and easily accessible. RCRA requires there to be adequate space between containers and aisles for the movement of emergency equipment to easily access any one container to make repairs or remove the container.

5.2.1 Waste Accumulation Time Limits
6 CCR 1007-3, Section 262.34(a), 262.34(a)(2)

Waste materials accumulated in the 90-Day Accumulation Area may be stored in the area for a maximum of 90 days prior to transfer to a Treatment, Storage and Disposal Facility (TSDF) for final disposition. This time clock begins the moment waste accumulation begins in the 90-Day Accumulation Area.

Full 55-gallon drums from the SAAs brought to the 90-Day Accumulation Area must have been marked with an accumulation start date as required in Section 1. The time clock starts from the date on the drum, not the date when the drum is placed in the 90-Day Accumulation Area.

5.2.2 90-Day Accumulation Container Types
40 CFR 265.171, 265.172, 265.176, & 265.177, 6 CCR 1007-3, Section 262.34(a)(1)

All containers used in the 90-Day Accumulation Areas must be United Nations Specification (UN Spec) transportation containers and must be compatible with the waste.

TSDFs may have their own requirements for containers used for shipment of waste, such as over packs.

5.2.3 90-Day Accumulation Containers Labeling Requirements
40 CFR 262.31, 262.32(a)&(b), 6 CCR 1007-3, Section 262.34(a)(2)&(3)

The waste container must at all times be labeled with the phrase "Hazardous Waste" that is clearly visible on the container. Before transporting hazardous waste off-site, the generator must label each container in accordance with DOT regulations on hazardous materials per 49 CFR Part 172.

Before transporting hazardous waste off-site, the waste must be packaged in accordance with the applicable DOT regulations under 49 CFR Parts 173, 178, and 179.

The side of the container is labeled with a preprinted Uniform Hazardous Waste label, specific for the waste stream. The Accumulation Start Date is marked in the Accumulation Start Date section of the Hazardous Waste Label.

The appropriate DOT Hazard Warning Label must be placed on the container next to the Hazardous Waste Label. A double arrow up label must be placed on each side of the container.

The waste container must be marked with the date when the first aliquot of waste was placed into the drum. The start date is entered in the appropriate box on the preprinted Uniform Hazardous Waste label and on the top of the drum.

The top of the container (e.g., drum) must be marked with the waste name (e.g., Aqueous Lab Waste) and container number. The container number is unique for each container, and consists of the waste stream, month and year of generation, and number of the barrel for that particular waste stream started in a given month (xx-mmyyyy-nn). For example, the third barrel of Aqueous Lab Waste generated in December, 2001 is labeled AW-122001-03.

5.2.4 Container Management
6 CCR 1007-3, Sections 262.34(a)(1) and 265.77

Containers holding ignitable or reactive waste must be located at least 50 feet (15 meters) from the facility's property line.

A container holding hazardous waste that is incompatible with waste in containers nearby must be separated from the other wastes.

All containers must be kept in a clean condition. Any spills of waste materials onto the container are required to be cleaned up as soon as possible. All labels must be intact and in good condition. Replace any worn, mutilated, or defaced labeling on the containers.

The containers must be in good condition at all times. The container must be replaced if it becomes damaged (e.g., distended, cracked, or dented). If a container has been damaged, arrange for a replacement container and transfer the material. The new container must be properly labeled.

PAR laboratory staff are required to ensure that all containers of hazardous waste are closed at all times when not in use. The definition for "in use" is when a staff member is in direct control and in the presence of the container during waste transfer operations.

5.2.5 Container Spill Management Requirements
40 CFR 262.34 and Subparts I, AA, BB, CC of 40 CFR 265

Containers that contain liquids must be stored in such a way to contain a leak. This may be accomplished by use of a spill pad or drip pad that is capable of containing the entire contents of the largest container. Additionally, it is acceptable to use an over pack container to contain any spillage.

All spill pads are to be cleaned regularly. Any spilled material is collected and placed in the proper waste containers.

5.2.6 Inspections of the 90-Day Accumulation Area
40 CFR 265.174

Weekly inspections of the 90-Day Accumulation Area are required by RCRA. The inspection must cover container condition; container labeling, container closure condition, and accumulation start time. The waste management staff shall use the 90-Day Accumulation Area inspections logs to document the weekly inspections.

6. PAR WASTE STREAMS
40 CFR 262.11

Paragon generates various hazardous waste streams including analytical process wastes, unaltered sample waste, unused chemicals, empty containers, planchet waste, universal waste, mixed waste, radioactive waste, PCB waste, and nonhazardous waste.

NOTE: All process waste streams have a written waste determination.

6.1 ANALYTICAL PROCESS WASTES
Individual laboratories generate different waste streams and may have multiple waste streams based on the analyses performed. The analytical process materials generated at Paragon must be evaluated to determine if they qualify as a hazardous waste under RCRA. On an ongoing case-by-case basis, the analytical data plus process knowledge about the waste stream will be used to write a waste determination. Once the waste determination is completed, the waste will be disposed of appropriately. Sample digestates and extracts are identified as process waste.

Waste characterization analysis is performed for radioactive satellite containers and drums of process waste. Copies of all analyses are retained on file and a waste determination form is completed.

Waste reduction is a requirement of RCRA. To meet this requirement, the process wastes that are multi-phased and potentially radioactive are divided by phases. Each phase is analyzed and a detailed written waste determination is completed. The waste is disposed of per the determination in the appropriate waste stream.

6.2 UNALTERED SAMPLES AS WASTES
40 CFR 261.4(d)

Some samples upon completion of analysis are returned to the client. The samples are packaged for return shipment per SOP 027 directives. Permission to return the samples is obtained from the client prior to sample shipment. Unaltered samples that are not designated for client return are held for 90 days after invoicing, unless otherwise specified by the client.

After a work order is invoiced, the samples may be moved from the various sample storage areas to the sample archive storage area to be held until disposal. The appropriate waste stream is assigned to all samples based on analyses reported in Paragon's Laboratory Information Management System (LIMS). The samples are segregated in the sample archive storage area by waste streams and by the month the samples are available for disposal. Once the specified archival time has ended, the samples are disposed of in the appropriate waste stream. Samples are disposed of on a monthly basis. Sample disposal is tracked per sample container to ultimate disposal through LIMS. Records of disposal are maintained by the Waste Compliance Officer.

6.3 UNUSED CHEMICALS AS WASTE
Chemicals that are not completely used prior to their expiration date or are not needed shall be brought to the waste characterization area. A waste determination (see Section 4) will then be made as to whether the chemical classifies as a Hazardous Waste or not. If the chemical is a Hazardous Waste, it will be stored in an SAA (see Section 5) until disposal can be accomplished (see Section 7). The chemicals that are not Hazardous Waste will be disposed of according to all applicable State and Federal regulations.

Unused Chemicals that are classified as a hazardous waste will be classified as a P, U and/or characteristic waste according to applicable State and Federal regulation (see Section 4)

6.4 EMPTY CONTAINERS AS WASTE
40 CFR Part 261.7, 6 CCR 1007-3, Sections 262.7

Empty containers may come from the analysis of samples (i.e., pipet tips, digestion cups), from the disposal of samples, or from chemicals that have been disposed of or completely used. Any container that contained a RCRA defined Hazardous Waste may be considered RCRA Empty and exempt from RCRA disposal requirements if the container meets the definitions contained in 40 CFR Part 261.7.

6.5 PLANCHETS AS WASTE

Various analyses involve sample material to be placed on planchets. After analysis, these planchets are disposed into a drum designated for planchet waste only with the assumption the planchets may possibly be radioactive. A representative sample of the drum is analyzed for radioactivity and other possible hazards. The drum is then shipped for appropriate disposal.

Prescreen planchet waste is segregated as radioactive or nonradioactive. Radioactive planchets are disposed into the planchet waste drum. Nonradioactive planchets are nonhazardous based upon analytical knowledge, and are disposed of as sanitary waste.

Planchets used for swipes are determined to be radioactive or nonradioactive. Radioactive swipes are disposed in the planchet waste drum. Nonradioactive swipes are nonhazardous waste based on the analytical process. Nonradioactive swipes are disposed of in the sanitary waste.

6.6 UNIVERSAL WASTE

40 CFR 261.9, and Part 273, 6CCR 1007-3, Section 273.6, 273.11, 273.13-273.19

Universal wastes are widely generated wastes including fluorescent lamps and batteries. Some fluorescent lamps fail the TCLP test for mercury, lead, or other heavy metals, and are considered hazardous waste. The universal waste regulations reduce the management requirements for universal wastes to increase proper recycling or disposal, but still require the management of the waste to be conducted in a manner that protects human health and the environment. Paragon accumulates less than 5,000 kilograms (11,000 pounds) of universal waste and is considered a Small Quantity Handler of Universal Waste.

The universal waste must be handled and collected in a way that prevents releases of any waste or components to the environment. Paragon has fluorescent lamps that are both hazardous and nonhazardous. All used lamps are collected and stored in their original box or specially purchased cardboard boxes. The boxes are labeled with a Universal Label identifying the contents. The nonhazardous lamps are segregated from the hazardous lamps and labeled with a nonhazardous waste label.

On site disposal of universal waste is prohibited. The local landfill does not accept any type of fluorescent lamps. All hazardous and nonhazardous lamps are sent to a permitted TSDF.

All used batteries shall be given to waste management staff. The batteries are collected and recycled.

6.7 MIXED WASTE

Mixed waste is waste that is determined to be both hazardous and radioactive. Unaltered samples and process waste can be mixed waste. Storage and handling of mixed waste must meet the requirements for RCRA waste and radioactive waste. Storage requirements for mixed waste are the same as for RCRA waste except that mixed aqueous waste drums must be contained in over pack drums. The requirements for handling radioactive aspects of the waste are detailed in SOP 15 - Disposal of Radioactive Waste.

6.8 RADIOACTIVE WASTE

All of Paragon's waste streams have the potential to be radioactive. The handling of wastes determined to be radioactive are addressed in SOP 15 - Disposal of Radioactive Waste.

6.9 PCB WASTE

40 CFR 761.50 and 761.64

PCBs or Aroclors are regulated under TSCA. A TSCA PCB waste is a material that has PCBs at a concentration of 50 ppm or greater. There are additional and unique requirements for management of PCB wastes as opposed to RCRA. Most PCB wastes dealt with at Paragon fall under 40 CFR 761.64. This Section of the regulation provides unique handling and disposal requirements for PCB waste generated as a result of chemical analysis of PCBs. The requirements for PCB wastes include container labeling, container types, temporary storage, and final storage prior to disposal. Some PCB wastes may be TSCA only; however, some PCB wastes may contain TSCA PCB and RCRA wastes. In this case, both TSCA and RCRA requirements apply. This will be most noticeable in storage and accumulation times.

Occasionally Paragon will receive samples that are radioactive and contain PCBs ≥50ppm. Paragon policy is to return these samples to the client after analysis. The samples are returned per DOT and EPA regulations.

6.9.1 <u>PCB Container Types For Long Term Storage</u>

40 CFR 761.40

The containers used to contain PCB wastes must be labeled with an EPA approved "Caution Contains PCBs" label. Paragon has available

both the large PCB Mark ML and the small PCB Mark MS labels. One of these labels must be used on all containers used to contain PCB Wastes.

If the waste is also a RCRA Waste, the appropriate Hazardous Waste Label must be placed on the container and all other RCRA labeling requirements apply.

All PCB waste containers in SAAs and Long Term Storage must be dated with the date the waste was added to the containers.

If there is an inner and outer containment system being used, both containers must be labeled with the appropriate labels.

6.9.2 Storage of PCB Waste
40 CFR 761.65

The Long Term Storage area must meet the construction requirements for the walls, roof, flooring, and curbing as detailed in the regulations. Rain and moisture must be kept from reaching the containers of PCB waste and the floor and curbing must provide the required containment volume. There must not be any types of openings to allow liquids to leak from the containment area. The storage area must not be located in the 100-year flood plain.

PCB wastes must be shipped within 9 months of the start date on the container. If the material is a RCRA waste, the maximum storage time will be 90 days.

All entries to the Long Term Storage area must be marked with the EPA-approved "Caution Contains PCBs", large PCB Mark ML label.

6.9.3 PCB Storage Area Inspections
Monthly inspections are required for PCB waste. Paragon's policy is to conduct weekly inspections on Short Term and Long Term Storage areas. The criterion for inspection is the same as for RCRA as described in Sections 1 and 1. PCB RCRA waste is inspected per the regulations for both TSCA and RCRA.

6.10 NON RCRA HAZARDOUS WASTE
Waste from the above waste streams that is determined to not be a RCRA Hazardous waste is classified as a non hazardous waste. Included in the nonhazardous waste description is floor sweepings from routine cleaning and sanitary trash. These wastes must have a written waste determination, including sanitary waste that is sent to the local landfill. Many of the waste streams

generated at Paragon are nonhazardous based on process and analytical knowledge.

7. WASTE DISPOSAL REQUIREMENTS

7.1 GENERAL

Paragon utilizes the services of several TSDFs for disposal of wastes. TSCA PCB wastes will be incinerated at an approved TSCA incineration facility. The facility will also be capable of handling destruction of RCRA components.

A staff member that has completed the US DOT Hazardous Materials Shipper Training must conduct the final manifesting and shipping operations.

Waste determinations are completed for some process wastes. The data are then sent to the local Publicly Operated Treatment Works (POTW) for permission to discharge through the sanitary sewer system. After written notification to dispose is received from the POTW, the waste is discharged through Paragon's holding tanks into the sanitary sewer system.

Sample containers (e.g., bottles and jars) that have been emptied into SAA containers or 90-Day Accumulation Area containers must be RCRA Empty and defaced before disposal in the sanitary solid waste. Empty sample containers that held radioactive materials must be washed, rinsed, defaced, and scanned for radioactivity before disposal as sanitary waste.

7.2 WASTE DISPOSAL OPERATIONS

All waste will be disposed of according to the waste determination specific to the waste. Waste determinations for all waste streams except unaltered samples will be hand written and kept on file. The unaltered sample waste determination is performed by LIMS electronically from data input from client information and process knowledge.

Laboratory personnel will dispose of unaltered sample wastes according to waste packs created in LIMS. The waste pack will list the waste stream for the samples. The sample will be placed into an SAA or waste container in a 90-Day Accumulation Area, that is appropriate for the LIMS characterized waste.

Laboratory personnel will dispose of all other types of waste according to the waste determination kept on file by the waste management staff. These wastes will be disposed into an SAA or 90-Day container designated for that specific waste stream.

Waste that is determined to be Non RCRA Hazardous will be disposed of properly. Non RCRA Hazardous waste may or may not be able to be disposed of in a sanitary waste stream or the sanitary sewer system. The waste management staff will give disposal instructions for these types of waste. The exception to this

statement is routine floor sweeping material, mop residue from non-spill cleaning activities and sanitary trash. These wastes can be disposed of in sanitary waste streams.

8. SAFETY AND TRAINING FOR PERSONNEL PERFORMING WASTE DISPOSAL

40 CFR 262.34(a)(4) & 265.16(a), 6 CCR 1007-3, Section 262.34(a)(4) & 265.16(a)

The safety hazards associated with waste disposal involve potential spread of hazardous and radioactive material contamination, and loading and moving the waste containers. All personnel shall utilize the appropriate personal protective equipment for the task at hand. This will include, at a minimum, gloves, lab coat, and safety glasses. At other times, respirators and Tyvek coveralls may be required. All operations involving moving containers (e.g., full 55 gallon drums) shall utilize suitable moving devices such as barrel dollies and use of steel-toed shoes. Waste disposal procedures are addressed Section 7.

Personnel handling hazardous waste must be trained with classroom and on-the-job training that teaches them to perform their jobs to maintain compliance with the hazardous waste regulations.

A staff member that has completed the US DOT Hazardous Materials Shippers Training must conduct the final manifesting and shipping operations.

9. REFERENCES

9.1 Colorado Department of Public Health and Environment Hazardous Waste Regulations.

9.2 Guide to Generator Requirements of the Colorado Hazardous Waste Regulations.

9.3 Code of Federal Regulations 40CFR 260 to 279.

9.4 Code of Federal Regulations 40CFR 761.

9.5 RCRA Regulations and Key Word Index, 2001 Edition.

9.6 RCRA Unraveled, 2001 Edition.

DOCUMENT REVISION HISTORY

11/7/07: Section 6.2 “Some samples upon completion of analysis are returned to the client.” Added “ The samples are packaged for return shipment per SOP 027 directives. Permission to return the samples is obtained from the client prior to sample shipment.” Also added “Records of disposal are maintained by the Waste Compliance Officer.” Added DOCUMENT REVISION HISTORY Section, added Forms.

A. SAA Key

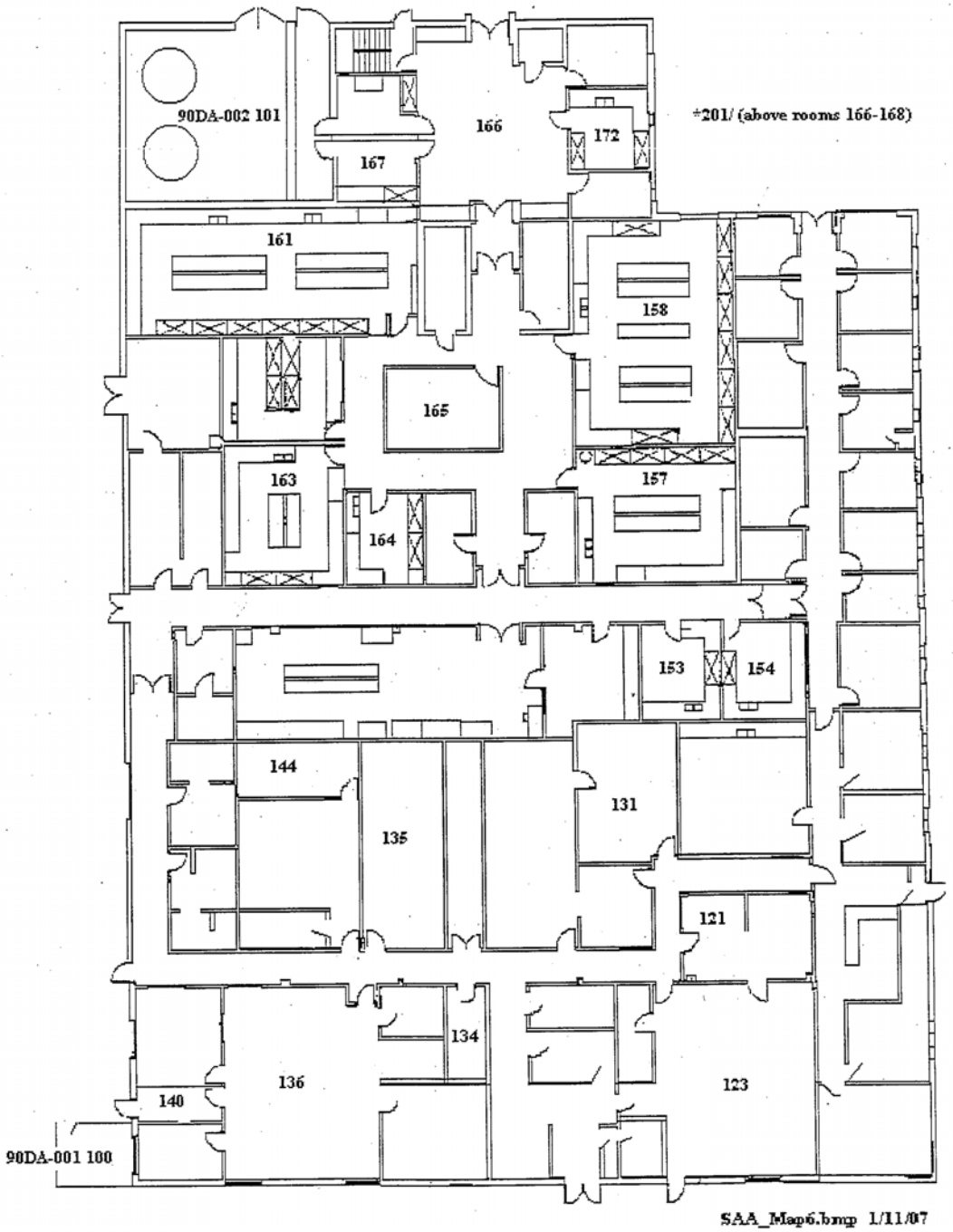
Paragon Analytics

Satellite Area Designation Area Name/SAA-Room Number/ SAA specific designation	**Room Identification**
Sample Rec./SAA-166/001	Sample Receiving
Pre-Screen/SAA-172/001	Pre-Screen Sample Prep. Lab
Actinides/SAA-161/002	Actinides-Waters Lab
Actinides/SAA-161/001	Actinides-Waters Lab
Strontium/SAA-158/005	Radium and Strontium Lab
Strontium/SAA-158/001	Radium and Strontium Lab
Strontium/SAA-158/002	Radium and Strontium Lab
Strontium/SAA-158/003	Radium and Strontium Lab
Strontium/SAA-158/004	Radium and Strontium Lab
WCL/SAA-167/001	Waste Characterization Lab
WCL/SAA-167/002	Waste Characterization Lab
WCL/SAA-167/003	Waste Characterization Lab
WCL/SAA-167/004	Waste Characterization Lab
Grinding/SAA-164/001	Sample Prep./Grinding Lab
Grinding/SAA-164/002	Sample Prep./Grinding Lab
Low-Level SAA-163/01	Ultra Low-Level Rad. Prep. Lab
Wet Chem./SAA-157/001	Wet Chemistry Lab
Wet Chem./SAA-157/002	Wet Chemistry Lab
Wet Chem./SAA-157/003	Wet Chemistry Lab
Tritium/SAA-153/001	MicroPrecipitation Lab
SVOCs/SAA-144/001	GC/MS Semivolatiles Lab
GCMS/SAA-201/001	GC/MS Volatiles Lab
HPLC/SAA-131/001	HPLC/TOC Lab
Fuels/SAA-135/001	Fuels Lab (Room 135)
Fuels/SAA-135/002	Fuels Lab (Room 135)
Metals/SAA-136/001	Metals Lab
Metals/SAA-136/002	Metals Lab
Metals Hallway/SAA-140/001	Metals Lab Hallway
Org. Standards/SAA-134/001	Organic Standards Lab/GPC Room
Org. Standards/SAA-134/002	Organic Standards Lab/GPC Room
Org. Extractions/SAA-123/001	Organic Extractions Lab
Org. Extractions/SAA-121/001	Organic Extractions Glass Room
Org. Extractions/SAA-121/002	Organic Extractions Glass Room
Org. Extractions/SAA-121/003	Organic Extractions Glass Room
Org. Extractions/SAA-121/004	Organic Extractions Glass Room
Org. Extractions/SAA-121/005	Organic Extractions Glass Room
Org. Extractions/SAA-121/006	Organic Extractions Glass Room
Sample Archive/SAA-165/001	Sample Warm Storage/Archive Area
Rad Standards/SAA-154/001	Rad Standards Lab

B. SAA Map

Satellite Accumulation Areas (SAAs) & 90-Day Storage Areas (key follows)

Paragon Analytics



C. SAA Description *Paragon Analytics*

C1

Room Identification	Sample Receiving
Satellite Area Designation	1/001, located in hood on southwest side of room
Process Description	Receipt of incoming samples Residual chlorine test on aqueous samples
Acceptable Waste Streams	Solid waste that has contacted sample liquids and solids; Aqueous lab waste
For Questions or When Container is Full, Contact:	Charles Orchard

Paragon Analytics

D. Satellite Accumulation Area Weekly Checklist *

Rad Standards SAA-27/001 ***Rad Standards Lab***	**Date / Initial**		**Date / Initial**		**Date / Initial**		**Date / Initial**		**Date / Initial**	
SAA	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No
1. Is the area clearly defined as an SAA?										
2. Is the area accessible?										
3. Is the area clean and free of debris?										
4. Is the area free of ignition sources?										
5. Is the total volume of Hazardous Waste below 55 gallons?										
6. Is the total volume of Acutely Hazardous Waste below 1 quart?										
7. Is the SAA in the Paragon Contingency Plan?										
8. Is the SAA under control of the process operator?										
9. Is the process generating waste still active?										
10. Is a spill kit readily available?										
Container Labels	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No
11. Are labels clearly visible when entering the SAA?										
12. Are labels in good condition?										
13. Are the words "Hazardous Waste" on each label?										
14. Are the contents of the container listed?										
Container Condition	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No
15. Is the container compatible with contents?										
16. Is the container in good condition? (ex. not leaking, dented, bulging, corroding, etc.)										
17. Can each side of the container be inspected?										
18. Are all containers closed?										
19. Is the outside of the container/secondary container clean and free of residue?										
20. Are incompatible waste in secondary containment?										
21. Is ignitable/reactive waste at least 50 feet from property line?										
22. Are all PCB inspection criteria met, including dated labels and 30-day hold times?										

* Note: Inspections of short-term storage of PCB and PCB-RCRA wastes are done on a weekly basis. The criteria used for each inspection (i.e., PCB and PCB-RCRA) are the same. PCB only and PCB-RCRA wastes may be held for a maximum of 30 days.

_____ A

Paragon Analytics

Satellite Accumulation Area Weekly Checklist (continued)

Comments (Initial and Date each comment)			Corrective Action Complete?	
Initial	Date		Yes	No

_____ B

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 008 REVISION 8

TITLE: **INITIAL RECEIPT OF RADIOACTIVE SAMPLES & EXTERNAL RADIATION EXPOSURE RATE AND REMOVABLE RADIOACTIVE MATERIAL CONTAMINATION SURVEY OF INCOMING RADIOACTIVE MATERIAL PACKAGES**

FORMS: **008, 009, 201, 214** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE 1/19/07

LABORATORY MANAGER _____ DATE 1-19-07

HISTORY: Rev0, 9/04/92; Rev1, 3/31/94; Rev2, 4/09/96; Rev3, 3/15/99; Rev4 (combined with SOP 209), 1/26/00; Rev5, 9/13/00; Rev6, 6/28//02; Rev7, 2/9/04 and 11/10/05 (re-released w/o revision); Rev8, 1/19/07.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures for conducting (1) the radioactive external exposure rate survey of all sample shipping containers received by the laboratory; and (2) the DOT radioactive survey of all incoming radioactive material packages for external radiation exposure rate and removable radioactive contamination. Radiation exposure rate guidelines, which determine acceptance or rejection of samples or materials and the manner in which they are processed, are described in this SOP. Directions for calibration of the radiation survey equipment used are presented in SOP 013. Detailed sample receipt and login processes are discussed in SOP 202.

2. OVERVIEW

2.1 Upon receipt, sample receiving personnel survey all sample shipping containers and incoming radioactive material packages for external radiation exposure rate. A DOT Survey form (Form 008) is completed. Additional steps taken are contingent upon the radiation rate levels determined by the external radiation exposure rate survey results. The steps taken are based on whether the surveyed items are samples or DOT-classified radioactive materials.

2.2 In general, sample shipments are accepted so long as external radiation exposure rates do not exceed 0.5mR/hr. If the radiation survey results are below 0.5mR/hr but are higher than two times the laboratory background levels, then the samples are only "provisionally" logged in (see SOP 202). The samples are then routed through a formal prescreening process (see SOP 703). The Radiation Safety Officer (RSO) may designate some client's samples as "always prescreen." The RSO, based on the prescreening results, determines acceptance or rejection of the samples. If the client's samples are not designated as "always prescreen" and the initial receipt survey results are less than two times laboratory background levels,

then the samples are accepted and processed for login (sample prescreening is not required).

2.3 Radioactive material packages are those labeled as (1) Excepted Radioactive Material, (2) Low Specific Activity (LSA) Radioactive Material, or (3) Radioactive Material I, II, or III, per 49 CFR 173 or IATA Dangerous Goods Regulations. The Colorado Rules and Regulations Pertaining to Radiation Control also apply.

In addition to the external radiation rate exposure survey, shipping containers for incoming radioactive material packages are also subjected to an external wipe test. The resultant wipe is counted and the results are recorded by the instrument printout (see SOP 010). Further wipe testing is conducted on all primary radioactive material containers (results recorded on Form 009). The wipe tests constitute the removable radioactive material contamination survey.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

4.1 Ludlum Model 19 MicroRoentgen (Micro R) meter or equivalent

4.2 Ludlum Model 1000 Scaler with Model 43-10 Alpha Scintillation Detector or equivalent

4.3 Ludlum Model 1000 Scaler with Model 44-7 End Window Geiger-Mueller Detector or equivalent

4.4 Oxford LB5100 Gas Flow Proportional Counter

4.5 filter papers, 47mm, Whatman #42 or Rad-Wipe Smears, or other equivalent

4.6 planchets, steel, 46mm

5. PROCEDURE

5.1 Where possible, the Project Manager (PM) will inform Sample Control staff of deliveries from clients whose samples may be radioactive. An Incoming Project Notice (IPN) form (Form 214) or a COC faxed from the field may be used for this purpose.

5.2 Calibrate all radiation survey equipment per SOP 013.

5.3 EXTERNAL RADIATION SURVEY OF SHIPPING CONTAINERS

5.3.1 This step applies to all incoming sample and radioactive materials containers. Ideally, shipping containers (i.e., coolers, ice chests, etc.) from radiological contractors are identified and segregated in the receiving area upon receipt. Coolers from radiological contractors may be identified via the return address information indicated externally on the cooler, or by the Chain-of-Custody (COC) paperwork contained inside.

NOTE: Per SOP 202, intactness of the chain-of-custody seals must be noted prior to opening.

5.3.2 Visually inspect the shipping container for damage that compromises the container's integrity. ***Notify the RSO immediately if any DOT classified radioactive material containers are damaged.***

5.3.3 Check the exposure rate at the container's surface using the Ludlum Model 19 Micro R survey meter. ***Notify the RSO immediately if any package exceeds the external radiation exposure rate limitations presented in Table 1 below:***

Table 1: RADIATION EXPOSURE RATE LIMITATIONS FOR SHIPPING CONTAINERS

		Incoming Radioactive Material Packages
Non-Exclusive Use Radioactive Material Shipment Type	***Maximum Allowable Surface Dose Rate at Surface (mR/hour)***	***Transport Index (TI) Maximum at One Meter (mR/hour)***
Excepted Radioactive Material (e.g., environmental samples)	0.5	N/A
Low Specific Activity (LSA)	0.5 *	N/A
Radioactive I	0.5	0.0
Radioactive II	50	1.0
Radioactive III	200	10

* In-house Paragon Limitation

Note that sample shipping containers must yield incoming radioactive survey results of less than 0.5 mR/hour.

NOTE: Due to radioactive material license limitations, Paragon will not accept Radioactive Material - LSA, N.O.S. packages yielding a greater than 0.5 mR/hour external surface radiation exposure rate, without prior approval by the RSO.

Paragon will not accept incoming radioactive material packages that require a Radioactive II or III DOT Warning label, without prior approval by the RSO.

5.3.4 Record the results of the external radiation survey on Form 008.

5.3.5 If the sample shipping container is not from a client whose samples are designated as "always prescreen," and is not labeled with any of the DOT classifications listed above, and if the external radiation survey results of the sample shipping container yields results are below two times the laboratory background level, then the samples are accepted for normal login processing per SOP 202. Prescreening is not required.

5.3.6 All sample shipping containers yielding external radiation exposure rate survey results less than 0.5 mR/hr may be processed. Open the sample cooler. ***If any samples containers are leaking or broken, contact the RSO immediately.***

5.3.7 Provisionally login samples (SOP 202) for clients whose samples are designated as "always prescreen," if the external sample shipping container radiation exposure rate is less than 0.5mR/hr. ***If the external sample shipping container radiation exposure rate is greater than 0.5mR/hr, notify the RSO immediately.***

5.3.8 If the client's samples are not designated as "always prescreen" and the radiation survey results are less than 0.5mR/hr but are greater than two times the laboratory background levels, then accept the samples for provisional login and prescreening.

5.3.9 If the item is a DOT classified radioactive material package and the criteria listed in Table 1 are not exceeded, then accept the package. If the shipment contains samples, then route the samples to prescreening (SOP 703). If the limits presented in Table 1 are exceeded, process the material per SOP 009.

5.3.10 Begin completing the Sample Condition Upon Receipt Form (Form 201). As described in SOP 202, acceptance or rejection of the samples is determined by the RSO based on the prescreening results.

5.4 SHIPPING CONTAINER WIPE TESTING

For all DOT classified radioactive material packages, the shipping container is also subjected to an external wipe test. ***After opening the shipping container, if any of the sample containers are leaking or broken, contact the RSO immediately.***

5.4.1 Wipe a filter paper or Rad-Wipe over a 4" x 4" square area of the container's external surface.

5.4.2 Count the wipe per SOP 010.

5.4.3 Record the results on Form 009 or retain printout from instrument.

5.5 WIPE TESTING OF SAMPLE CONTAINERS

This step applies to all packages from clients that may ship radioactive material samples to Paragon. The package may not need to be classified as a DOT Radioactive Material shipment.

5.5.1 Make a composite wipe over all the sample containers.

5.5.2 Count the wipe per SOP 010.

5.5.3 If the results exceed the limits indicated in Table 3, then each container must be wipe tested individually.

5.5.4 Record the results on Form 009 or retain printout from instrument.

Table 2: REMOVABLE EXTERNAL RADIOACTIVE CONTAMINATION LIMITS FOR OUTER SHIPPING CONTAINERS

Radionuclides	*dpm/cm^2*
Beta/Gamma emitting radionuclides; all radionuclides with half lives less than ten days; natural uranium; natural thorium; U-235; U-238; Th-232; Th-228; and Th-230 when contained ores or physical concentrates	22
All other alpha emitting radionuclides	2.2

Table 3: REMOVABLE EXTERNAL RADIOACTIVE CONTAMINATION LIMITS FOR SAMPLE CONTAINERS

Radionuclides	*dpm/100 c^{m2}*
Beta/Gamma emitting radionuclides;	200
All other alpha emitting radionuclides	20

NOTE: Sample control personnel should consult with the RSO if there is any uncertainty as to whether a shipment requires both external shipping and primary sample container surveys.

5.6 NOTIFICATION OF REGULATORY AUTHORITIES IN THE EVENT OF A PACKAGE THAT HAS BEEN INVOLVED IN AN TRANSPORTATION ACCIDENT

In the event a package received at or shipped to Paragon has been involved in an accident, the RSO must immediately notify the Radiation Control Division of the Colorado Department of Public Health and Environment Laboratory and Radiation Services Division and the U.S. DOT as per the requirements of 49 CFR.

6. QUALITY CONTROL (QC)

Applicable quality control procedures are detailed in SOP 014.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

7.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

7.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

7.1.3 The radioactive material check source must be stored in its container when not in use.

7.1.4 Food and drink are prohibited in all lab areas.

7.2 WASTE DISPOSAL

All used wipes that have radioactive material contamination shall be disposed of as Low Level Radioactive Waste.

8. REFERENCES

8.1 49 CFR 173.

8.2 IATA Dangerous Goods Regulations.

8.3 “Rules and Regulations Pertaining to Radiation Control,” Colorado Department of Health, Radiation Control Division, 2001.

DOCUMENT REVISION HISTORY

1/19/07: Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

SAMPLE LOGIN / DOT SURVEY

Client _____ Workorder No. _____ Project/Site _____

Shipping Container ID ____ ____ ____ ____ ____ ____ ____ ____

External Micro R Meter Reading (μ R/hr) ____ ____ ____ ____ ____ ____ ____ ____

Background Micro R Meter Reading (μ R/hr)_____ Date _____ Initials _____

Notify RSO immediately if shipping container's meter reading is more than twice background reading!!

Samples received from clients designated as "always prescreen" must be routed through the prescreening process (see SOP 202).

If twice background is exceeded, RSO or designee will complete the following Table:

CLIENT SAMPLE ID	CONTAINER DESIGNATION	EXPOSURE RATE (μ R/hr)

Further action (e.g., prescreening, wipe testing per SOP 008, etc.) will be directed by the RSO. As applicable, sample disposition will be communicated via LIMS Project Specifications.

Where applicable, attach LB5100 prescreening and/or wipe testing results.

Form 008r6.doc (6/26/04)

SAMPLE LOGIN SURVEY

PARAGON ANALYTICS, INC.
REMOVABLE RADIOACTIVE MATERIAL CONTAMINATION SURVEY

ALPHA DETECTOR: Ludlum Model 1000 Serial #95539 With 43-10 Alpha Detector, Serial #PR094423
BETA DETECTOR: Ludlum Model 1000 Serial # 95543 With 44-7 End Window G-M Detector, Serial #PR094207

RADIOACTIVE MATERIAL CALIBRATION SOURCE INFORMATION

Manufacturer	Radionuclide	Activity(dpm)	TOC Date	Half Life(years)	Activity @ TOA
ANALYTICS	AM-241	9624	9/1/1993	432.2	#VALUE!
ANALYTICS	Cs-137	9378	9/23/1993	30	#VALUE!

ALPHA & BETA EFFICIENCY DETERMINATIONS

	Background Counts	Gross Counts	Net CPM	Alpha Efficiency	MDA(DPM)	MDA (DPM/100Sq.cm)
Alpha	Number	Number	#VALUE!	#VALUE!	#VALUE!	#VALUE!
Beta	Number	Number	#VALUE!	#VALUE!	#VALUE!	#VALUE!

Background Count Time= 5 Minutes

RESULTS OF REMOVABLE RADIOACTIVE MATERIAL CONTAMINATION SWIPE TESTS ON INCOMING SAMPLE CONTAINERS

DATE SWIPES TAKEN: Enter
Location of Swipes: Count Time 5 Minutes

Swipe #	SampleID	Gross Alpha Counts	Gross Beta Counts	Calculated Alpha DPM/300sq cm	Calculated Beta DPM/300sq cm	Calc. Alpha DPM/100sq cm	Calc. Beta DPM/100sq cm
1	Cooler 1	0	0			0.0	0.0
2	Cooler 2	0	0			0.0	0.0
3	Cooler 3	0	0			0.0	0.0
4	Cooler 4	0	0			0.0	0.0
5	Cooler 5	0	0			0.0	0.0
6	Cooler 6	0	0			0.0	0.0
7	Cooler 7	0	0			0.0	0.0
8	Cooler 8	0	0			0.0	0.0

Paragon Analytics

CONDITION OF SAMPLE UPON RECEIPT FORM

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

1.	Does this project require any **special handling** in addition to standard Paragon procedures?		YES	NO
2.	Is **pre-screening** required per SOP 008?		YES	NO
3.	Are custody **seals** on **shipping containers** intact?	N/A	YES	NO
4.	Are custody **seals** on **sample containers** intact?	N/A	YES	NO
5.	Is there a **COC (Chain-of-Custody) present** or other representative documents?		YES	NO
6.	Is the **COC** (if applicable) **complete and legible**?	N/A	YES	NO
7.	Are **bottle IDs legible** and in **agreement** with **COC sample IDs**?	N/A	YES	NO
8.	Is the COC in agreement with samples received? (**# of samples, # of containers, matrix**)	N/A	YES	NO
9.	Were **airbills** present and/or removable?	N/A	YES	NO
10.	Are all **aqueous samples** requiring preservation **preserved correctly**? (excluding volatile organics)	N/A	YES	NO
11.	Are all aqueous **non-preserved samples** at the **correct pH**?	N/A	YES	NO
12.	Is there **sufficient sample** for the requested analyses?		YES	NO
13.	Were all samples placed in the **proper containers** for the requested analyses?		YES	NO
14.	Are all samples within **holding times** for the requested analyses?		YES	NO
15.	Were all sample containers received **intact**? (not broken or leaking, etc.)		YES	NO
16.	Are all samples requiring no headspace (volatiles, reactive cyanide/sulfide, radon), headspace free? **Size of bubble**: ____ < green pea ____> green pea	N/A	YES	NO
17.	Were samples checked for and free from the presence of **residual chlorine?** (Applicable when PM has indicated samples are from a chlorinated water source; note if field preservation with sodium thiosulfate was not observed.)	N/A	YES	NO
18.	Were the sample(s) **shipped on ice**?	N/A	YES	NO
19.	Were cooler temperatures measured at 0.1-6.0°C?	N/A	YES	NO

***IR gun used** *(circle one)* : **#2** - Oakton InfraPro II, SN2922500201-0066; **#4** - Oakton InfraPro II, SN2372220101-0002

Cooler #'s								
Temperature (°C)								
No. of custody seals								
DOT Survey/ Acceptance Information: External µR/hr reading								
Background µR/hr reading								

Were external µR/hr readings ≤ two times background and within DOT acceptance criteria? **YES / NO** (If no, see Form 008.)

Additional Information: PROVIDE DETAILS BELOW FOR A NO RESPONSE TO ANY QUESTION ABOVE EXCEPT #1 AND #2

If applicable, was the client contacted? **YES / NO / NA** Contact Name:_____ Date/Time:_____

Project Manager Signature/ Date: _____

Form 201r18.xls (6/26/04)

Kit: Y / N **Rush?** Y / N **Prescreen?** Y / N ***Paragon Analytics***

INCOMING PROJECT NOTICE

Date: _____ **Copy to:** Sample Control

Initiator: _____

Date(s) expected: _____

Client: _____ Assigned PM: _____

Address: _____ Client Contact: _____

_____ Phone: _____

Report to: _____ Fax: _____

Proj. Name/Number: _____

# Samp	Matrix	Analysis/Method	Price	Sub Lab	# x Cont. Type	Preserv.	Tot. Bottles
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		

QC Level: _____ Disposal or handling? $5 / $10 / $15 / $_____ / RTC

Report Level: _____ TAT (working days): 20 / 15 / 10 / 5 / 3 / 2 / 24hr /____

EDD: N / Y Format: Report: Wet Weight / Dry Weight / As Received

Kit to:

Date kit needed: _____ **am / pm**

Attention: _____

Company: _____

Address: _____

_____

Phone: _____

Potential Radioactivity:

Do the samples contain radioactive materials?	Y / N
Are any samples potentially mixed hazardous materials?	Y / N
Are any samples from a known RAM site?	Y / N

Additional Special Handling:

Include: COC(s) Bubble Wrap Labels Seals Blue Ice Temp. Blks

Comments: Rush Special Test Special Analyte Special Charge Detection Limits (see attached)

Kit Prepared by: _____ Date: _____ Picked up by: _____ Date: _____

i:\oprtns\misc\forms\IPN_Form214r5.xls (10/29/03)

CONFIDENTIAL

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 009 REVISION 7

TITLE: INCOMING RADIOACTIVE MATERIAL PACKAGES THAT EXCEED REMOVEABLE RADIOACTIVE MATERIAL CONTAMINATION LIMITS

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/12/07

QUALITY ASSURANCE MANAGER _____ DATE 1/12/07

LABORATORY MANAGER _____ DATE 1-12-07

HISTORY: Rev0, 10/26/92; Rev1, 3/31/94; Rev2, PCN #485, 6/03/95; Rev3, 3/15/99; Rev4, 2/11/02; Rev5, 4/04/03; Rev6, 2/13/04 and 11/10/05 (re-released w/o revision); Rev7, 1/12/07.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) mandates that the Radiation Safety Officer (RSO) be notified immediately when incoming samples or radioactive material packages fail to meet the regulatory criteria established for removable radioactive contamination. This SOP applies to excepted radioactive material packages, Low Specific Activity (LSA), and Radioactive I, II, and III radioactive material packages. The specific procedures used to conduct removable radioactive material contamination surveys of incoming radioactive material packages are detailed in SOP 008.

2. SUMMARY

The RSO must be notified immediately when incoming samples or radioactive material packages fail to meet the criteria set forth by the Colorado Radiation Health Regulation RH 17.15.8 and/or the United States Department of Transportation (US DOT) regulations contained in 49CFR 173.443. **The regulatory limit is 22 dpm/cm^2 for beta-gamma emitting radionuclides; radionuclides with half-lives of less than 10 days; natural uranium; natural thorium; and U-235, U-238, Th-232, Th-228 and Th-230 contained in ores or physical concentrates. The limit is 2.2 dpm/cm^2 for all other alpha emitting radionuclides.** Upon notification, the RSO discusses the problem with the appropriate Project Manager (PM). The RSO or PM contacts the client to resolve the situation.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to inform the Sample Receiving Manager and the RSO of any problems that may occur during the performance of these procedures.

3.2 It is the responsibility of the Sample Receiving Manager to ensure that the package has been properly decontaminated prior to release from the receiving area or handling by the general staff.

3.3 It is the responsibility of the RSO to ensure that the activity limits provided in this procedure are current and in compliance with applicable regulations.

4. APPARATUS AND MATERIALS

Ludlum Model 19 MicroRoentgen (Micro R) meter or equivalent

5. PROCEDURE

5.1 Perform a survey of incoming packages per SOP 008.

5.2 If contamination exceeds the limits indicated in Section 2.0 of this SOP, Table 5.1 of SOP 008, or Colorado RH 17.15.8, notify the Sample Receiving Manager and the RSO immediately.

5.3 The RSO promptly notifies the appropriate PM. The RSO or PM contacts the client to resolve the situation.

6. SAFETY, HAZARDS AND WASTE DISPOSAL

6.1 SAFETY AND HAZARDS

6.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

6.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), when handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

6.2 WASTE DISPOSAL will be performed in accordance with the Paragon Waste Management Plan

7. REFERENCES

6.1 "Rules and Regulations Pertaining to Radiation Control", Colorado Department of Public Health and Environment (CDPHE), 2001.

6.2 Code of Federal Regulations (CFR), Title 49, Chapter 1, Subchapter C, October 2002.

DOCUMENT REVISION HISTORY

1/12/07: Section 2, changed phrase **"The regulatory limit is 22 dpm/cm^2 for alpha-beta emitting radionuclides…"** to only include beta-gamma emitting radionuclides, not

alpha emitters. Section 3, added specific responsibilities for the RSO and Sample Receiving Manager. Added Section 4, APPARATUS AND MATERIALS. Section 5.2, referenced Waste Management Plan. Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 010 REVISION 4

TITLE: **SURVEY OF LABORATORY AREAS FOR RADIOACTIVE CONTAMINATION**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/13/07

QUALITY ASSURANCE MANAGER _____ DATE 2/13/07

LABORATORY MANAGER _____ DATE 2-19-07

HISTORY: Rev0, 9/4/92; Rev1, 10/26/93; Rev2, 8/25/02; Rev3, 2/9/04 and 11/10/05; Rev4, 2/8/07.

re-released w/o revision 7/20/08 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used to survey any areas within the laboratory facilities (e.g., laboratories, storage areas) where radioactive materials have been or are being used. To comply with Paragon's radioactive materials license requirements, area surveys must be performed weekly in any area where radioactive materials have been used.

2. SUMMARY

To determine if removable radioactive contamination is present, the area must be surveyed using wipes and counted for both alpha and beta-emitting radioactive materials. Wipes should be taken over a 100 cm^2 area (~4inch x 4inch). Each wipe shall be analyzed using the appropriate counting equipment for the type of radiation suspected. The results shall be reported in units of dpm/100cm^2 area.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Facility, Sample, and Waste Control Manager to ensure that the surveys are performed properly and timely, to review the survey results, and to maintain the historical survey data for a period of at least two years after the survey is completed.

The Facility, Sample, and Waste Control Manager must ensure that any necessary decontamination procedures are followed, and must notify the Radiation Safety Officer (RSO) any time there is a survey result above the action level described in the Procedures section.

3.2 It is the responsibility of the Laboratory QA Manager, or designee, to maintain current and accurate maps of the facility, which may be copied from the LQAP or other source, and be used to perform these surveys.

3.3 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.4 It is the responsibility of all personnel who work with these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

4.1 removable radioactive material contamination survey laboratory maps

4.2 Defensap™ smears or 2" filter paper or equivalent

4.3 envelopes

4.4 laboratory gloves

4.5 planchets, 47mm

4.6 permanent-ink marker

4.7 Oxford LB-5100 gas flow proportional counter or equivalent

4.8 NE Electra with Dual Phosphor Alpha/Beta Probe

4.9 RadiacWash™ , or equivalent detergent with chelating agent

5. PROCEDURE

5.1 SURVEY LOCATIONS

5.1.1 All areas that could have been contaminated by radioactive material should be smeared (wipe tested). These areas include but are not limited to floors, walls, benchtops, and hoods.

5.1.2 Smear locations should be identified on the appropriate survey map for each specific laboratory.

5.2 PROPER SMEAR TECHNIQUES

5.2.1 Wipe smear paper with medium pressure over a 100cm^2 area (~ 10cm x 10cm or 4in x 4in).

5.2.2 Place smear in an envelope marked with the appropriate smear number or use an integrated smear/folder combination. The smear number should correspond to the location number on the removable radioactive material contamination forms or on the area maps.

5.3 SMEAR COUNTING

5.3.1 The smear should be counted for removable contamination in the Oxford LB-5100 gas flow proportional counter.

5.3.2 The smear sample is placed in a 47mm planchet and the smear ID is written on the bottom of the planchet. The smears are loaded and

counted in the Oxford LB-5100 gas flow proportional counter as directed by SOP 724.

5.3.3 The smears are counted for 1 minute or long enough to reach a minimum Lower Limit of Detection (LLD) of 10 dpm/100cm^2 for alpha and 20 dpm/100cm^2 beta-emitters.

5.3.4 The LB-5100 generates a report providing the activity in dpm/100cm^2, the 2 sigma total propagated uncertainty (TPU) in dpm/100cm^2, and the Minimum Detectable Activity (MDA) in dpm/100cm^2. The results shall be reviewed to determine any areas that exceed the Action Levels of 10 dpm/100cm^2 alpha, 100 dpm/100cm^2 beta, or in excess of 100dpm/100cm^2 combined alpha and beta contamination.

(a) CALCULATE BACKGROUND COUNT RATE:

$$R_b = \frac{C_b}{T_b}$$

where:

R_b = Background count rate (cpm)

C_b = Total background counts

T_b = Background count time (min)

(b) 2 SIGMA TOTAL PROPAGATED UNCERTAINTY:

$$2sTPU = \frac{2(\,SmpCts + (BkgCPM) + (SmpCts * Xtalk)\,)^{1/2}}{\text{Efficiency}}$$

(c) MDA CALCULATION:

$$MDA = \left(4.66\sqrt{\frac{R_b}{T_b}} + 2.71/T_b \right) \Big/ EFF$$

where:

R_b = Background count rate (cpm)

T_b = Background count time (min)

EFF = Instrument Counting Efficiency

5.3.5 Any area whose smears exceed the Action Levels shall be cleaned with RadiacWash™ and surveyed using an NE Electra with Dual Phosphor Alpha/Beta Probe. A confirmatory wipe test will be performed following the cleaning, and alpha-beta will be determined to verify that

the removable contamination levels are below the action levels. Repeat this process until the removable radioactive material contamination levels in the affected area are below the action levels.

6. SAFETY, HAZARDS AND WASTE DISPOSAL

6.1 SAFETY AND HAZARDS

6.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

6.1.2 Wear gloves, safety glasses, and lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or radioactive materials or within a laboratory area.

6.1.3 The radioactive material check source(s) must be stored in its container when not in use.

6.1.4 Food and drink are prohibited in all lab areas.

6.2 WASTE DISPOSAL

All used wipes that contain radioactive material contamination shall be disposed of as Low Level Radioactive Waste.

7. REFERENCES

7.1 "Rules and Regulations Pertaining to Radiation Control", Colorado Department of Health, Radiation Control Division, 2001.

7.2 Paragon Analytics Radiation Protection Plan.

DOCUMENT REVISION HISTORY

11/10/05: Rev3, re-released without revision.

2/8/07: Expanded RESPONSIBILITIES Section. Added items to APPARATUS AND MATERIALS. Updated and corrected calculations. Minor format updates, defined acronyms. Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 012 REVISION 6

TITLE: **CONTAMINATION SURVEYS USING PORTABLE SURVEY METERS (E.G., ELECTRA, MICRO REONTGEN)**

FORMS: **014, ~~028~~, 219** **(use current iteration)**

Form 028 was consolidated with Form 219. Text references were corrected. DAS 8/13/07

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/13/07

QUALITY ASSURANCE MANAGER _____ DATE 8/10/07

LABORATORY MANAGER _____ DATE 8/13/07

HISTORY: Rev0, 9/4/92; Rev1, PCN #200, 4/5/94; Rev2, 3/16/99; Rev3, 8/27/02; Rev4, 2/9/04; Rev5, 3/24/05. Was retired then reinstated with revision - Rev6, 8/10/07. re-released w/o revision 7/20/08 DAS

1. SCOPE AND APPLICATION

Portable survey meters that detect contamination and radiation are available for personnel use to perform surveys on equipment, personnel or in areas where radioactive material is stored or analyzed. This Standard Operating Procedure (SOP) describes the methods and procedures used to ensure that the meters are functioning correctly, that proper calibration and performance checks are performed, and that surveys are performed in the proper manner.

2. SUMMARY

One of the most important aspects of an efficient and productive radiation protection program is pro-active contamination control. The control of personnel contamination is a significant part of this program. By following the procedures outlined in this SOP, the spread of contamination will be minimized.

All laboratory personnel who are engaged in preparing or analyzing samples or standards that may be radioactive, shall survey their hands, feet, and any other area suspected of contacting radioactive materials if so directed by LIMS special instructions or the Radiation Safety Officer (RSO). Additionally if a spill is suspected or occurs while aliquotting, the technician shall perform a survey of the area in question. Periodic surveys of sample storage areas for radiation are also performed to ensure that dose is in compliance with the State of Colorado Rules pertaining to Radiation Control.

Furthermore, all laboratory personnel who have entered a controlled area are responsible for performing a personal contamination survey upon leaving the controlled area. This survey is typically conducted using a hand and foot monitor (e.g., Berthold, SOP 029), or by a conducting a survey using the Electra as described herein.

All laboratory radiation and contamination surveys are conducted using a survey meter equipped with a dual phosphor alpha-beta scintillation detector (e.g., Electra), a meter equipped with a Sodium Iodide gamma scintillation detector (Micro R Meter), and

contamination swipes that are subsequently analyzed on a Gas Flow Proportional counter.

3. RESPONSIBILITIES

3.1 The RSO is responsible for maintaining an adequate supply of properly functioning radiation survey equipment. Any needed repairs or replacements shall be coordinated by the RSO, the RSO shall maintain meter service records. The RSO shall also coordinate the periodic surveys conducted of radioactive materials storage areas.

3.2 Project Managers are responsible for working with the RSO to create LIMS special instructions as necessary pertaining to samples to be processed for their projects.

3.3 It is the responsibility of all laboratory staff to consult the LIMS special instructions and to observe the requirements and procedures described in this SOP.

4. APPARATUS AND MATERIALS

4.1 NE Electra survey meter with 100cm^2 dual phosphor alpha-beta scintillation detector or equivalent

4.2 Ludlum model 12 or model 192 NAI micro Reontgen meter

5. PROCEDURES

5.1 CALIBRATION OF PORTABLE HEALTH PHYSICS INSTRUMENTS
Any instrument that is at its calibration due date must be taken out of service and sent to an outside vendor for recalibration. The Steps below describe how this is accomplished.

5.1.1 When an instrument is due for calibration, remove the instrument from service and give it to the RSO. A temporary replacement instrument will be provided by the RSO.

5.1.2 The instrument will be packaged and shipped to a licensed outside vendor for calibration.

5.1.3 The vendor will perform the calibration. As appropriate, the vendor will calibrate the instrument's response to its attached check source, following calibration of the instrument. The vendor will affix a label to the instrument indicating the calibration date and the due date of the next calibration.

5.1.4 The vendor will return the instrument to Paragon. The vendor will supply a calibration certificate including all calibration data. The calibration certificate will be maintained by the RSO.

5.1.5 The temporary replacement instrument will be returned to the RSO once the re-calibrated instrument is returned to Paragon.

5.1.6 The daily instrument check (see below) must be performed before the instrument can be used.

5.2 PORTABLE HEALTH PHYSICS INSTRUMENTS PERFORMANCE CHECKS
Each portable survey instrument shall have a calibration or response check performed daily before use (document in logbook, Form 014). If the instrument fails the check, the instrument shall be checked again. If the instrument fails a third time, tag the instrument out according to SOP 317 and notify the RSO.

5.2.1 VISUAL INSPECTION

5.2.1.1 Confirm that the instrument has a sticker indicating calibration by an outside vendor within the last 12 months. If the instrument has not been calibrated by an outside vendor within the last 12 months, notify the RSO. Also, confirm that there are no placards indicating that the instrument has been removed from service (SOP 317).

5.2.1.2 Confirm that all instrument parts are present and that all detector windows are not perforated.

5.2.1.3 Visually inspect the cable connections at both the instrument and detector to ensure that all connections are tight and secure.

5.2.2 BATTERY CHECK

5.2.2.1 Verify that the batteries in the instrument are within the operating range specified on the dial of the instrument (Model 19 and 192) or by noting if the battery symbol lights up on the panel (Electra).

5.2.2.2 If the batteries are not in the operating range specified or the battery symbol lights up, change the batteries before use.

5.2.3 INSTRUMENT PERFORMANCE CHECK USING RADIOACTIVE MATERIAL CHECK SOURCE
The instrument must be checked using an appropriate radioactive material check source to ensure proper meter response. It is imperative that the proper check source be used with the appropriate probe (e.g., an alpha check source used with an alpha probe, or a gamma check source used with a gamma detector).

5.2.3.1 PERFORMANCE CHECK FOR GAMMA SCINTILLATION DETECTORS (MODEL 19 AND 192)

Place the active area of the check source directly on the detector. Hold the source in this position for approximately 20 seconds and observe the meter reading. The meter should read within plus or minus 10% of the reference reading obtained by exposing the instrument to the check source in a constant and reproducible manner 10 or more times. The average value will be used as the reference reading (ANSI N323A, 1997 Section 4.8).

The reference reading obtained upon receipt of the instrument from the calibration vendor must be verified against historical reference reading data before use. If the instrument is not functioning properly, the RSO should be notified in writing, and the instrument removed from service per SOP 317. Record the results in the appropriate instrument logbook (Form 014).

5.2.3.2 PERFORMANCE CHECKS AND INTEGRATED BACKGROUND AND EFFICIENCY DETERMINATIONS FOR NE ELECTRAS (DUAL PHOSPHOR ALPHA-BETA DETECTORS)

5.2.3.2.1 Performance Checks: Turn the instrument on and let it stabilize. Record the background count per minute (cpm) in the appropriate instrument log book containing (Form 219).

Place the detector over the active area of each source and record the cpm values for the large area alpha and beta check sources, and the alpha and beta electroplated planchet sources in the instrument logbook (Form 219). The meter should read within plus or minus 10% of the reference reading obtained by exposing the instrument to the check sources in a constant and reproducible manner, 20 or more times. The average value will be used as the reference reading (ANSI N323A, 1997 Section 4.8).

If the instrument is not functioning properly, the RSO should be notified in writing, and the instrument removed from service per SOP 317.

5.2.3.2.2 Background Determination for Integrated Counts: Push the integrate button and count the background for sixty (60) seconds. Record the background count for both alpha and beta on Form 219. For the alpha/beta scintillation detector, alpha results will be recorded on the left facing page and beta results on the right facing page of the logbook.

5.2.3.2.3 Alpha Efficiency Determination for Integrated Counts: The detector is placed directly on the alpha particle standard plate. Push the integrate button on the Electra and count the check standard for 60 seconds. Record the gross alpha counts on Form 219. Calculate the alpha efficiency as follows:

$$\alpha \text{ Efficiency} = \frac{\text{(Gross Alpha CPM - Alpha Background CPM)}}{\text{Alpha Source DPM}}$$

5.2.3.2.4 Beta Efficiency Determination for Integrated Counts: The detector is placed directly on the beta particle standard plate. Push the integrate button on the Electra and count the standard for 60 seconds. Record the gross beta counts on PAI Form 219. Calculate the beta efficiency as follows:

$$\beta \text{ Efficiency} = \frac{\text{(Gross Beta CPM - Beta Background CPM)}}{\text{Beta Source DPM}}$$

5.3 USE OF SURVEY METERS IN THE LABORATORY

If instructed by LIMS special instructions, all employees shall use an NE Electra Survey Meter to survey their hands, feet, and any other area suspected of contacting radioactive materials before leaving the laboratory. This survey is performed as follows:

5.3.1 SURVEY OF HANDS AND FEET

Verify that the instrument is functioning properly (e.g., the battery is charged, the instrument background is acceptable, and the instrument has been calibrated within the last 12 months). Use caution in handling the instrument with potentially contaminated hands to avoid

contaminating the instrument. Consult the RSO if you have any questions or if any problems arise.

5.3.1.1 Slowly pass each hand (front and back) over the active area of the detector. Keep the hand as close as possible without touching the detector (i.e., about 1cm or less distance).

5.3.1.2 Pass the active detector area over the sole of each foot.

5.3.1.3 Each hand or foot pass should be performed slowly, requiring at least 10 seconds to completed.

5.3.1.4 If radioactive material is detected in excess of 12cpm Alpha and 650cpm Beta, then decontamination of the affected areas is required. The first decontamination step is to wash with soap and water. Resurvey the area after washing. If the area is still contaminated, call the RSO or designee for instructions regarding further decontamination measures.

5.3.2 SURVEY OF LAB COATS PRIOR TO SENDING OFFSITE

A survey of lab coats shall be performed using an Electra prior to placing in the vendor removal basket. The survey should focus on the sleeves near the cuffs and the front waist area of the lab coats (areas where sample contact could be made).

5.3.2.1 Slowly pass the Electra over the area of interest (more easily done while wearing the lab coat).

5.3.2.2 If a hit at or above limits (see below) is detected, verify by resurveying. If activity is still found, notify the RSO or designee.

5.3.2.3 If no contamination is found, place lab coat in vendor removal basket.

5.3.2.4 If contamination is found in excess of 12cpm Alpha and 650cpm Beta, the RSO shall document and decontaminate as needed. If the lab coat can not be decontaminated, then it will be placed in the Radioactive waste container for disposal.

5.3.3 SURVEY OF EQUIPMENT AND AREAS

5.3.3.1 Slowly pass the Electra over the area or article of interest. Please note that some items are not practical to survey with a meter in this manner. This is due to shape or contours of the article or area. The article or area shall have enough of an accessible area to assure that any contamination if present

will be detected. If the instrument or article does not have an accessible area, a swipe survey shall be performed. Consult with the RSO for further directives.

5.3.3.2 Document any areas of contamination above 12cpm Alpha and 650cpm Beta on a Map of the area or article or as instructed by the RSO. These limits also apply to personnel contamination surveys using the Electra.

6. SAFETY, HAZARDS AND WASTE DISPOSAL

6.1 SAFETY AND HAZARDS

6.1.1 The building is equipped with safety showers, eyewash stations, fire extinguishers, fire blankets, and first aid kits. All laboratory personnel must be trained in the use and location of these items.

6.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), or handling materials or equipment potentially contaminated with chemicals or radioactive materials.

6.1.3 Food and drink are prohibited in all lab areas.

6.2 WASTE DISPOSAL

Any residual materials used in personnel or equipment decontamination operations shall be evaluated and, if indicated, be disposed of as Low Level Radioactive Waste.

7. REFERENCES

7.1 “Rules and Regulations Pertaining to Radiation Control,” Colorado Department of Health, Radiation Control Division, 2001.

7.2 Paragon Analytics, Radiation Protection Plan (RPP), current revision.

7.3 ANSI N323A, 1997

DOCUMENT REVISION HISTORY

8/10/07: Reinstated SOP, updated, and combined with SOPs 007, 013 and 031. Augmented RESPONSIBILITIES. Incorporated Forms. Added DOCUMENT REVISION HISTORY.

11/3/07: Added Lab Coat Survey posting as ‘Operator’s Aid’ to SOP; updated Form 014 image.

Paragon Analytics

Ludlum Model 19 (SN 89429)
Survey Instrument Check Source Test and Background Reading Logbook

Analyst	Date	Time	Check Source* Reading (μR/hr)	Background (μR/hr)	Analyst	Date	Time	Check Source* Reading (μR/hr)	Background (μR/hr)

Acceptable Range for Check Source Reading 210 μR/hr to 260 μR/hr.
Notify RSO immediately if acceptable range is exceeded.

Reviewed By/Date: ________________________________ **Form 014r6b.frm (9/27/01)**

*** Unique Check Source Identifier - SN0291**

______________ **A** ***Paragon Analytics***

Electra Check Logbook (units are counts/minute)

Electra ____________

DATE	α Bkg	α Low	α High	COMMENTS	INIT.
	β Bkg	β Low	β High		

C. Limits _________ **date** Calib. _________ **date**

	α Bkg	β Bkg	α Low	β Low	α High	β High
Low						
High						

Electra ____________

α Bkg	α Low	α High	COMMENTS	INIT.
β Bkg	β Low	β High		

C. Limits _________ **date** Calib. _________ **date**

	α Bkg	β Bkg	α Low	β Low	α High	β High
Low						
High						

Electra ____________

α Bkg	α Low	α High	COMMENTS	INIT.
β Bkg	β Low	β High		

C. Limits _________ **date** Calib. _________ **date**

	α Bkg	β Bkg	α Low	β Low	α High	β High
Low						
High						

CONTINUED NEXT PAGE

______________ **B**

Paragon Analytics

Electra Check Logbook (units are counts/minute)

Electra ____________

DATE	α Bkg	α Low	α High	COMMENTS	INIT.
	β Bkg	β Low	β High		

C. Limits _________ **date** Calib. _________ **date**

	α Bkg	β Bkg	α Low	β Low	α High	β High
Low						
High						

Electra ____________

α Bkg	α Low	α High	COMMENTS	INIT.
β Bkg	β Low	β High		

C. Limits _________ **date** Calib. _________ **date**

	α Bkg	β Bkg	α Low	β Low	α High	β High
Low						
High						

Electra ____________

α Bkg	α Low	α High	COMMENTS	INIT.
β Bkg	β Low	β High		

C. Limits _________ **date** Calib. _________ **date**

	α Bkg	β Bkg	α Low	β Low	α High	β High
Low						
High						

Reviewed by / date ___________________________

Form 219r2.doc (7/18/07)

Attention:

Per SOP 012, all lab coats must be surveyed prior to leaving the building:

1.) **Survey your lab coat with an Electra before placing it in the dirty lab coat hamper.**

2.) **Concentrate on the ends of the sleeves and the waist area. However, the entire lab coat should be surveyed.**

3.) **Survey areas where the lab coat contacted sample material.**

Action Limits are:

Alpha 12cpm

Beta 650cpm

If these Limits are exceeded, place lab coat in a bag and notify the RSO or designee. Then a survey should be performed on the individual who wore the lab coat to verify that the individual is free of contamination.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 015 REVISION 6

TITLE: DISPOSAL OF RADIOACTIVE WASTE

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/7/07

QUALITY ASSURANCE MANAGER _____ DATE 11/7/07

LABORATORY MANAGER _____ DATE 11-7-07

HISTORY: NEW, 11/10/93; Rev1, 5/30/97; Rev2, 2/03/00; Rev3, 4/03/02; Rev4, 3/17/03; Rev5, 9/22/03 and 7/18/05 (re-released without revision); Rev6, 11/7/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures used to handle and dispose of radioactive and mixed wastes. This SOP applies to all radioactive waste streams in all laboratories.

Paragon has three general categories of waste streams: nonradioactive (hazardous), radioactive, and mixed hazardous/radioactive wastes. The handling and disposal of hazardous waste is addressed in SOP 003 - Management of Nonradioactive Hazardous Waste. Mixed waste is handled and disposed of according to both this SOP and SOP 003 because the waste is both hazardous and radioactive.

Paragon utilizes radioactive materials under a radioactive material license issued by the Colorado Department of Public Health & Environment (CDPHE), Radiation Control Division. Therefore, all regulatory references, in regards to radioactive materials and waste, are to the Colorado Radiation Control Regulations. These regulations are derived from those found in Chapter 10 of the Code of Federal Regulations (CFR).

2. SUMMARY

It is extremely important that the radioactive components of the waste streams are segregated from the nonradioactive (hazardous) components. If the waste streams are combined, a mixed waste containing both hazardous and radioactive components as defined by the Resource Conservation & Recovery Act (RCRA), may be created. The mixing of hazardous and radioactive wastes shall be systematically minimized in order to limit the production of mixed waste.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who perform this procedure to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. REAGENTS AND APPARATUS

4.1 Solidification Media

4.2 Waste Containers: Containers used for disposal of radioactive waste must be United Nations Specification (UN Spec). The types of containers authorized include UN Spec 5 gallon pail, 30 gallon open head drum, 30 gallon closed head drum, 55 gallon open head drum, 55 gallon closed head drum, and 85 gallon open head salvage drum.

4.3 Ludlum Model 1000 Scaler with Ludlum Model 43-10 Alpha Scintillation Detector or equivalent.

4.4 Ludlum Model 1000 Scaler with Ludlum Model 44-7 End Window Geiger-Mueller Detector or equivalent.

4.5 Tennelec Model LB5100 simultaneous Alpha and Beta Counter.

4.6 Bicron Electra with 100 cm^2 Dual Phosphor Alpha-Beta Scintillation Detector.

4.7 Ludlum Model 19 Micro R Radiation Survey Meter or equivalent.

4.8 Ludlum Model 3 Radiation Survey Meter With End Window G-M Detector or equivalent.

4.9 Filter papers for removable radioactive material contamination surveys.

4.10 Removable radioactive material contamination wipes that dissolve in liquid scintillation cocktail, for low energy beta removable contamination surveys.

5. PROCEDURES

5.1 WASTE DISPOSAL

5.1.1 Sample Disposal

Samples are collected for disposal after a specified archival time. The archival time is a function of the client contract (may be Paragon standard or otherwise). Paragon's standard archival time is 90 days past the date of invoice. Archival time may be extended according to client-specific requirements. Typically, the Paragon PM notifies the client before samples are disposed. Samples are disposed into a container that is specified for a particular waste stream (i.e., radioactive solid, radioactive liquid, mixed solid, mixed liquid). This container may be a Satellite Accumulation Area (SAA) container or a UN SPEC container. Movement of sample volume from the laboratory storage areas to archival, into SAAs, and through to final disposal is tracked in LIMS. SAA management is described in SOP 003.

5.1.2 Process Waste Disposal

Process waste generated at Paragon that is radioactive or mixed shall be placed into a container that is compatible with the waste stream. Mixed waste shall be placed into the container that is present in a Satellite Accumulation Area (SAA). When the SAA containers become full (refer to SOP 003), the contents shall be transferred into a UN SPEC container in a 90-Day Accumulation Area. The UN SPEC containers shall be compatible with the waste streams they contain.

5.1.3 Records of disposal are maintained by the Waste Compliance Officer.

5.2 RADIOACTIVE WASTE CLASSIFICATION FOR OFF-SITE DISPOSAL

There are three main types of radioactive waste that are addressed in this procedure: Low Level Radioactive Waste (LLRW), High Level Radioactive Waste (HLW), and Transuranic Waste (TRU). These waste types are defined in Colorado Radiation Control Regulations RH 14.2. LLRW radioactive waste will be for all practical purposes the only radioactive waste generated at Paragon. However, it is necessary to understand HLW and TRU waste in order to understand LLRW waste.

5.2.1 Low Level Radioactive Waste (LLRW)

LLRW is defined as waste other than that generated by US Government defense or research and development activities, HLW, TRU, byproduct material as defined in Section II e (2) of the Atomic Energy Act of 1954 (as amended on November 8, 1978), or wastes from extraction industries involving minerals other than radium. LLRW does not necessarily imply low levels of radioactive material concentrations. For example, limitations on activity concentrations for LLRW materials are in the Curie per gram range, that is well above environmental levels.

5.2.2 High Level Radioactive Waste (HLW)

HLW materials are materials such as irradiated reactor fuel, liquid wastes from reprocessing irradiated reactor fuels, or solids into which any of the above described liquid wastes have been converted. In short, HLW refers to materials that originated from operations involving nuclear fuels. Paragon will not, under any circumstances, generate High Level Radioactive Waste.

5.2.3 Transuranic Waste (TRU)

TRU materials are wastes containing transuranic elements in activity concentrations exceeding 100 nCi/gram (3700 Bq/gram). Disposal entities (e.g., the Benton County, Washington or Barnwell, South Carolina Radioactive Waste Disposal sites) may impose additional administrative limitations upon TRU activity concentration. The Radiation Safety Officer (RSO) can provide information on current limitations.

5.3 LOW LEVEL RADIOACTIVE WASTE DISPOSAL REQUIREMENTS

The main body of radioactive waste generated at Paragon is LLRW. PAR will not generate any HLW due to the nature of our operation and license restrictions. Also, it is unlikely that Paragon will generate TRU waste (e.g., material with any activity greater than 100 nCi/gram). Sample remainders that contain TRU waste will be returned to the client for final disposition. The LLRW waste generated at Paragon is composed of samples contaminated with radioactive material and laboratory process effluents contaminated with radioactive materials. The following requirements for preparing these wastes for disposal are in accordance with Colorado Radiation Control Regulations 4.22 through 4.26:

5.3.1 Determination of Radioactive Waste Class

The radioactive waste class (A, B or C) must be determined in accordance with Colorado Radiation Control Regulation RH 4.22. Paragon is required to determine the waste class based upon both the activity concentration of long-lived radionuclides for which institutional controls may not be totally effective, and the activity concentrations of the shorter-lived radionuclides for which institutional controls are effective. Based upon Paragon's radioactive materials license limitations, no class B or C waste shipments will ever be made. The requirements for Class B and C radioactive material waste shipments are beyond the scope of this SOP.

5.3.2 Class A Waste Classification Protocols

A waste may be classified as a Class A radioactive waste if it meets the following criteria:

- The activity concentrations of any radionuclide(s) present that are listed in Table 1 may not exceed 0.1 times the value in Table 1 of 10 CFR 61.55 and;
- The activity concentrations of any radionuclide(s) present that are listed in Table 2 of 10 CFR 61.55 may not exceed the activity concentration value in Table 2, Column 1 of 10 CFR 61.55 and/or;
- The radionuclide(s) present are not listed in either Table 1 of 10 CFR 61.55 or Table 2 of 10 CFR 61.55 and;
- The material is stable (e.g., soils) or unstable (e.g., waters).

5.3.3 Class A Radioactive Waste Disposal Requirements

- All waste must be packaged so as to meet the conditions of the license issued to the operator of the site to which the material is being sent for disposal. For example, Perma-Fix of Florida requires that all shipments of radioactive liquids be packaged in an over packed container.

- No wastes shall be packaged for disposal in cardboard or fiberboard boxes or containers.
- Liquid wastes with activity concentrations in excess of 0.002 uCi/g shall be packaged such that sufficient absorbent material is present to absorb twice the volume of the liquid.
- Solid waste containing liquids shall contain as little free standing and noncorrosive liquid as is reasonably achievable, but the total volume of the liquid shall not exceed 1% of the total volume.
- The waste shall not be readily capable of explosive detonation, explosive decomposition, reaction at normal temperatures and pressures, or of explosive reaction with water. Wastes may be shipped to a Temporary Storage and Disposal Facility (TSDF) for treatment and removal of the hazardous waste codes prior to disposal at a radioactive waste disposal facility.
- No waste shall be capable of generating quantities of toxic gases, vapors, or fumes that are harmful to persons transporting, handling, or disposing of the waste. This provision does not apply to radioactive gaseous waste packaged in accordance with Colorado Radiation Control Regulation RH 4.23.1.8.
- No waste shall be pyrophoric. Any pyrophoric materials contained in any waste material shall be treated, prepared, and packaged to be nonflammable and nonhazardous. Wastes may be shipped to a TSDF for treatment and removal of the hazardous waste codes prior to disposal at a radioactive waste disposal facility.
- Gaseous radioactive material wastes shall be packaged at a gauge pressure that does not exceed 1.5 atmospheres at 20 degrees Celsius, nor more than 100 curies (3700 GBq) of activity per container. It is extremely unlikely that Paragon will ever generate a gaseous radioactive waste.
- Waste containing hazardous, biological, pathogenic or infectious material shall be treated to eliminate the nonradiological hazards. Wastes will be shipped to a TSDF for treatment and removal of these additional waste codes prior to disposal at a radioactive waste disposal facility.

5.4 PREPARATION OF RADIOACTIVE MATERIAL FOR LLRW DISPOSAL

5.4.1 Collection of Radioactive Material

5.4.1.1 *Bulk Liquids Contaminated With Radioactive Material*
Radioactive Material may be deposited into a waste

accumulation container (e.g., sample remainders deposited into a UN Spec 20 Liter Jerry Can). The waste liquids may later be transferred to a larger UN Spec Container such as a tight head 55 gallon drum. The waste material will be characterized for radionuclide composition and activity at a later date.

5.4.1.2 *Radioactive Material Contaminated Solids*
Radioactive material solids contained in individual containers (e.g., soil or water samples in discreet sample containers), may be collected and composited into the waste container. The radionuclide composition and activity concentration will be determined by characterization of a composite sample or evaluation of the laboratory analyses for each sample.

5.4.1.3 *Liquid Scintillation Waste*
To the maximum extent practical, analytical operations involving Liquid Scintillation Counting (LSC) shall use LSC cocktails that do not qualify as hazardous materials. All LSC wastes will be collected in open head drums. The liquid scintillation waste is composed of the liquid scintillation vial, liquid scintillation cocktail, and dissolved sample. The LSC cocktail sample mixture shall not be removed from the vial and disposed of in bulk. The vials will be segregated into separate drums based upon classification as Exempted LSC Waste, LLRW, or Mixed LLRW. The Colorado Radiation Control Regulation 4.21 exempts tritium and carbon-14 in LSC cocktail waste from disposal concerns with respect to radioactive material provided the activity concentration is less than 0.05 uCi/gram (50,000 pCi/gram).

Additional requirements for liquid scintillation waste follow:

- Any samples with less than 0.05 uCi/gram (50,000 pCi/gram) of tritium or carbon-14 shall be deposited in the Exempted LSC Waste Drum. Exempted LSC wastes will be sent to a facility with a radioactive materials license for incineration. The resultant ashes will be disposed in a radioactive waste disposal facility.
- LSC vials containing tritium or carbon-14 in excess of 0.05 uCi/gram (50,000 pCi/gram) or any other radionuclides dissolved in nonhazardous cocktails, shall be deposited in the LLRW LSC Waste Drum. LLRW LSC wastes will be sent to a facility with a radioactive materials license for incineration.

Facilities that currently meet these requirements are Perma-Fix of Florida and DSSI in Kingston, Tennessee. The materials will be incinerated and the resultant ashes will be disposed in a radioactive waste disposal facility.

- LSC vials containing tritium or carbon-14 in excess of 0.05 uCi/gram (50,000 pCi/gram) or any other radionuclides dissolved in hazardous cocktails, shall be deposited in the Mixed LLRW LSC Waste Drum. The Mixed LLRW LSC wastes will be sent to a facility with a radioactive materials license and a TSDF permit for incineration. The materials will be incinerated, the EPA Hazardous Waste Codes removed as possible, and the resultant ashes disposed in a radioactive waste disposal facility or a radioactive/hazardous waste disposal facility as necessary.
- All types of LSC Vials shall be packaged in 55 gallon open head UN Spec drums. The empty drum shall have a 3" layer of a sorbent such as Floor dry poured onto the bottom. A 4-5 inch layer of LSC vials will then be added to the drum. Another 3" layer of floor dry will be added, then more vials, and so on until the drum is full.

5.4.2 Determination of Radionuclidic Composition and Activity

The concentration of radionuclides may be determined by analytical evaluation and/or process knowledge. If analytical evaluation is needed, sampling of the waste streams shall be performed. The minimum tests required for a complete analytical evaluation are given below:

- Gross Alpha/Beta
- Gamma Spectroscopy
- Tritium
- Carbon-14
- Radium-226
- Radium-228
- Strontium-90
- Technetium-99
- Isotopic Thorium

- Isotopic Uranium
- Isotopic Plutonium
- Am-241

The data from the above analyses or process knowledge will be used to fill out the Uniform Low Level Radioactive Waste Manifest.

5.4.3 Packaging of Radioactive Material

5.4.3.1 *Bulk Liquids Contaminated with Radioactive Material*
The following requirements apply to bulk liquids contaminated with radioactive material:

- Bulk liquids must be noncorrosive.
- Liquids with an activity concentration less than 0.002 uCi/g (2000 pCi/g) will be packaged in a Tight Head UN Spec container. The filled container will then be placed in a UN Spec Open Head Over pack container.
- Liquids with an activity concentration greater than 0.002 uCi/g (2000 pCi/g) will be packaged into a tight head UN Spec container with a maximum volume of 15 gallons. This 15 gallon container will be placed in a 55 gallon UN Spec Open Head Drum and surrounded with a sorbent material such as Floor Dry.

5.4.3.2 *Solid Low Level Radioactive Waste*
Solid LLRW will be packaged in a UN Spec container. The size of the drum used may be up to 55 gallon, as appropriate. The drum should have a liner in place. Any free liquids present in the soils must be less than 1% of the total volume and noncorrosive.

5.4.3.3 *Liquid Scintillation Waste*
The containers must be UN Spec 55 Gallon Open Head Drums.

5.4.4 Preparation of Radioactive Material Waste Packages for Shipment

5.4.4.1 A removable radioactive material contamination survey is performed according to PAR SOP 010 - Radioactive Contamination Area Surveys. The results must be within the limits required by 49 CFR 173.443. These limits are 22 dpm/cm^2 for beta-gamma radionuclides, all radionuclides with half lives less than 10 days, natural uranium, natural thorium

and U-235, U-238, Th-232, Th-228, and Th-230 when contained in ores and physical concentrates. The limit for any other alpha-emitting radionuclide is 2.2 dpm/cm^2.

5.4.4.2 External exposure rate measurement shall be taken at the container surface and at one meter from the container surface. Please see PAR SOP 008, Table 5.1 for external radiation level limits by shipment type.

5.4.4.3 *Manifest Preparation*
The manifest must contain information about the generator, waste characteristics, and other classification information. The information required is given in the following Sections:

- Generator Name, Address, and EPA ID #
- Weight of waste
- Physical form
- Waste Class A, Stable (S) or Unstable (U)
- Waste description
- Solidification media or absorbent material, if applicable
- Radionuclide(s)
- Chemical form
- Activity of each radionuclide
- Waste form
- Radiation exposure rates at the surface and at one meter from the container
- Quantity of waste to be shipped
- One time shipment or continuous
- Source material present (Kilograms), if applicable

6. SAFETY, HAZARDS, AND WASTE DISPOSAL

The safety hazards associated with this procedure involve potential spread of radioactive material contamination and moving the waste containers. Radioactive material contamination in the environment is a possibility during waste preparation operations. These operations shall be supervised by the RSO with appropriate monitoring and personnel protective equipment being utilized. Any operations involving moving containers (e.g., 55 gallon drums containing contaminated soil), shall utilize suitable moving devices such as barrel dollies and use of steel-toed shoes. Waste disposal procedures are addressed in the body of the procedure.

7. REFERENCES

7.1 Colorado Department of Health Rules and Regulations Pertaining To Radiation Control.

7.2 Chapter 10 of the Code of Federal Regulations.

7.3 Chapter 49 of the Code of Federal Regulations.

7.4 Paragon Analytics SOP 003.

DOCUMENT REVISION HISTORY

11/7/07: Added "Typically, the Paragon PM notifies the client before samples are disposed." to Section 5.1.1. Added "Records of disposal are maintained by the Waste Compliance Officer." As Section 5.1.3. Added DOCUMENT REVISION HISTORY Section.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 016 REVISION 6

TITLE: ELECTRON CAPTURE DETECTOR LEAK TESTS

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 10/3/07
QUALITY ASSURANCE MANAGER _____ DATE 10/2/07
LABORATORY MANAGER _____ DATE 10/4/07

HISTORY: Rev0, 11/20/92; Rev1, 4/05/94; Rev2, PCN #478, 5/26/95; Rev3, 5/15/99; Rev4, 4/09/02; Rev5, 2/9/04 and 11/10/05 (re-released w/o revision); Rev6, 10/2/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures used to perform a leak test for an electron capture detector (ECD). This SOP applies to radioactive materials sources in electron capture detectors that emit beta radiation. ***The leak tests must be performed every six months.*** Paragon does not possess any other radioactive material sealed sources that require leak testing as per Colorado Radiation Regulations 6 CCR 1007-1 (current version).

2. SUMMARY

There is always a possibility that sealed radioactive sources may leak radioactive materials. To prevent the spread of radioactive contamination, it is necessary to test these sources for leakage.

The leak test is performed by wiping all surfaces that contact or are in close proximity to the radioactive source. These areas include: detector housings, exits, and any openings that the source may contact. The wipe may be performed using a *NUC-WIPE*™ or other suitable wipe that will dissolve in the liquid scintillation counter (LSC) cocktail. The wiping media is placed in a scintillation vial and LSC cocktail is added. The wipe is allowed to dissolve, and then the vial is counted in a Beckman LS6000TA Liquid Scintillation Counter or comparable instrument. Finally, the amount of removable radioactive contamination is calculated.

3. RESPONSIBILITIES

3.1 The Organics Department Manager or designee is responsible for managing and performing all necessary ECD leak tests, and for taking appropriate corrective actions as necessary.

3.2 Paragon's Radiation Safety Officer (RSO) shall provide oversight for the requirements and procedures stated in this SOP, and shall maintain leak test records.

3.3 Radiochemistry Department staff shall analyze the leak test wipes in accordance with SOP 704, and submit the test results to the Organics Department Manager or designee.

3.4 It is the responsibility of all personnel who work with these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

4.1 *NUC-WIPE*™ or other wipe material that will dissolve in the LSC cocktail

4.2 Liquid scintillation vials, 20mL

4.3 Beckman LS6000TA Liquid Scintillation Counter or equivalent

5. REAGENTS

Liquid scintillation cocktail, Packard Ultima Gold™ LLT or equivalent

6. PROCEDURES

6.1 WIPE TEST

Obtain a *NUC-WIPE*™ or equivalent wipe and wipe all areas that are in contact with or in close proximity to the sealed source. Wipe every surface with a uniform medium pressure. Place the wipe in a 20mL LSC vial that is labeled with the sample identification number on the cap. Complete the following information on Form 040: date of test, the name of the individual performing the leak test, standard identification, and sample identification information.

6.2 LEAK TEST ANALYSIS

Add 20mL of the liquid scintillation cocktail to the LSC vial. The LSC vial shall be held for at least one hour prior to placing in the LSC instrument, in order to ensure dissolution of the wipe prior to counting.

6.3 LIQUID SCINTILLATION COUNTING

The vial shall be placed into the LSC and counted for at least 30 minutes to achieve a minimum detection limit of 0.005 microcuries per sample. The counting procedures are outlined in SOP 704. If the contamination is less than 0.005 uCi/sample, then it is considered within acceptable limits. If the contamination exceeds the 0.005 uCi/sample limit, then the detector must be tagged out of service and serviced by an entity licensed to receive and service ECD detectors.

6.4 LEAK TEST RECORD

A record of the leak test will be completed and filed in the radiation safety files. All test records including raw data and results will be maintained for inspection.

7. QUALITY ASSURANCE

Refer to SOP 704.

8. CALCULATIONS AND INTERPRETATION OF DATA

8.1 CALCULATIONS

Net Standard CPM = Gross STD CPM -- Background CPM

Efficiency =Net STD CPM / Ni-63 STD DPM

LLD = 4.66*(Bkg CPM/Count Time)$^{1/2}$ / (Eff * 2.22X10^{6} dpm/uCi)

Net Sample CPM = Gross Sample CPM -- Background CPM

Removable Activity(uCi) = Net Sample CPM/(Eff*2220000 dpm/uCi)

8.2 INTERPRETATION OF DATA

If the removable activity of the sample exceeds 0.005 µCi/sample , then the radioactive source is contaminated and must be removed from the laboratory, cleaned, and serviced.

9. SAFETY, HAZARDS AND WASTE DISPOSAL

9.1 SAFETY AND HAZARDS

9.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

9.1.2 Gloves, safety glasses, and a lab coat shall be worn in the laboratory areas.

9.2 WASTE DISPOSAL

Refer to SOP 704.

10. REFERENCES

Colorado Radiation Regulations 6 CCR 1007-1 (current version)

DOCUMENT REVISION HISTORY

10/2/07: Expanded RESPONSIBILITIES. Updated regulatory references to Colorado Radiation Regulations 6 CCR 1007-1 (current version). Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 017 REVISION 5

TITLE: EFFLUENT MONITORING AND RELEASE

FORMS: 015 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 4/25/07

QUALITY ASSURANCE MANAGER _____ DATE 4/24/07

LABORATORY MANAGER _____ DATE 4-26-07

HISTORY: Rev0, PCN #217, 4/13/94; Rev1, 5/15/99; Rev2, 4/3/02; Rev3, 3/7/03; Rev4, 2/9/04 and 4/1/05; Rev5, 4/26/07.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the processes used to sample and monitor effluent releases from the laboratory facilities. The procedures that follow apply to sampling, analysis, and regulatory compliance for effluent released into the sanitary sewer system from Paragon's wastewater system.

2. SUMMARY

2.1 Paragon's wastewater system is composed of one 3000-gallon sump, two 8000-gallon holding tanks, and two pumps with a control panel. Water from laboratory operations flows into the sump and is pumped into one or both of the tanks. The tanks can be used independently by opening or closing the appropriate flow valves. The pumps are controlled via the control panel and they can be operated manually or automatically.

2.2 Boxelder Sanitation District is the local agency that oversees discharge of wastewater from Paragon. Boxelder Sanitation District's Prohibitions and Limitations on Wastewater Discharge, Part 8, is the document that governs the discharge of wastewater from Paragon. Radioactive components are addressed in Part 802 (I) of this document, which refers to the Colorado Department of Public Health and Environment (CDPHE) publication "Rules and Regulations Pertaining to Radiation Control".

2.3 The wastewater from Paragon's laboratory processes must have a pH between 5 and 10 before release (Boxelder Sanitation District, Prohibitions and Limitations on Wastewater Discharge 802 (O)). There are additional regulatory limits that must be complied with and documented. To comply with these regulations, waste determinations must be documented for waste discharged into the system from laboratory processes, and representative samples may be obtained, as appropriate, from the holding tanks for analysis.

2.4 All wastewater (excluding sanitary systems) from laboratory processes is neutralized in the wastewater system. The neutralized effluent is stored in holding tanks. Samples are taken from the holding tanks before any effluent is released to the sanitary sewer system. The samples are held until the end of the current month, and then analyzed for gross alpha and beta radioactivity, tritium, and total metals. The Waste Compliance Officer or the Radiation Safety Officer (RSO) may request additional analyses. The total metals analysis is performed on a composite sample from the entire sampling period. Results of the analysis are not needed prior to discharge in routine operations and conditions, because process knowledge of in-house samples and limitations of Paragon's radioactive materials license will keep discharges less than regulatory limits at a volume of 7800 gallons (approximate volume of daily discharge).

3. RESPONSIBILITIES

It is the responsibility of all personnel who work with these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

4.1 baking soda or equivalent caustic material

4.2 nitric acid, HNO_3, concentrated

4.3 nitric acid, 20%

4.4 bottles, wide-mouth, plastic, 500mL

4.5 pH strips

4.6 transfer pipets, disposable, glass

5. PROCEDURES

5.1 TANK SAMPLING

5.1.1 Check the volume of the tank(s) using the gauges on the wall.

5.1.2 Isolate the tank to be discharged by opening the valve to the other tank and turning off the valve to the tank to be discharged.

5.1.3 Purge the discharge line by opening the discharge valve for 3 to 5 seconds.

5.1.4 Collect a sample using the sampling port.

5.1.5 Verify that the pH of the tank is between 5 and 10. If the pH needs to be adjusted, then refer to Section 5.2 for the procedure. Repeat steps 5.1.3 through 5.1.5 until pH is between 5 and 10.

5.1.6 Open the discharge valve to release contents of the tank. Discharge time is approximately 30 minutes, depending on the volume to be discharged. However, discharge time may be limited by Boxelder Sanitation District in order to control volume discharged into the system at any given time. Check with Boxelder Sanitation District for limitations on discharge time.

5.1.7 Complete the tank discharge log (Form 015) with the following information: sample ID number (TWMMDDYY), date, time, initial pH, tank number, volume discharged, and any comments. When more than one tank is sampled in a day, use -A, -B etc. for 1st and 2nd sample etc.

5.1.8 Label the sample bottle with the same information entered onto the tank discharge log.

5.1.9 Place the sample in a holding bin until the end of the sampling period. Close the discharge valve when the discharge is complete.

5.2 ADJUSTING THE pH

5.2.1 Baking soda should be added to the sump at regular intervals to maintain the pH at approximately 7.

5.2.2 If the pH of the tank is acidic (pH less than 5), add baking soda to the tank until the pH is within the release criteria (pH 5-10).

5.2.3 If the pH of the tank is basic (pH greater than 10), add acid (concentrated HNO_3) until the pH is within the release criteria (pH 5-10).

5.3 COMPOSITE SAMPLE

5.3.1 Obtain a small volume of approximately 5mL from each sample taken during the sample period.

5.3.2 Place the aliquoted volume from the samples in a 500mL plastic bottle preserved with 20% HNO_3.

5.4 SAMPLE ANALYSIS

5.4.1 Create a separate chain of custody log (Form 015) for the composite sample, and the group of tank samples taken during the sampling period.

5.4.2 Forward the samples and the chain of custody to the Sample Control Department for login and distribution.

5.4.3 Tank samples are to be analyzed for tritium and gross alpha and beta.

5.4.4 The composite sample is to be analyzed for total RCRA metals plus nickel, copper, and zinc.

NOTE: Additional analyses may be requested by the RSO and/or Waste Compliance Officer.

5.5 RECORDS

5.5.1 Copies of discharge logs/discharge chain of custody forms and logbooks, are forwarded to the Boxelder Sanitation District's Pretreatment Coordinator, if requested, at the end of the sampling period.

5.5.2 Copies of the results of the total metals analysis are forwarded to the Boxelder Pretreatment Coordinator, if requested, at the end of the sampling period.

5.5.3 Copies of results from the tritium and gross alpha/beta analyses and discharge logs are forwarded to Paragon's Radiation Safety Officer for review of compliance with the Colorado Department of Public Health publication, Rules and Regulations Pertaining to Radiation Control.

5.5.4 A logbook that details discharges via the sanitary sewer system, other than laboratory wastewater, is maintained by the Waste Compliance Officer. The Waste Compliance Officer reviews the data for compliance with RCRA 10CFR, and Prohibitions and Limitations on Wastewater Discharge, Part 8.

6. QUALITY ASSURANCE/MONITORING

All QA/QC requirements for specific analyses are included in the individual laboratory test procedures.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

7.1.1 The building is equipped with safety showers, eyewash stations, fire extinguishers, fire blankets and first aid kits. All laboratory personnel must be trained in the use and location of these items.

7.1.2 Gloves, safety glasses and a lab coat, shall be worn in the laboratory areas.

7.2 WASTE DISPOSAL

Not Applicable.

8. REFERENCES

8.1 Colorado Department of Public Health, "Rules and Regulations Pertaining to Radiation Control", 2001.

8.2 Boxelder Sanitation District, "Prohibitions and Limitations on Wastewater Discharge", Part 8.

8.3 Paragon Analytics, Radiation Protection Plan (RPP).

8.4 Paragon Analytics, Chemical Hygiene Plan (CHP).

8.5 Paragon Analytics, Waste Management Plan (WMP).

DOCUMENT REVISION HISTORY

4/26/07: Added detail Tank discharge log (Form 105) to Section 5.1.7 and Tank discharge chain-of-custody record into Section 5.5.1. Minor editorial corrections. Added DOCUMENT REVISION HISTORY. Attached Form.

Paragon Analytics
A Division of DataChem Laboratories, Inc.

225 Commerce Drive Fort Collins, CO 80524
800-443-1511 or (970) 490-1511 (970) 490-1522 Fax

Accession Number (LAB ID): ______

Page ____ of ____

Project Name/No.: Tank Samples **Sampler(s):** __________ **Report Due:** 30 Days **Disposal:** Standard

Report To: **Dave Burns**
Phone: **970-490-1511 (Ext 223)**
E-mail: **dburns@paragonlabs.com**

Lab ID	Sample ID	Date	Time	Tank #	Gallons	Sample pH	Matrix	Preservative	No. of Containers	E900.0 Gross Alpha / Beta	E906.0 Tritium		
							W	None	1	X	X		
							W	None	1	X	X		
							W	None	1	X	X		
							W	None	1	X	X		
							W	None	1	X	X		
							W	None	1	X	X		
							W	None	1	X	X		
							W	None	1	X	X		
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							W	None	1	X	X		

Comments:	Relinquished By	Received By
	Signature: ______	**Signature:** ______
	Printed Name: ______	**Printed Name:** ______
	Date: ______ **Time:** ______	**Date:** ______ **Time:** ______
	Company:	**Company:**

Form 015r3 (4/24/07)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 024 REVISION 3

TITLE: DISPOSAL OF SHORT LIVED RADIONUCLIDES BY DECAY IN STORAGE

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ for _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE 1/19/07

LABORATORY MANAGER _____ DATE 1-19-07

HISTORY: Rev0, 7/31/97; Rev1, 2/11/02; Rev2, 4/07/03; Rev3, 2/13/04, 3/10/05, 1/19/07 (re-release without revision).

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures used to manage the disposal of short-lived radionuclides by decay in storage. This SOP applies to disposal by decay in storage of short-lived radionuclides with half lives of 60 days or less.

2. SUMMARY

This procedure is used for disposal of radiochemical standards and samples that contain only known short-lived radionuclides and **DO NOT CONTAIN ANY CHEMICAL CONSTITUENT THAT WOULD MAKE IT A RCRA HAZARDOUS WASTE.** Any materials contaminated with radionuclides having a half life greater than 60 days must be disposed of as a Low Level Radioactive Waste (refer to SOP 015). These radionuclides ***with half lives less than 60 days*** will be stored until at least 10 half lives have elapsed. Following the decay period, the materials will be surveyed in a low background area to ensure that all radiation levels are indistinguishable from background levels. Prior to disposal, all radioactive material labels must be removed or defaced. The material may then be disposed in the normal (sanitary) trash.

3. RESPONSIBILITIES

It is the responsibility of the technician to perform these procedures according to this SOP and to inform the Radiation Safety Officer (RSO) and Waste Compliance Officer of any problems that may occur during the performance of these procedures.

4. APPARATUS AND MATERIALS

4.1 Ludlum Model 19 MicroRoentgen Meter or equivalent

4.2 NE Electra with DP6A Dual Phosphor Alpha/Beta Scintillation Detector or equivalent

4.3 Materials for defacing labels, including items such as black paint or permanent markers.

5. REAGENTS

None.

6. PROCEDURE

6.1 CLASSIFICATION OF MATERIALS FOR DISPOSAL BY DECAY IN STORAGE

Records are reviewed for radionuclide content to ensure that all radionuclides present have half lives of 60 days or less and **that there are no chemical constituents that would make the material a RCRA Hazardous Waste**. This data may be obtained from a Radioactive Material Standard Certificate that details radionuclide composition or from analytical reports on samples. However, when reviewing analytical reports, sample data must be available for **all** radionuclides to ensure that long lived radionuclides present in the sample are not missed. All materials that are classified as short-lived may be set aside for decay in storage.

6.2 DECAY IN STORAGE PERIOD

Materials that are classified as short-lived are set aside for a period of at least 10 half lives of the radionuclide with the longest half life. The total decay in storage time is calculated by multiplying the longest half life by a factor of 10. The earliest disposal date is calculated by adding the 10 times the half life to the current date. The disposal date is marked on the label.

6.3 STORAGE LOCATION

Materials that are set aside for decay in storage shall be kept segregated from other materials.

6.4 SURVEY PRIOR TO DISPOSAL

Following the decay in storage period, the material is removed to a low background area and surveyed with a Micro Roentgen Meter and a NE Electra with a Dual Phosphor Alpha/Beta Scintillation detector. In order, for the material to be disposed of, there can be no radiation detected above background. *The material must be indistinguishable from background.* If no radiation levels above background are found, the material is cleared for disposal.

6.5 REMOVAL OF LABELS OR MARKINGS INDICATING THE PRESENCE OF RADIOACTIVE MATERIAL

All labels or other marking that indicate the presence of radioactive material must be removed or defaced prior to disposal. The labels may be removed or defaced using black paint or permanent marker. The labels must be removed or defaced to prevent unnecessary public concerns resulting from radioactive material labels being discovered by a citizen or sanitary landfill personnel.

6.6 DISPOSAL

The decayed, surveyed, and defaced materials may disposed of in the normal (sanitary) trash providing the above conditions have been met *without exception*.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

7.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

7.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), or when handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

7.2 WASTE DISPOSAL

The waste generated by these procedures is disposed as described in SOP 003 - Management of Nonradioactive Hazardous Waste.

8. REFERENCES

"Rules and Regulations Pertaining to Radiation Control", Colorado Department of Public Health and Environment, Laboratory and Radiation Services Division, Section 4, 2001.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 026 REVISION 2

TITLE: RADIOACTIVE MATERIALS INVENTORY CONTROL USING LIMS

FORMS: NONE

APPROVED BY:
TECHNICAL MANAGER _____ DATE 2/9/07
QUALITY ASSURANCE MANAGER _____ DATE 2/9/07
LABORATORY MANAGER _____ DATE 2-9-07

HISTORY: Rev0, 9/22/03; Rev1, 3/24/05; Rev2, 2/9/07.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

Paragon Analytics operates under Radioactive Material Licensing conditions prescribed by the Colorado Department of Public Health and Environment (CDPHE), Laboratory and Radiation Services Division. These Radioactive Material Licensing conditions dictate that Paragon must control possession of radioactive material by both activity and volume. Paragon manages these requirements by performing radioactive material prescreening on samples and incoming radioactive materials. The data obtained from prescreening, plus other general, sample description information, is entered into Paragon's Laboratory Information Management System (LIMS). LIMS provides the Radiation Safety Officer (RSO) or designee with the means to efficiently monitor the total activity and volume of radioactive material in house.

2. SUMMARY

The backbone of radioactive material control at Paragon is the sample receipt process. Procedures for the initial receipt and login of samples are detailed in Paragon SOP 202. Per SOP 202, Sample Control staff arrange for the samples to be prescreened, as applicable, for radioactive material. Sample Control staff also enter all relevant sample information, including sample volume, into LIMS. As needed, the samples are prescreened per procedures outlined in Paragon SOP 703. The data obtained from the prescreen analysis of the samples is entered into LIMS by the Project Manager (PM) or the RSO. At this time, the RSO has the information necessary to manage the radioactive materials inventory.

3. RESPONSIBILITIES

3.1 Sample Control staff are responsible for the initial receipt and login of samples and for arranging for prescreen analyses, as detailed in SOP 202.

3.2 Qualified laboratory personnel are responsible for conducting the prescreen analyses as described in SOP 703.

3.3 The Project Manager (PM), RSO or designee is responsible for entering the prescreen data into LIMS.

3.4 The RSO is responsible for reviewing the prescreen data and ensuring that the conditions of the Radioactive Materials License are met.

4. APPARATUS AND MATERIALS

4.1 Prescreening instrumentation per SOP 703.

4.2 Paragon Analytics LIMS.

5. PROCEDURE

5.1 INITIAL SAMPLE RECEIPT

Samples are received and initially logged in by Sample Control staff per Paragon SOP 202. Samples that are designated for prescreening are held in the Sample Control Walk-In Cooler (RU #20), until the prescreen data is received by the PM, RSO or designee, and the samples are released to the lab.

5.2 SAMPLE PRESCREENING

Sample prescreening operations are conducted per Paragon SOP 703. The sample prescreen data are delivered to the PM, RSO or designee.

5.3 INPUT OF SAMPLE PRESCREEN DATA INTO LIMS

The PM, RSO or designee inputs the prescreen data into LIMS as follows:

5.3.1 From the LIMS main menu, select the 'Waste Management' menu option, then select 'Prescreen Rad Inventory'. Enter the sample workorder number in the order number field, then click on the 'Add Samples From Login' button.

5.3.2 The sample data will appear on the screen including workorder number, matrix, sample volume, activity concentration and total activity for alpha, beta, and tritium. Enter the activity concentrations from the prescreen report in pCi. LIMS will calculate the total activity for each sample and all samples in the workorder.

5.3.3 Click on the 'Evaluate Rad/Disposal' status button. This will assign handling classes and disposal type.

5.3.4 Click on the 'Activity Report (pCi)' button and review the report. ~~This report will be included with the LIMS Project Instructions to provide all laboratory staff with a detailed report of activity concentrations and total activities for each sample and the entire workorder.~~ ; correct as necessary DAS

5.3.5 The LIMS Project Instructions must now be generated. Go to the 'Sample Control' menu and click on the 'Potential Hazards' button.

Press Ctrl +F and input the workorder number in the dialog box. Then click 'Find'. The workorder information will appear on the screen.

5.3.6 Click the 'Prescreen Data Released' button, then the 'Handling Instructions Released' button, then click the 'Update HI Now Codes' (i.e., Handling Instructions Codes) button.

5.3.7 Click on the 'Preview Handling Instructions' button, and review the Project Instructions report; make any changes that are necessary.

5.4 EVALUATION OF RADIOACTIVE MATERIALS INVENTORY

The RSO or designee may check the radioactive materials inventory at any time by going to the LIMS 'Waste Management' menu and selecting 'RAD Inventory'. The total activities, license activity limit, % remaining, and the license balance information will be provided. Additionally, any workorder may be selected to review the associated activities.

5.5 REDUCTION OF RADIOACTIVE MATERIALS INVENTORY BY LABORATORY SAMPLE DISPOSAL

Samples are maintained in Paragon's radioactive materials inventory until disposal. In LIMS, samples are designated for disposal via the creation of a "waste package". The total activity for each sample in the disposal unit is automatically removed from the laboratory's radioactive materials inventory upon physical disposition of the "waste package". This is accomplished per the following procedures:

5.5.1 To add samples to a waste package in LIMS, go to the 'Waste Management' menu, then select 'Sample Disposal'.

5.5.2 Enter the workorder number in the order number field, then click on the 'Find' button. Double click on the samples that are to be disposed. The samples selected for disposal will appear in the 'Selected Bottles for Disposal' window to the right of the sample information.

5.5.3 Waste Management staff then physically creates the waste package by gathering together all of the samples in a particular waste stream to be disposed of per the identities listed in the LIMS waste package report generated in Step 5.5.2 above. The Waste Management staff will then dispose of the designated samples in the appropriate waste stream container.

5.5.4 Once the samples in the waste package have been physically disposed of, the Waste Management staff will indicate in LIMS that disposal is complete. LIMS will then automatically remove the samples from the radioactive materials inventory.

6. SAFETY, HAZARDS AND WASTE DISPOSAL

6.1 SAFETY AND HAZARDS

6.1.1 The building is equipped with safety showers, eyewash stations, fire extinguishers, fire blankets, and first aid kits. All laboratory personnel must be trained in the use and location of these items.

6.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), or handling materials or equipment potentially contaminated with chemicals or radioactive materials.

6.1.3 Food and drink are prohibited in all lab areas.

6.2 WASTE DISPOSAL

Wastes are disposed of in the manner that is appropriate to the waste stream; detailed procedures are provided in Paragon SOPs 003 and 015.

7. REFERENCES

7.1 Paragon Analytics, SOP 202, Login and Distribution of Samples, current revision.

7.2 Paragon Analytics, SOP 703, Sample Prescreening, current revision.

7.3 Paragon Analytics, SOP 003, Management of Nonradioactive Hazardous Waste, current revision.

7.4 Paragon Analytics, SOP 015, Disposal of Waste, current revision.

DOCUMENT REVISION HISTORY

2/9/07: References to SOP 201 removed since this SOP was combined with SOP 202 then retired. Added DOCUMENT REVISION HISTORY Section.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 027 REVISION 1

TITLE: PACKAGING SAMPLES FOR RETURN TO CLIENT

FORMS: NONE

APPROVED BY:
TECHNICAL MANAGER _____ DATE 9-11-06
QUALITY ASSURANCE MANAGER _____ DATE 9/8/06
LABORATORY MANAGER _____ DATE 9-11-06

HISTORY: Rev 0, 5/15/03 and 4/1/05; Rev1, 9/11/06.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures for packaging samples to be returned to the client. The samples will be classified as one of the following groups prior to packaging: nonhazardous, hazardous, radioactive for transportation, and both hazardous and radioactive for transportation. The classified samples will be packaged according to both regulatory requirements and Paragon's requirements for the class of sample(s) being shipped.

2. SUMMARY

Samples to be packaged for return to the client are classified based upon analytical results, including sample prescreen results and historical or process knowledge as appropriate. All samples returned to the client by Paragon are packaged to ensure that the contents do not leak under conditions normally incident to transportation. All outgoing sample shipments meet, at a minimum, the requirements defined by Title 49 of the Code of Federal Regulations (49CFR) for general packaging. Further, sample shipments that are hazardous or hazardous and radioactive, meet the requirements of 49 CFR and/or International Air Transportation Association (IATA) Dangerous Goods Regulations. Hazardous samples are required to be shipped with specific types of outer and inner containment known as UN specification packaging. Because the process of hazard determination, labeling, manifesting, packing and shipping is complicated, a flow chart to help illustrate the process is included as Appendix A.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP, applicable regulations, and to know what regulations are applicable to what shipping provider, and to complete all documentation required for review. Any anomalies or out-of-control events must be noted and corrective action taken and documented.

3.2 Only personnel who have completed Department of Transportation (US DOT) hazardous materials shipper training and who possess a working knowledge of US DOT and IATA hazardous material shipping regulations, may oversee the

preparation and shipment of samples with hazardous constituents. The Facilities/Waste Manager is responsible for ensuring that appropriate training has been provided and for retaining all shipping records.

3.3 The Paragon Project Manager (PM) is responsible for coordinating the shipment with the client, obtaining the correct address and any site-specific protocols for sample return.

4. APPARATUS AND MATERIALS

4.1 Plastic coolers (Coleman or equivalent)

4.2 Double-walled fiber board boxes, minimum burst strength of 275 psi or greater

4.3 Shipping tape, 2" width or greater

4.4 Plastic liners

4.5 Industrial heat sealing apparatus and accompanying poly bags

4.6 Zip-lock poly bags

4.7 Floor Dry™ sorbent material or equivalent

4.8 Bubble wrap bags

4.9 Assorted cushioning materials (bubble wrap, foam sheets, foam peanuts)

4.10 UN Specification 4G fiber-board boxes

4.11 UN Specification 1A2 and 1H2 open-head drums

4.12 Other UN Specification shipping containers, as needed

4.13 Ludlum Model 19 MicroRoentgen (Micro R) meter or equivalent

4.14 Oxford LB5100 Gas Flow Proportional Counter or equivalent

4.15 Whatman™ 42 filter papers (47mm), Rad-Wipe smears, or equivalent

4.16 47mm steel planchets

5. PROCEDURE

5.1 NOTIFICATION OF SAMPLES TO BE RETURNED TO CLIENT

Waste management personnel inform the Paragon PM when samples are available for return to client. Sample return and disposal information is maintained in the Paragon Laboratory Information Management System (LIMS). A written list, typically a LIMS printout, is forwarded to the PM. The PM obtains client

approval for sample return. The PM also obtains information regarding any client and/or site-specific protocols for sample return. After client approval for sample return has been received, the PM informs waste management personnel that they may package the samples for shipment.

5.2 CLASSIFICATION OF SAMPLES FOR TRANSPORTATION

5.2.1 Evaluate the samples for the presence of radioactivity. Create appropriate shipping documents as necessary based on the absence of or level of radioactivity present.

5.2.1.1 If the samples do not meet the requirements for radioactive as described in 49 CFR 173 or IATA Part 10.3, then the material is not considered radioactive for transportation. No special packaging for radioactive concerns is needed. However, Hazardous material regulation may still be applicable.

5.2.1.2 If the samples do meet the definition of radioactive material as described in 49 CFR 173 or IATA Part 10.3, they are considered radioactive materials for transportation purposes.

NOTE: Sample shipments that meet the definition of Class 7 Radioactive I, II or III hazards as defined in 49CFR or IATA require special handling in excess of this SOP. If a client has requested return of samples that meet these criteria, contact the RSO immediately.

5.2.1.3 DOT Excepted Packages for limited quantities of Class 7 are defined in 49 CFR 173.421. If the listed criteria is met, the package is exempt from packaging requirements and only needs the applicable UN number marked on the outside of the package and Radioactive on the inside container.

5.2.1.4 IATA Excepted Package is defined in IATA 10.5. These items must be shipped according to the limitations and specifications listed in Section 10.5.

5.2.2 Evaluate the samples to determine their hazardous materials status. Materials are considered to be hazardous for transportation by the US DOT if they possess any of the following characteristics:

- ***Explosive:*** The sample contains explosive materials capable of detonation or ignition. (Hazard Class 1)
- ***Flammable Gas:*** The sample is a gas that is capable of ignition. (Hazard Class 2)
- ***Flammable Liquid:*** The sample has a flash point of less than or equal to 141ºF (60.5°C). (Hazard Class 3)
- ***Flammable Solid:*** The sample is spontaneously combustible or dangerous when wet. This class includes solid materials that are capable of self-ignition, combustion, or reaction. (Hazard Class 4)
- ***Oxidizers:*** The sample contains materials that are capable of giving up oxygen that can enhance or accelerate the combustion of fuel sources. (Hazard Class 5)
- ***Poisons:*** The sample contains non-gaseous materials that are known to be so toxic as to provide a hazard to health during transportation. A list of these materials may be found in the Hazardous Materials Table, 49CFR172.101. (Hazard Class 6)
- ***Radioactive Materials:*** The sample meets the criteria prescribed in 49 CFR173 or IATA 10.3. (Hazard Class 7)
- ***Corrosive Liquid:*** The sample is a liquid with a pH of less than 2.0 or pH greater than 12.5. (Hazard Class 8)
- ***Miscellaneous Hazards:*** The sample is a material that presents a hazard to transportation, but does not meet the definition of any other hazard classes. A list of miscellaneous hazards may be found in the Hazardous Materials Table, 49CFR172.101. (Hazard Class 9)

5.2.2.1 If the sample does not possess any of the above listed characteristics, it is classified as **"non-hazardous"** with respect to transportation. No special documentation is required.

5.2.2.2 If the sample <u>does</u> possess one or more characteristics that classify it as a **"hazardous material"**, assemble the required documentation.

NOTE: Only personnel who have completed Department of Transportation, Hazardous Materials Shipper training and who possess a working knowledge of US DOT and IATA hazardous material shipping regulations may oversee the manifesting of samples with hazardous constituents. Directions for completion manifests can be found in 49CFR Subpart C and IATA Section 8. Preprinted documents are available to aid with manifest preparation.

- Obtain from the RSO a US DOT hazardous material manifest with emergency response information for ground shipments or an IATA Shippers Declaration of Dangerous Goods with emergency response information for air shipments.

- Obtain from the RSO the DOT Hazard Class Warning label and proper shipping name marking. This information is found in 49 CFR 172.101, columns 3 and 2 respectively, or the IATA Dangerous Goods Regulations, Section 4, columns C and B respectively.

- For shipments that include radioactive samples, ensure that the appropriate language listed in Section 5.2.1.2 of this procedure is included as additional handling information on either type of manifest.

5.3 SELECTION OF AN APPROPRIATE SHIPPING CONTAINER

5.3.1 If the sample shipment is classified as: Non-hazardous and Non-regulated (US DOT) with respect to radioactivity, Exempt (IATA) with respect to radioactivity **OR** Radioactive Material, Excepted Package-Limited Quantity of Material, UN2910, choose one of the following outer containers as appropriate to the sample matrix:

5.3.1.1 For soils and solids, choose a double-walled fiberboard box with burst strength of at least 275psi. Assemble with 2" polyethylene shipping tape. Secure the bottom flaps with at least two strips of tape and allow at least 3 inches of overhang on each side.

5.3.1.2 For non-regulated, exempt liquids, choose a plastic cooler or a UN specification 1A2 or 1H2 5-gallon drum. Note: the use of UN Specification containers is not required in this case, but may be more efficient in some situations.

5.3.1.3 For radioactive, excepted quantity liquids, choose a UN specification 1A2 or 1H2 5-gallon drum.

5.3.2 If the sample shipment is classified as hazardous, select the UN specification packaging system for the materials being shipped. UN specification 1A2 (steel drum with removable head), 1H2 (plastic drum with removable head), or 4G (fiberboard box) outer packages with glass or plastic inner packages are Paragon's preferred combination packaging systems and are typically kept in stock.

5.3.2.1 For ground shipments, consult column 8B of 49CFR172.101 to locate the packaging reference for 49CFR173. Go to that citation and choose the combination packing option appropriate for the shipment.

5.3.2.2 For air shipments, consult Section 4, column K of the IATA Dangerous Goods Regulations to locate the packaging instruction reference. Go to that citation in Section 5 of IATA and choose the combination packing option appropriate for shipment.

5.3.3 If either 49CFR or IATA regulations indicate requirement of a type of packaging that is not readily available, consult the Waste Management Officer or RSO for guidance.

5.3.4 If a 4G fiberboard box is the preferred combination packaging, assemble and pack the container according to manufacturer's instructions.

5.4 PACK THE CONTAINER

All samples are packed, at a minimum, according to the standard of strong outside packaging (49CFR171.8) that will not allow the contents to leak under the conditions normally incident to transportation. These instructions apply to all packagings other than UN 4G systems.

5.4.1 Line the interior of the chosen container with a plastic liner.

5.4.2 Wrap individual sample bottles in cushioning material. Use bubble wrap bags if available or bubble wrap sheets.

5.4.3 Place each sample container in secondary containment. Use a zip-lock bag for solid samples or a heat-sealed plastic bag for liquid samples.

5.4.4 For solid samples, place approximately 4" of additional cushioning material (e.g., bubble wrap, foam peanuts or foam sheeting) on the bottom and 2" of additional cushioning material along the sides of the package. Insert the sample containers, but do not over pack the container. Place cushioning material in the voids and on top of the package.

5.4.5 For liquid samples, add two inches of Floor Dry or other approved sorbent material to the bottom of the container. Add the bagged samples leaving enough space to allow sorbent material to completely surround samples. Cover the samples in Floor Dry. Ensure that the liquid sample material is compatible with the sorbent used through testing or process knowledge.

5.4.6 Seal the inner plastic liner with a knot or by twisting and taping with packing tape.

5.4.7 Place paperwork in a large zip-lock bag. If possible, tape the bag to the inside lid of the cooler or box. Otherwise, place the zip-lock bag on top of the shipment. Paperwork includes:

- Chain-of –custody;
- If required and assembled during step 5.2.1.2, letter of transmittal and "RADIOACTIVE" label;
- Any additional information provided by the PM according to client and site specific requirements.

If a "RADIOACTIVE" label is included, ensure that it is attached such that it will be visible immediately upon opening the package.

5.4.8 Seal the shipping container. For coolers and boxes, seal with shipping tape. Ensure that the shipping tape goes completely around the outside of the container.

5.5 LABEL THE CONTAINER

5.5.1 Place a double arrow label on the outside of the container to indicate package orientation.

5.5.2 Label package with Paragon's return address and the consignee's address.

5.5.3 If previously obtained from SOP section 5.2.2.2, place the proper DOT

Hazard Class Warning label on the opposite side of the container. Place the proper shipping name marking on the container above the DOT Hazard Class Warning label.

5.5.4 Place the completed Bill of Lading or IATA Shippers Declaration of Dangerous Goods in a poly envelope and affix to the package or to package 1 of a multiple piece shipment.

5.6 ADDITIONAL REQUIREMENTS FOR RADIOACTIVE MATERIAL SHIPMENTS

5.6.1 Perform a swipe test for removable contamination. Wipe a filter paper or Rad-Wipe over a 4" x 4" (100 cm^2) square area of the container's external surface. Count the wipe per SOP 010. The removable radioactive material contamination on the package must be less than 220dpm/100 cm^2 alpha and 2200dpm/100 cm^2 beta/gamma.

5.6.2 Survey the external surface of the package. Obtain a Ludlum Model 19 Micro Roentgen (Micro R) meter or equivalent. Verify that the daily instrument checks for calibration and background have been completed per SOP 007. Perform a survey of the container. The external dose rate reading must not exceed 0.5mRem/hour (500uRem/hour) at the surface of the package.

5.7 Ship the sample return package(s) by available carrier such as FEDEX Ground, FedEx, UPS (non-hazardous or excepted shipments), or an approved common carrier (truck line) for large shipments.

6. SAFETY AND HAZARDS AND WASTE DISPOSAL

6.1 SAFETY AND HAZARDS

6.1.1 The building is equipped with safety showers, eyewash stations, fire extinguishers, fire blankets and first aid kits. All laboratory personnel must be trained in the use and location of these items.

6.1.2 Wear gloves, safety glasses and a lab coat when working with any samples or chemicals or when handling materials or equipment potentially contaminated with chemicals.

6.1 WASTE DISPOSAL

All used wipes that have radioactive material contamination shall be disposed of as low level radioactive waste (LLRW).

7. REFERENCES

7.1 Code of Federal Regulations, Title 49, Chapter 1, October, 2005.

7.2 International Air Transportation Association Dangerous Goods Regulations, Resolution 618, Attachment A, 47th Edition, January, 2006.

7.3 Rules and Regulations Pertaining to Radiation Control, Colorado Department of Health, Radiation Control Division, 2005.

DOCUMENT REVISION HISTORY

9/11/06: Updated text as needed and references to reflect current regulations. Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 029 REVISION 2

TITLE: **CALIBRATION AND USE OF THE BERTHOLD LB 1043 AS HAND AND FOOT MONITORS**

FORMS: **221 (use current iteration)**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 10/3/07
QUALITY ASSURANCE MANAGER _____ DATE 10/2/07
LABORATORY MANAGER _____ DATE 10/4/07

HISTORY: Rev1, 7/13/04 (re-released without revision 6/23/05); Rev2, 10/2/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) provides instructions for the calibration, performance checks, maintenance, and continuous use of the Berthold LB 1043 AS hand and foot monitors, located at the routine personnel exits from controlled laboratory areas at Paragon Analytics.

Laboratory staff use these monitors to survey for potential hand and foot contamination from alpha and beta particle-emitting radionuclides. The monitors are capable of discriminating between alpha and beta radiation, allowing for separate action levels for the two types of contamination. Other types of radiation, such as gamma and X-rays are not measured by this instrument.

This procedure is an integral part of the laboratory's efforts to keep the dose of ionizing radiation to the employee and members of the general public "As Low As Reasonably Achievable" (ALARA). The user is cautioned that this procedure is intended to supplement, not replace, other established ALARA practices as defined in the laboratory's Radiation Protection Plan (RPP). Users should note that detection levels for this type of instrumentation are relatively high, as compared to analytical detection limits achieved in the laboratory. Consequently, the user should be mindful that an instrument determination of "NOT CONTAMINATED" is not a definitive assessment of a lack of radioactive contamination. The consistent use of other ALARA practices, such as good housekeeping and the use of personal protective equipment, is critical.

2. SUMMARY

2.1 CALIBRATION AND ALARMS

The monitors are operated in a mode to provide raw count data, rather than calculated activity units (e.g., Becquerels); evaluation of counting efficiencies is done on a separate worksheet. NIST-traceable sources, manufactured to provide a 100cm^2 active surface area, are used in the calibration. A ^{241}Am source is used in the alpha efficiency calibration, and a ^{137}Cs source is used in the beta efficiency calibration. The monitors are calibrated to sound an alarm at a count rate that is

consistent with established activity action levels for alpha and beta contamination. Alpha and beta alarm levels are set separately.

2.2 WEEKLY PERFORMANCE CHECKS

Weekly performance checks are completed on each monitor while the instrument remains in service. The sources used for the weekly performance checks may be the same sources used for calibration, or they may be other sources, the use of NIST-traceable sources for the weekly performance check is not required. Acceptance criteria for weekly performance checks are established from the initial performance checks and may be updated, if necessary, after sufficient historical data is accumulated. Routine maintenance during the weekly checks may include replacing the P-10 gas cylinder, replacing the detector windows, and routine cleaning.

2.3 CONTINUOUS USE

Continuous operation of the hand and foot monitors involves the individual employees surveying themselves for hand and foot contamination prior to leaving the controlled laboratory areas.

3. RESPONSIBILITIES

3.1 Radiation Safety Officer (RSO)

3.1.1 It is the RSO's responsibility to provide adequate training to the Primary Instrument Technician to ensure that the Technician is able to demonstrate proficiency in the operation, calibration, and maintenance of the instruments. Demonstration of proficiency by the Technician shall include a hands-on demonstration, successful performance checks and recalibration, and a manual recalculation of results. The RSO shall maintain records of the proficiency demonstration.

3.1.2 It is the responsibility of the RSO to review and approve the calibration data to ensure that the proper alarm levels are set in the instruments, and to ensure that the hand and foot monitors are used.

3.1.3 In the event that a monitor is determined to be out of normal operating specifications, it is the RSO's responsibility to ensure that the instrument is removed from use (SOP 317), that the necessary services to return the instrument to use are procured, and to provide the employees with an alternate method for performing personal surveys.

3.2 Primary Instrument Technician

3.2.1 The Primary Instrument Technician will have completed all radiation safety training required for general laboratory personnel, and will have documented previous experience in the calibration and use of radiation detection instrumentation. The Primary Instrument Technician shall

provide a demonstration of proficiency (described above), before performing any procedure unsupervised.

3.2.2 It is the responsibility of the Primary Instrument Technician to perform the instrument calibrations, weekly instrument checks and routine maintenance, including replacement of the detector windows and weekly cleaning of the hand and foot detectors, as described in this SOP. In the event that the instrument fails to meet established acceptance criteria the primary instrument technician will remove the instrument from service, properly tag the instrument per SOP 317, and immediately notify the RSO.

The Primary Instrument Technician is responsible for maintaining an adequate supply of P-10 gas to ensure the continuous operation of the instrument during working hours, as well as overnights, weekends, and holidays. This allows for employees who may work off-shifts or non-routine schedules.

3.3 Each Employee

3.3.1 It is the responsibility of each employee to properly survey themselves before leaving a controlled laboratory area in which radiological materials may have been used.

In the event of an indication from the instrument that the employee is potentially contaminated, it is the employee's responsibility to minimize the extent of the laboratory contamination and help facilitate decontamination of themselves and the lab area.

DO NOT LEAVE THE LABORATORY AREA, remain in the immediate vicinity.

Travel only as far back into the lab area as necessary to call for assistance. Notify the RSO immediately!

3.3.2 As needed, each employee is responsible for providing any assistance the RSO may need to evaluate the extent of contamination, to decontaminate an employee or their clothing, and to identify the root cause of the incident.

3.3.3 In the event of an instrument malfunction, it is the employee's responsibility to use an alternate instrument to perform a personal survey before leaving the lab area, and to notify the RSO as soon as possible of the malfunction.

4. APPARATUS AND MATERIALS

4.1 Berthold LB 1043 AS hand and foot monitor.

4.2 Mylar film, 0.3 mg/cm^2, or equivalent.

4.3 P-10 gas, 90% argon + 10% methane, high purity.

4.4 Low pressure regulator, <0.1 mbar.

4.5 Tacky-Mat shoe cleaning mat, Lab Safety Supply 3BB-1631-5, or equivalent

5. PROCEDURE

5.1 OPERATING CONDITIONS

5.1.1 Proper instrument operation relies on the low flow of P-10 gas through the detectors. The line pressure for the P-10 supply should be less than 0.1 mbar (0.00145 lb/sq.in.). A low pressure regulator should be used and the flow rate should be adjusted so that the ball gauges on the front of the instrument read approximately "5" both in and out.

5.1.2 Each hand and foot monitor has a tacky-mat directly in front of the instrument. A new sticky surface should be exposed, or the mat should be replaced, at least weekly.

5.1.3 The instrument should be clean, especially the covers for the hand and foot detectors.

5.1.3.1 The hand detectors should be wiped at least weekly with a disinfecting agent, for sanitary maintenance.

5.1.3.2 The foot detectors should be gently blown or vacuumed at least weekly to remove visible dirt and debris. This helps to minimize the background measurements and optimize the detector sensitivity.

5.1.4 The mylar window coverings over the detectors must be intact and should be replaced as soon as any tear or puncture is noticed. This repair must be performed by the RSO or another qualified individual, and must be done per the instrument manufacturer's instruction manual.

5.2 CALIBRATIONS

5.2.1 The calibration of the instrument consists of determining the instrument efficiency coefficients and background count rates, and setting the appropriate alarm settings to achieve the following action levels:

Alpha	1000 dpm	hand	(= 16.7 dps)
Beta	4000 dpm	hand	(= 66.7 dps)

Alpha	2000 dpm	foot	(= 33.4 dps)
Beta	8000 dpm	foot	(= 133 dps)

5.2.2 See I:\oprtns\safety\hand and foot cals.xls (**Attachment 1**). Record the alpha and beta instrument background count rate for each detector, using the Steps outlined below. These values are recorded for informational purposes only, they are not used to set the threshold alarm levels in the instrument.

5.2.2.1 Approach the instrument without stepping on the foot platform.

5.2.2.2 Press the "DISPLAY" button on the front panel.

5.2.2.3 Read the detector 1 alpha background, and record the result.

5.2.2.4 Repeatedly press the "DISPLAY" button, recording the other background results in the appropriate spaces on the calibration worksheet.

5.2.3 Determine the alpha counting efficiencies for each detector as follows:

5.2.3.1 Obtain 100cm^2 surface area alpha and beta sources.

5.2.3.2 Record the decay-corrected current source activities on the calibration worksheet.

5.2.3.3 For each detector, place the alpha source housing against the detector grate, obtain a standard count over the pre-set count duration.

5.2.3.4 Using the "DISPLAY" button on the front panel (see Step 5.2.2 above), record the observed net count rate on the calibration worksheet.

5.2.3.5 Repeat this process until five observations are recorded for each detector.

5.2.3.6 Alternately, if the calibration sources are used for daily performance checks, the most recent five observations may be entered into the calibration worksheet.

5.2.3.7 In the specified column on the calibration worksheet, enter the average of the five readings.

5.2.3.8 Determine the individual detector efficiencies. Divide the

average result by the current source activity, in dps.

5.2.4 Repeat Steps 5.2.3 using the beta source.

5.2.5 Set the appropriate alarm level for each detector.

5.2.5.1 Using the threshold alarm levels in dps (see 5.2.1), multiply this number by the calculated detector efficiency (Steps 5.2.3 and 5.2.4) to obtain threshold alarm levels, in cps.

5.2.5.2 Calculate the average alpha and beta threshold alarm level for all four hand detectors. These values will be used to set the instrument.

5.2.5.3 Calculate the average alpha and beta threshold alarm level for both foot detectors. These values will be used to set the instrument.

5.2.5.4 Obtain the security lockout code from the RSO. This will allow the user to reset threshold count rates in the instrument.

5.2.5.5 Begin by entering the lockout code into the instrument keypad.

5.2.5.6 Using the flowchart in **Figure 1**, reset the threshold alarm levels to those calculated above. DO NOT CHANGE ANY OF THE PRE-SET INSTRUMENT SETTINGS, OTHER THAN THE THRESHOLD ALARM LEVELS, WITHOUT THE EXPRESS APPROVAL OF THE RSO.

5.2.5.7 Affix a label, shown at the bottom of Attachment 1, to the instrument indicating the date of calibration and the responsible Technician (the template for the label can be found at I:\oprtns\safety\hand and foot cals.xls). Any similar label with the same information is acceptable.

5.2.6 The instrument is now calibrated and ready for use.

5.3 WEEKLY PERFORMANCE CHECKS

Instrument background and efficiency checks are performed weekly. Results are recorded in the Hand and Foot Monitor Check Logbook (Form 221, **Attachment 2**), and are evaluated against established control limits.

5.3.1 Measure the instrument background count rates following the procedures described in Step 5.2.2, except that the results are entered

into the Hand and Foot Monitor Logbook (Form 221).

Control limits are established as follows:

5.3.1.1 Interim control limits are established after initial setup of the instrument or after significant service or repairs. Interim control limits are based on the initial background measurements taken for alpha and beta activity for each detector, and are calculated as:

initial value ± (initial value * 3/sqrt(bkg cps * ct time seconds))

5.3.1.2 If sufficient data is collected to establish historically derived limits (i.e., 20-30 data points), calculate the control limits as follows:

mean value ± (3*standard deviation)

5.3.2 Measure the instrument alpha and beta count rates. In this case, the sources used do not necessarily need to be NIST-traceable or have an area of 100cm^2, but the same sources must be used consistently. Follow the procedure described in Steps 5.2.3 (alpha) and 5.2.4 (beta) and enter the results into the Hand and Foot Monitor Logbook (Form 221). Control limits are established as follows:

5.3.2.1 Interim limits are based on the initial source count rate for alpha and beta activity for each detector, and are calculated as:

initial value ± (initial value * 3/sqrt(source cps * ct time seconds)).

5.3.2.2 If sufficient data is collected to establish historically derived limits (i.e., 20-30 data points), calculate the control limits as follows:

mean value ± (3*standard deviation)

5.3.3 In the event that any weekly performance check measurement is outside established control limits, the instrument is removed from service, per SOP 317, and corrective action is referred to the Radiation Safety Officer.

5.4 CONTINUOUS USE

Any employee working in a radiologically-controlled area must use the hand and foot monitor before leaving the area.

5.4.1 Approach the hand and foot monitor and wait until the display panel reads “READY”.

5.4.2 Step onto the pedestal and place both feet all the way forward until both shoes touch the front bar, activating the instrument’s optical sensors.

5.4.3 Place both hands into the hand openings far enough to push the finger-tip lever fully in. This causes the hand detectors to close around the employee’s hands and activates the switches at the employee’s wrists.

5.4.4 Remain still until the instrument completes the count, shows all detector symbols as green, and the display panel reads “NOT CONTAMINATED”.

5.4.5 The employee is free to leave the area.

5.4.6 If the instrument detects alpha or beta contamination above the threshold alarm levels determined above, or if the instrument malfunctions, the detector symbols will be shown as either yellow (malfunction) or red (contamination) and an audible alarm will briefly sound.

5.4.6.1 In the event of an indication from the instrument that the employee is potentially contaminated, it is the employee’s responsibility to minimize the extent of the laboratory contamination and help facilitate decontamination of themselves and the lab area.

DO NOT LEAVE THE LABORATORY AREA. Remain in the immediate vicinity. Travel only as far back into the lab area as necessary to call for assistance.

Notify the RSO immediately.

5.4.6.2 Provide any assistance the RSO may need to evaluate the extent of the contamination, decontaminate the employee or their clothing, and identify the root cause of the incident.

5.4.6.3 In the event of an instrument malfunction, it is the employee’s responsibility to use an alternate instrument to perform a personal survey before leaving the lab area, and to notify the RSO as soon as possible of the malfunction.

5.5 General instructions for the use of other hand-held survey equipment is provided in SOP 031.

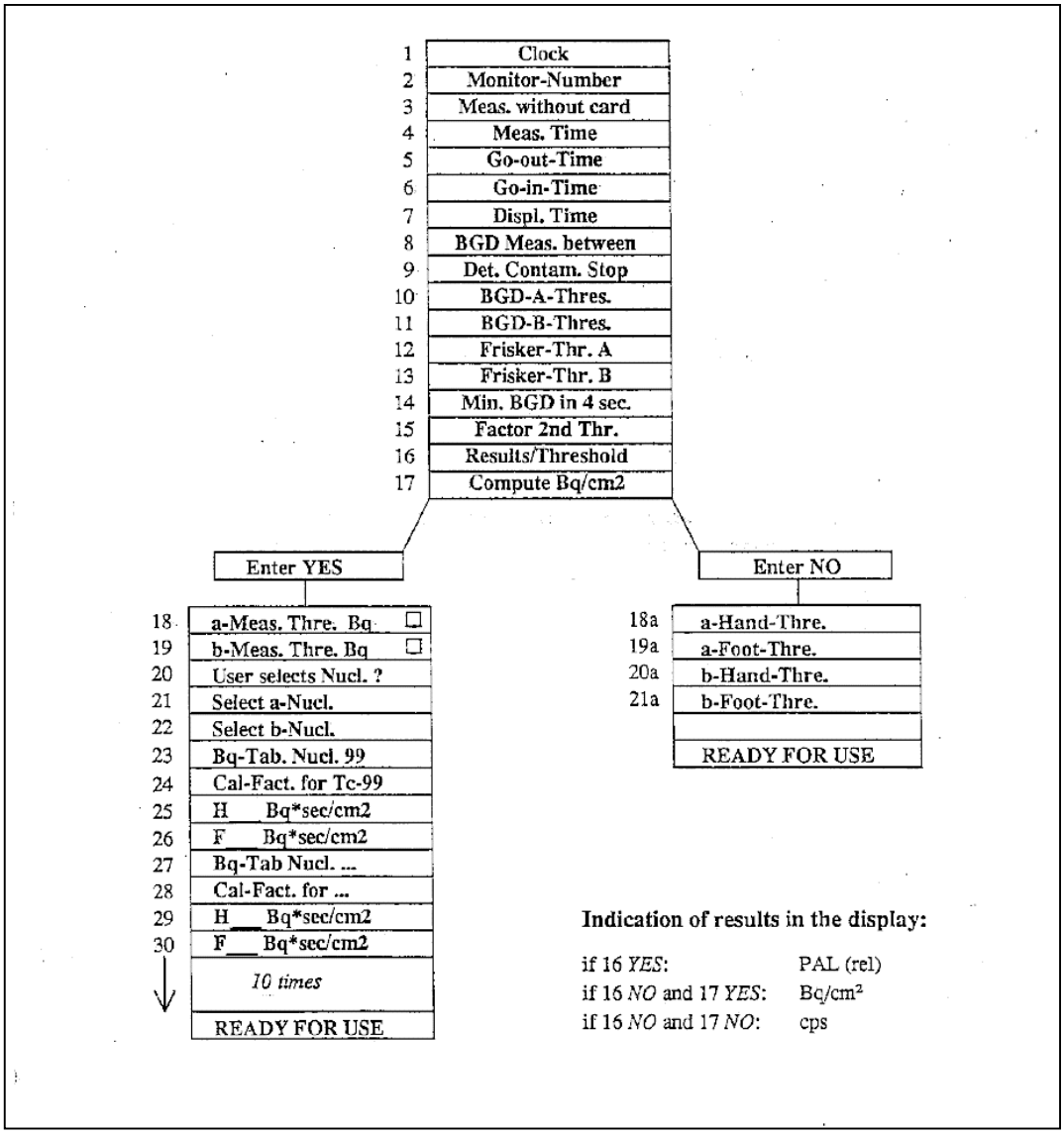
6. REFERENCES

Contamination Monitor LB 1043 AS Operating Manual, EG&G Berthold.

DOCUMENT REVISION HISTORY

10/2/07: Updated format, no technical revisions. Added DOCUMENT REVISION HISTORY.

Figure 1
Dialog Flow Chart



Attachment 1

I:\oprtn\safety\hand and foot calibration.xls

LB 1043 AS Hand and Foot Monitor Calibration

Calibration Date: SN:
Location:

Alpha Source ID:
Nuclide: Half-Life (years): Current Activity(dps):
Activity (dps): Source Cal.Date:

	Det. #	Alpha Bkg. (cps)	Alpha Source (cps) 1st ct.	Alpha Source (cps) 2nd ct.	Alpha Source (cps) 3rd ct.	Alpha Source (cps) 4th ct.	Alpha Source (cps) 5th ct.	Alpha Source (cps) Average	Counting Efficiency	Alarm Level (dps)	Threshold (cps)
L. hand, outside	1									16.7	
L. hand, inside	2									16.7	
R. hand, inside	3									16.7	
R. hand, outside	4									16.7	
									AVERAGE =		
L. foot	5									33.4	
R. foot	6									33.4	
									AVERAGE =		

Beta Source ID:
Nuclide: Half-Life (years): Current Activity(dps):
Activity (dps): Source Cal.Date:

	Det. #	Beta Bkg. (cps)	Beta Source (cps) 1st ct.	Beta Source (cps) 2nd ct.	Beta Source (cps) 3rd ct.	Beta Source (cps) 4th ct.	Beta Source (cps) 5th ct.	Beta Source (cps) Average	Counting Efficiency	Alarm Level (dps)	Threshold (cps)
L. hand, outside	1									33.4	
L. hand, inside	2									33.4	
R. hand, inside	3									33.4	
R. hand, outside	4									33.4	
									AVERAGE =		
L. foot	5									133.0	
R. foot	6									133.0	
									AVERAGE =		

LB 1043 AS Calibration Completed _____ (date)
per SOP 029 Initials _____
Calibration expires in one year.

Attachment 2

_____ A

SN 80117 (North Hall, RadChem)

Paragon Analytics

Hand & Foot Monitor Check Logbook (units are counts/second)

Detector #1

DATE	α Bkground / β Bkground	Low α Reading / Low β Reading	High α Reading / High β Reading	INIT.

Detector #2

α Bkground / β Bkground	Low α Reading / Low β Reading	High α Reading / High β Reading	INIT.

Detector #3

α Bkground / β Bkground	Low α Reading / Low β Reading	High α Reading / High β Reading	INIT.

COMMENTS:

CONTROL LIMITS

	α Bkgnd	β Bkgnd	Low α	Low β	High α	High β
Low						
High						

CONTROL LIMITS

	α Bkgnd	β Bkgnd	Low α	Low β	High α	High β
Low						
High						

CONTROL LIMITS

	α Bkgnd	β Bkgnd	Low α	Low β	High α	High β
Low						
High						

CONTINUED NEXT PAGE

_____ B

SN 80117 (North Hall, RadChem)

Paragon Analytics

Hand & Foot Monitor Check Logbook (units are counts/second)

Detector #4

DATE	α Bkground / β Bkground	Low α Reading / Low β Reading	High α Reading / High β Reading	INIT.

Detector #5

α Bkground / β Bkground	Low α Reading / Low β Reading	High α Reading / High β Reading	INIT.

Detector #6

α Bkground / β Bkground	Low α Reading / Low β Reading	High α Reading / High β Reading	INIT.

COMMENTS:

CONTROL LIMITS

	α Bkgnd	β Bkgnd	Low α	Low β	High α	High β
Low						
High						

CONTROL LIMITS

	α Bkgnd	β Bkgnd	Low α	Low β	High α	High β
Low						
High						

CONTROL LIMITS

	α Bkgnd	β Bkgnd	Low α	Low β	High α	High β
Low						
High						

Reviewed by / date _____

Form 221r3.doc (4/7/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 030 REVISION 1

TITLE: OPERATION OF THE HYDRAULIC WASTE COMPACTOR

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/8/05
QUALITY ASSURANCE MANAGER _____ DATE 11/8/05
LABORATORY MANAGER _____ DATE 11-8-05

HISTORY: Rev0, PCN #222, 4/14/94; Was retired, reactivated, reformatted and released without technical revision 7/7/2003; Rev1, 11/22/04 and 11/10/05 (re-released w/o revision).

re-released w/o revision 2/29/08 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary for the safe operation of the Hydraulic Waste Compactor.

2. SUMMARY

Waste barrels are placed inside the compaction chamber. The door is shut and the waste is compacted at approximately 2500 psi.

3. RESPONSIBILITIES

3.1 This procedure shall be performed under the direction of the Waste Compliance Manager. The Waste Compliance Manager will perform all training of personnel that have been designated to operate this piece of equipment.

3.2 Two people are needed to perform this procedure. This is due to the fact that two individuals are needed to place the drum inside the compactor and for safety purposes during the operation of the machine.

3.3 Safety inspections shall be performed on the compactor quarterly, this inspection is to include but is not limited to: (1) hydraulic fluid level, (2) electrical cord condition, (3) plunger stability and (4) proper operation of the safety catch. The items shall be documented in a maintenance logbook or on a form signed and retained by the Waste Compliance Manger.

3.4 The instrument shall be operated only on level solid ground (e.g., a concrete pad).

3.5 If the instrument is contaminated with radioactive material, as described in Section 6.2, the Radiation Safety Officer (RSO) shall be notified and appropriate steps shall be taken to minimize the spread of the contamination. The machine shall be decontaminated as directed by the RSO.

4. APPARATUS AND MATERIALS

- Compactor
- Drum Dolly
- Lab Coat
- Drum Liners
- Gloves
- Steel Toe Boots
- Radiological Contamination Survey Swipes
- NE Electra

5. REAGENTS

Radiac Wash™

6. PROCEDURE

6.1 HAZARDOUS WASTE, RADIOACTIVE/MIXED WASTE PROCEDURE

6.1.1 Cover the plunger with a plastic barrel liner.

6.1.2 Place the drum inside the compaction chamber making sure that the bottom of the drum completely encircles the raised circular base plate.

6.1.3 Remove the bung and lid from the top of the barrel.

6.1.4 Cut the bottom off of a plastic barrel liner, pull one end over the top of the drum and attach it about 2 inches from the top. Pull the other end over the plunger and attach it just above the push plate. The plunger may need to be slightly lowered to accomplish this.

6.1.5 Completely close and latch the door with the door latch.

6.1.6 Push both hydraulic levers towards the back of the unit.

6.1.7 Turn on the electric motor on the back of the unit. This will start the compaction process.

6.1.8 When the pressure on the pressure gauge indicates about 2500 pounds per square inch (psi), pull the bottom lever forward to retract the plunger. You can also pull the lever forward after the desired compaction is complete.

6.1.9 When the plunger reaches the top of the unit, after the compaction, the top lever will automatically push forward to stop the process.

6.1.10 Turn the motor off when the process is complete.

6.1.11 Remove the drum liners from the drum and the plunger and place in the drum.

6.1.12 Perform radiation surveys as necessary per Section 6.2.

6.2 POST COMPACTION RADIATION SURVEYS

6.2.1 Remove the drum and perform a swipe survey the top outside of the drum and plunger.

6.2.2 Count the swipes and if the areas surveyed are contaminated above 10 dpm/100cm2 alpha and 100 dpm/100cm2 beta, notify the RSO for guidance on further surveys and decontamination efforts.

6.2.3 If decontamination is necessary, decontaminate the areas with Radiac Wash and water then resurvey. Repeat this process as necessary until limits are acceptable.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 The employees implementing this procedure shall be trained to operate the unit in addition to reading and understanding this procedure.

7.2 Two individuals are needed to place most drums in the compactor, this process should be done so that both individuals are on either side of the drum.

7.3 If the instrument fails to operate in the manner prescribed above or if the procedure cannot be implemented as described above, stop the process and notify the Safety Manager and the Waste Compliance Manger.

7.4 Do not bypass the safety catch on the door latch.

7.5 Unplug the instrument after use and during maintenance checks.

8. REFERENCES

None.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 052 REVISION 8

TITLE: DATA PACKAGE REVIEW PROCEDURES FOR STABLE CHEMISTRY METHODS

FORMS: NONE

APPROVED BY:
TECHNICAL MANAGER _____ DATE 9-11-06
QUALITY ASSURANCE MANAGER _____ DATE 9/8/06
LABORATORY MANAGER _____ DATE 9-11-06

HISTORY: Rev0, 12\4\92; Rev1, PCN #192, 3/31/94; Rev4, 4/12/00; Rev5, 9/20/02; Rev6, 4/22/04; Rev7, 3/9/06; Rev8, 9/11/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps required to review laboratory data package reports generated by the Reporting Group. An overview of the tiered review process, which is supplemented by method-specific review checklists, is also discussed. Procedures for managing changes that need to be made to the data are also discussed.

2. SUMMARY

All analytical data generated at Paragon are extensively reviewed before submission to our clients. Raw data are reviewed for accuracy and completeness within each Department before being submitted to the Reporting Group. Reports generated by the Reporting Group are then reviewed at three distinct levels:

- ***first level report review*** - usually performed by the reporter who compiles the report
- ***second level report review*** - usually performed by the analyst who performed the work or a designee within the Department
- ***third level report review*** - performed by the Project Manager

Method-customized checklists that specify analytical and report review requirements, are used by the Reporting Group to perform the first level report review. After the first two levels of review have been performed and documented, the report is transmitted to the Reports Management Department where the client's report is finalized. The assigned Project Manager then performs the final review of the report before it is submitted to the client. Changes made to the data during the review processes, are made by authorized analysts, under the direction of Senior personnel. Documentation of these data changes occurs either by hand-annotation of review checklists, or via audit trails programmed into Lims. Should a client inquiry investigation (Project Manager is focal point of contact) result in resubmission of data, the appropriate changes are guided by Senior personnel with documentation occurring as a revised data package case narrative, completion of an NCR

(SOP 928) and /or audit trails in LIMS.

3. RESPONSIBILITIES

3.1 The Reporting Group is responsible for the generation, compilation, and first level review of the complete report. This Group must ensure that any computer automation used to calculate the final results is functioning properly and has been verified and documented.

3.2 The Department Manager, qualified analyst or other designee is responsible for the second level report review. This level of report review ensures that the reported data match the raw data and that all data are of acceptable quality and conform to the parameters of the applicable method.

3.3 It is the responsibility of all personnel who perform data review to document any anomalies, out-of control or non-compliant events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented in a Quality Assurance Summary Sheet (QASS), Non-Conformance Report (NCR), or narrative comment.

4. APPARATUS AND MATERIALS

This procedure requires access to the computer system(s) from which the report to be reviewed is generated. A hand calculator may be needed to perform manual calculations during the review process. Re-verification of software-generated or manually-generated values shall be documented.

5. PROCEDURE

5.1 DATA PACKAGE REVIEW

5.1.1 After the analytical review has been completed, the data are compiled into reports via work order number. Each report may contain: raw data, LIMS-generated summary forms, and supporting documentation (as required by the client). The reporter or analyst who performs the ***first level report review*** of the data package and report, follows the guidelines stated below. If any requirements are not met, corrective action must be taken before the data are submitted to our client.

<u>Calibration Data</u>

- Initial calibration (ICAL), initial calibration verification (ICV), and initial calibration blank (ICB) data are method compliant, analyzed at the correct frequency, and are completely documented (if applicable).
- Continuing calibration verification (CCV) and continuing calibration blank (CCB) data are method compliant, analyzed at the correct frequency, and are completely documented (if applicable).

QC Samples

- Method blanks (MB) contain no target compounds above the reporting limit (or another limit, as specified by the method or client, such as the MDL for drinking water samples analyzed in accord with compliance monitoring).
- All applicable QC sample recoveries are within control limits established by applicable method and/or client.

Samples and Miscellaneous

- Extraction and analytical holding times have been met.
- Applicable extraction SOP was followed and sample preparation information is correct.
- Sample dilutions and/or multipliers/divisors are correct.
- Units are correct.
- Internal standard (IS) areas are within control limits, if applicable.
- Surrogate standard (SS) recoveries are within control limits, if applicable.
- Dual column confirmation data are included and correct, if applicable.
- Quantitative results and units are correct.
- TIC information is included, if applicable.
- All manual re-integrations, with before and after chromatograms, are presented with the data, if applicable.
- Accompanying documentation (checklists, LIMS generated forms, if applicable, etc.) is complete and correct.

Specific review issues and strategies may be needed to address client specific requirements.

5.1.2 A ***second level report review*** shall be performed by the Department that generated the data. The reviewer may be another qualified analyst, Department Manager, or designee using the guidelines listed above.

5.1.3 Additionally, the first and second level report review verifies the following:

- All sample data are present (primary and secondary analyses, if appropriate).

- The raw data are consistent with the final report forms.
- Work order numbers, client names and client sample identifications are correct on all LIMS forms.
- QC data are present and complete.
- Significant figures are correct.
- All case narrative comments are documented correctly.
- The reporting limits are correct.
- All cross-outs are completed properly (one line cross-out, initialed and dated).
- Data qualifiers, if applicable, are present and correct.
- Data that are manually entered into LIMS are subject to 100% review to prevent data entry errors.
- Report contains all necessary accompanying documentation (e.g., percent moisture form, run sequence logs, extraction benchsheets, etc.)

5.1.4 The Reporting Group shall correct all reporting errors. If errors are brought to the attention of the reporting group prior to the report being sent to the client, the data may require analysts providing new electronic and hardcopy raw data, re-importing of the raw data, re-processing of imported data or manual correction of results. If data have already been provided to the client, originally provided data will permanently remain in the client's Workorder Review directory. After data has been corrected, new report forms may be provided, depending on the correction, and an electronic version of the report will be provided in the client's Workorder Review directory with some designation that the report is a resubmission. The final resubmission is based on the project manager and/or the client's request.

5.1.5 Significant discrepancies or errors should be brought to the attention of the responsible analyst and or Department Manager to ensure proper resolution of the situation. Examples include holding time violations, surrogate failures, calibration failures, or QC sample failures not documented by an NCR form.

5.2 FINAL REVIEW

5.2.1 Final review or ***third level report review*** is performed by the Project Manager using the following guidelines:

Introductory Section

- Review the cover letter.
- Address and addressee are correct.
- Project name and number are correct.
- Number and type of samples are correct.
- Choices of analyses/methods are correct.
- Sample cross-reference table is correct.

Review QC Sample Results

- Extraction dates identical for QC and field samples.
- Correct QC samples are present.
- QC recoveries (LCS, LCSD, MS, MSD) are within control limits or an explanation is given in the case narrative and the NCR form, if applicable.

Sample Results and Miscellaneous

- Analyte lists and reporting limits are correct.
- Concentration units match matrix type.
- Header information is correct.
- Client ID's match Chain of Custody.
- Sample results are consistent in comparable tests (e.g., BTEX by SW 8021 and SW 8260).
- Surrogate recoveries are in control.
- Results are reported to the correct significant figures.
- Qualifiers are correct and consistent.
- Results for all requested samples are included.

Case Narratives

- Client name and work order number are correct.
- Test name is correct.
- Grammar and spelling are correct.
- All discrepancies are noted.

Invoice

- Review the invoice for the correct number of samples, tests, and prices.

- Verify that the purchase order (PO) number, addressee, and address are correct.

5.3 CORRECTION OF ERRORS IN DOCUMENTS

During the course of processing and reviewing sample preparations and analysis results, it may be necessary to correct documentation errors. Detailed requirements for the correction of manual documentation errors are prescribed in **SOP 303**. Changes made to the data during the review process shall only be made by authorized analysts and under the supervision of Senior personnel. In summary, manual entries may not be obliterated by erasure, use of correction fluid, or other means. In order to maintain the integrity of the documentation generated by the laboratory, changes to documentation must be made in the following manner:

- A single line must be struck through the error so that the original text remains legible;
- A corrected entry must be made adjacent to the error; and
- The person making the change must initial and date the corrective entry.

If corrections to computerized data are required, Paragon's LIMS controls the ability to make data changes and provides an electronic audit trail for corrections that are made.

If not clearly evident, the reason for the data change must be indicated.

6. REFERENCES

None.

DOCUMENT REVISION HISTORY

9/11/06: Procedures for managing changes made to data were added. DOCUMENT REVISION HISTORY added. Data review forms attached.

Wet Chemistry Data Review Check Sheet

Analysis:

W.O #	Method/ Analytes of Interest	MATRIX	QCA	Prep Batch ID	Anal. Batch ID	CLN UP	REASONS FOR DILUTION: PROTECT/ CONDUCT. SCREEN	DIL INTO RANGE	REDUCED ALIQUOT

Data Review Checklist:

	Rev. Y(es)N(o)NA	Rev. Y(es)N(o)NA	Comments
Is the **Calibration or Standardization** criteria within the acceptable limits?			
Is the **ICV/ICB** and all **CCV/CCB** sets within control?			
Are the **MB and LCS(D)** within control?			
Was there **Matrix QC** performed with each prep batch?			
Are there **20 or less** samples per prep batch?			
Are there **10 or less** samples per CCV/CCB? (**20** for titrametric analyses)			
Is the correct prep **Date and Time** entered into the LIMS Prep Batch?			
Are the **Sample Volumes** correctly entered into the LIMS Prep Batch?			
Are rhe LCS/MS/MSD **Spike Volumes** correctly entered into the LIMS Prep Batch?			
Are sample within the established **Hold Times**?			
Received by: (Initial & Date)-->			

Data Review Checklist for Manual LIMS Entry:

	Y(es)N(o)NA	Y(es)N(o)NA	Comments
Are all **Sample Values** correctly entered?			
Are all samples correctly **Flagged**? (U,J,N,B,Z,*)			
Are all **%R, RPD,** and **Spike Volumes** entered?			
Are all **Dilution Factors** entered?			
Are all **reporting limits** correct?			
Received by: (Initial & Date)-->			

Additional Comments:

i:oprtns\wtchm\forms\checklists\datarevchecklist.xls

Instrument Filename:

	Order Number	Client	LIMS Protocol	Run QC TestGrpName	Anal.RunID	QCA
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						

I:\oprtns\metals\limsdata\limstrak.xls

8011 Analytical Review Checklist
Paragon Analytics

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

First Reviewer/Date:_____ Second Reviewer/Date:_____

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
Extraction holding time criteria met? (14 days from collection liquids)						
Analytical holding time criteria met? (24 hours from extraction)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
All CCAL criteria met?						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____ HP_____						
Water / Soil / Other_____ HP_____						
Water / Soil / Other_____ HP_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____ HP _____						
Water / Soil /Other_____ HP _____						
Water / Soil /Other_____ HP _____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						
Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						

8011 Analytical Review Checklist
Paragon Analytics

Target Analytes reported within Calibration Range?				☐	☐	☐	☐	☐	☐
Manual Integrations documented before and after?				☐	☐	☐	☐	☐	☐
				☐	☐	☐	☐	☐	☐
Analytical Review				Y	N	NA	Y	N	NA
Were sample dilutions made?				☐	☐	☐	☐	☐	☐
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Any samples to be re-analyzed in another batch?				☐	☐	☐	☐	☐	☐
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____________
Analyte:___________________

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____________
Analyte:___________________

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GC/HPLC ICAL Data Review Checklist (Internal Standard)

Method:_____ Instrument ID:_____ Date analyzed:_____

first reviewer/date:_____ second reviewer/date:_____

	First Review			Second Review			
Initial Calibration Review QC Criteria	Y	N	NA	Y	N	NA	COMMENTS
Minimum of five point calibration analyzed?							
Are compounds properly identified and integrated?							
Manual integrations documented before and after?							
Internal standard recoveries within 50-200% criteria?							
Are average response factors used for quantitation?							
Are all the % RSDs <20%?							
Is the mean % RSD <20%?							
Are linear curve fits used for quantitation?							
Are all the corr. coef. >= 0.995 (R^2 = 0.990)							
Are quadratic curve fits used for quantitation?							
Minimum of six point calibration analyzed?							
Are all the CODs >= 0.990?							
Second source analytes (ICV) +/- 15% difference?							
One data point recalculated successfully?							
Additional comments:							

Recalculation Verification:

Verify a calibration factor in the ICAL using the equation below.

Response factor = $(A_s \times C_{is})/(A_{is} \times C_s)$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_s = Concentration of the analyte.
C_{is} = Concentration of the internal standard.

Verify the instrument concentration of a second source (ICV) compound using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Average response factor calibration:

$C_s = (A_s \times C_{is})/(A_{is} \times RF)$

RF = Average response factor from the ICAL
A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_{is} = Concentration of the internal standard.

Lab Sample ID:_____

Analyte:_____

Linear calibration:

$y = mx + b$ or $A_s/A_{is} = m(C_s/C_{is}) + b$ or $C_s = [(A_s / A_{is}) - b]C_{is}/m$

C_s = Concentration of the analyte.
m = The slope of the linear equation.
b = The intercept of the linear equation.

Lab Sample ID:_____

Analyte:_____

GC/HPLC ICAL Data Review Checklist (External Standard)

Method:_____ Instrument ID:_____ Date Analyzed:_____

1st Reviewer/Date:_____ 2nd Reviewer/Date:_____

	1st Review			2nd Review			
External Standard QC Criteria	Y	N	NA	Y	N	NA	COMMENTS
Instrument breakdown criteria met?							
Minimum of five point calibration analyzed?							
Standard preparation documented?							
Are compounds properly identified and integrated?							
Manual integrations documented before and after?							
Are average response factors used for quantification?							
Are all the %RSD ≤20%?							
Is the mean %RSD ≤20%?							
Are linear curve fits used for quantification?							
Is each $r^2 \geq 0.990$?							
Are quadratic curve fits used for quantification?							
Minimum of six point calibration analyzed?							
Is each COD ≥ 0.990?							
2nd source documented properly?							
different control # than 1st source?							
Is 2nd source concentration different than CCV conc.?							
Second source analytes (ICV) +/- 15% difference?							
One CF recalculated successfully?							
One compound in the ICV recalculated successfully?							
Additional comments:							

Recalculation Verifications:

1. Verify a calibration factor in the ICAL using the equation below.

   Calibration factor (CF) = peak area/standard concentration

2. Verify the instrument concentration of a second source (ICV) compound using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

2a. Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

2b. Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

Paragon Analytics — 8015Bmod GRO analytical review checklist

work order(s):_____ analytical batch ID:_____

instrument ID:_____ date analyzed:_____

prep batches included: HCG_____
HCG_____
HCG_____

first reviewer/date:_____ second reviewer/date:_____

	first review Y	first review N	first review NA	second review Y	second review N	second review NA
pH of aqueous samples ≤ 2?						
list exceptions here						
any preserved liquids? Y N analytical holding time met? (14 days from collection)						
list exceptions here						
any unpreserved liquids? Y N analytical holding time met? (7 days from collection)						
list exceptions here						
any solids? Y N analytical holding time met? (14 days from collection)						
list exceptions here						
any problems / observations during prep?						
If yes, refer to logbook						
all ICAL criteria met? refer to ICAL review sheet & list any compounds out of control below						
all CCAL criteria met? list any out of control target or surrogate compounds below						
ccv file GRO - ↑ ↓ surrogate - ↑ ↓ *circle appropriate arrow if* **N** *above*						
ccv file GRO - ↑ ↓ surrogate - ↑ ↓ *circle appropriate arrow if* **N** *above*						
ccv file GRO - ↑ ↓ surrogate - ↑ ↓ *circle appropriate arrow if* **N** *above*						
ccv file GRO - ↑ ↓ surrogate - ↑ ↓ *circle appropriate arrow if* **N** *above*						
all method blanks meet criteria? all target analytes below MDL (report limit)?						
water / soil / other_____ HCG ***circle one*** <MDL <RL >RL						
water / soil / other_____ HCG ***circle one*** <MDL <RL >RL						
water / soil / other_____ HCG ***circle one*** <MDL <RL >RL						
all LSC/LCSD's meet criteria? (all recoveries and RPDs in control?)						
water / soil / other_____ HCG _____						
water / soil / other_____ HCG _____						
water / soil / other_____ HCG _____						
all MS/MSD criteria met? (all recoveries and RPDs in control?)						
sample? MS /MSD **client specified?** Y N (circle one) **in control?**						
failed compounds okay in LCS/LCSD?						
failed compounds detected in samples?						
sample ? MS/MSD **client specified?** Y N (circle one) **in control?**						
failed compounds okay in LCS/LCSD?						
failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample **circle one if no MS/MSD**						

Paragon Analytics — 8015Bmod GRO analytical review checklist

	Y	N	NA	Y	N	NA
surrogate recoveries in control for samples reported?						
If **N** list samples with surrogate outside of control limits and confirmation files or other reasons to report						
target analytes reported within calibration range? if no list which samples need E						
manual Integrations documented before and after?						
if no return to analyst or document						
were sample dilutions made? **if Y list dilutions and reasons why**						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
sample dilution factor matrix / targets comments						
if CH_3OH extractions were done are the weights and volumes documented in run log?						
any samples to be re-analyzed in another batch? **if Y list samples and reasons why**						
sample confirm / dilute / other...						
sample confirm / dilute / other...						
sample confirm / dilute / other...						
sample confirm / dilute / other...						
sample confirm / dilute / other...						
sample confirm / dilute / other...						

If shaded box(es) have been checked above, then corrective actions are needed.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

DRO 8015B Modified Analytical Review Checklist
Paragon Analytics

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

First Reviewer/Date:_____Second Reviewer/Date:_____

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
Extraction holding time criteria met? (7 days from collection liquids and 14 days solids)						
Analytical holding time criteria met? (40 days from extraction, liquids and solids)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
All CCAL criteria met?						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____EX_____						
Water / Soil / Other_____EX_____						
Water / Soil / Other_____EX_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____EX_____						
Water / Soil /Other_____EX_____						
Water / Soil /Other_____EX_____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						
Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						
Surrogate Recoveries in control?						

DRO 8015B Modified Analytical Review Checklist
Paragon Analytics

Target Analytes reported within Calibration Range?						
Manual Integrations documented before and after?						
Analytical Review	Y	N	N A	Y	N	NA
Were sample dilutions made?						

Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments

Any samples to be re-analyzed in another batch?						

Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

Paragon Analytics 8021B Analytical Review Checklist

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

First Reviewer/Date:_____ Second Reviewer/Date:_____

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
pH of aqueous samples ≤ 2?						
Water analytical holding time criteria met? (14 days from collection or 7 if pH >2)						
Soil/Solid analytical holding time criteria met? (14 days from collection)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
All CCAL criteria met?						
Internal standard in control? (50-200% of midpoint standard or first daily CCV)						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____ HCB_____						
Water / Soil / Other_____ HCB_____						
Water / Soil / Other_____ HCB_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____ HCB _____						
Water / Soil /Other_____ HCB _____						
Water / Soil /Other_____ HCB _____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						
Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						

Paragon Analytics 8021B Analytical Review Checklist

	First Review			Second Review		
	Y	N	NA	Y	N	NA
Surrogate Recoveries in control?						
Target Analytes reported within Calibration Range?						
Manual Integrations documented before and after?						

Analytical Review	Y	N	NA	Y	N	NA
Were sample dilutions made?						

Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments

Any samples to be re-analyzed in another batch?						

Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Average response factor calibration:

$C_s = (A_s \times C_{is}) / (A_{is} \times \overline{RF})$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_{is} = Concentration of the internal standard.

Lab Sample ID:_____
Analyte:_____

Linear calibration:

$y = mx + b$ or $A_s/A_{is} = m(C_s/C_{is}) + b$ or $C_s = [(A_s / A_{is}) - b]C_{is}/m$

$\overline{RF}$ = Average response factor from the ICAL.
C_s = Concentration of the analyte.
m = The slope of the linear equation.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

8081 Analytical Review Checklist
Paragon Analytics

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

First Reviewer/Date:_____ Second Reviewer/Date:_____*

*Please do not re-evaluate data without having a second review on your changes. Also, Please initial and date your changes so that it does not appear to be the work of the analyst.

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
Extraction holding time criteria met? (7 days from collection liquids and 14 days solids)						
Analytical holding time criteria met? (40 days from extraction, liquids and solids)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
Performance Evaluation Mixture (PEM) degradation criteria met?						
All CCAL criteria met?						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____ EX_____						
Water / Soil /Other_____ EX_____						
Water / Soil /Other_____ EX_____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						

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8081 Analytical Review Checklist
Paragon Analytics

Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						
Surrogate Recoveries in control?						
TCMX (high)						
TCMX (low)						
DCB (high)						
DCB (low)						
Target Analytes reported within Calibration Range?						
Manual Integrations documented before and after?						
Analytical Review	Y	N	NA	Y	N	NA
Were sample dilutions made?						
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Any samples to be re-analyzed in another batch?						
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

8082 Analytical Review Checklist
Paragon Analytics

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

First Reviewer/Date:_____Second Reviewer/Date:_____

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
Extraction holding time criteria met? (7 days from collection liquids and 14 days solids)						
Analytical holding time criteria met? (40 days from extraction, liquids and solids)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
All CCAL criteria met?						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____ EX_____						
Water / Soil /Other_____ EX_____						
Water / Soil /Other_____ EX_____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						
Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						

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8082 Analytical Review Checklist
Paragon Analytics

Surrogate Recoveries in control?						
TCMX (high)						
TCMX (low)						
DCB (high)						
DCB (low)						
Target Analytes reported within Calibration Range?						
Manual Integrations documented before and after?						

Analytical Review				Y	N	NA	Y	N	NA
Were sample dilutions made?									
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Sample	Dilution factor	Matrix / Targets	Comments						
Any samples to be re-analyzed in another batch?									
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								
Sample	Confirm / Dilute / Other...								

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

8141 Analytical Review Checklist
Paragon Analytics

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

First Reviewer/Date:_____Second Reviewer/Date:_____

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
Extraction holding time criteria met? (7 days from collection liquids and 14 days solids)						
Analytical holding time criteria met? (40 days from extraction, liquids and solids)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
All CCAL criteria met?						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____ EX _____						
Water / Soil /Other_____ EX _____						
Water / Soil /Other_____ EX _____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						
Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						
Surrogate Recoveries in control?						

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8141 Analytical Review Checklist
Paragon Analytics

Target Analytes reported within Calibration Range?						
Manual Integrations documented before and after?						
Analytical Review	Y	N	NA	Y	N	NA
Were sample dilutions made?						
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Sample	Dilution factor	Matrix / Targets	Comments			
Any samples to be re-analyzed in another batch?						
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					
Sample	Confirm / Dilute / Other...					

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

8151 Analytical Review Checklist
Paragon Analytics

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

First Reviewer/Date:_____ Second Reviewer/Date:_____

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
Extraction holding time criteria met? (7 days from collection liquids and 14 days solids)						
Analytical holding time criteria met? (40 days from extraction, liquids and solids)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
All CCAL criteria met?						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
Water / Soil / Other_____ EX_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____ EX _____						
Water / Soil /Other_____ EX _____						
Water / Soil /Other_____ EX _____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						
Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						
Surrogate Recoveries in control?						
DCAA (high)						

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8151 Analytical Review Checklist
Paragon Analytics

DCAA (low)								
Target Analytes reported within Calibration Range?								
Manual Integrations documented before and after?								
Analytical Review					Y	N	NA	Y	N	NA
Were sample dilutions made?										
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Sample	Dilution factor	Matrix / Targets	Comments							
Any samples to be re-analyzed in another batch?										
Sample	Confirm / Dilute / Other...									
Sample	Confirm / Dilute / Other...									
Sample	Confirm / Dilute / Other...									
Sample	Confirm / Dilute / Other...									
Sample	Confirm / Dilute / Other...									
Sample	Confirm / Dilute / Other...									

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

GC/MS 8260B Analytical Review Checklist (Volatiles)

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Soils / Waters / Both 5mL / 10mL / 25mL

First Reviewer/Date:_____ Second Reviewer/Date:_____ MDL:_____

Paragon Analytics Inc.

	First Review			Second Review		
Prep Batch Review	Y	N	NA	Y	N	NA
Method blank, LCS, LCSD, MS and MSD associated with batch? (please circle)						
Is batch ≤ 20 samples? (≤ 18 samples + MS/MSD for AFCEE)						
Are MS/MSD client specific?						
Aqueous samples head space free? / pH of aqueous samples ≤ 2?						
Holding time criteria met? (14 days preserved aqueous and solids, 7 days non-preserved aqueous)						
All samples and standards injected within 12hr tune?						
Any problems/observations during prep?						
All samples and QC spiked correctly?						
Is there any sample remaining? (In case reanalysis is required)						
List anomalies with the condtion of sample vials/EnCores:						
False positives deleted prior to pulling TIC's?						
List work orders that require TIC's						
Analytical Review	Y	N	NA	Y	N	NA
All ICAL criteria met?						
All ICV criteria met?						
All CCAL criteria met?						
All Method Blank criteria met?						
All target analytes below MDL?						
Acetone Above/Below RL In Samples:						
Methylene chloride Above/Below RL In Samples:						
Other: Above/Below RL In Samples:						
Above/Below RL In Samples:						
All LCS/LCSD criteria met?						
Water (LCS / LCSD) All recoveries and RPDs in control						
Samples non-detect for failed compounds?						
Soil (LCS / LCSD) All recoveries and RPDs in control						
Samples non-detect for failed compounds?						
All MS/MSD criteria met?						
MS/MSD not analyzed due to insufficient sample / not requested						
All recoveries and RPDs in control?						
Failed compounds okay in LCS/LCSD?						
Samples non-detect for failed compounds?						

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GC/MS 8260B Analytical Review Checklist (Volatiles)

Analytical Review			Y	N	NA	Y	N	NA
Internal standard in control? (50-200% of midpoint standard or continuing calibration)								
IS1 H / L	Confirmed? Y / N Files:							
IS2 H / L	Confirmed? Y / N Files:							
IS3 H / L	Confirmed? Y / N Files:							
IS4 H / L	Confirmed? Y / N Files:							
Surrogate Recoveries in control?								
SS1 H / L	Confirmed? Y / N Files:							
SS2 H / L	Confirmed? Y / N Files:							
SS3 H / L	Confirmed? Y / N Files:							
SS4 H / L	Confirmed? Y / N Files:							
Were samples with targets outside calib. range diluted so the targets were within calib. range?								
Manual Integrations documented before and after?								
Were sample dilutions made?								
Sample	Dilution factor	Matrix / Targets / NTC / TIC Comments						
Sample	Dilution factor	Matrix / Targets / NTC / TIC Comments						
Sample	Dilution factor	Matrix / Targets / NTC / TIC Comments						
Sample	Dilution factor	Matrix / Targets / NTC / TIC Comments						
Sample	Dilution factor	Matrix / Targets / NTC / TIC Comments						
Sample	Dilution factor	Matrix / Targets / NTC / TIC Comments						
Any samples to be re-analyzed in another batch?								
Sample	Confirm / Dilute / Other...							
Sample	Confirm / Dilute / Other...							
Sample	Confirm / Dilute / Other...							
Sample	Confirm / Dilute / Other...							
Sample	Confirm / Dilute / Other...							
Sample	Confirm / Dilute / Other...							

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the concentration of a reported analyte using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Average response factor calibration:

$C_s = (A_s \times C_{is}) / (A_{is} \times \overline{RF})$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_{is} = Concentration of the internal standard.

Lab Sample ID:_____
Analyte:_____

Linear calibration:

$y = mx + b$ or $A_s / A_{is} = m(C_s / C_{is}) + b$ or $C_s = [(A_s / A_{is}) - b]C_{is}/m$

$\overline{RF}$ = Average response factor from the ICAL.
C_s = Concentration of the analyte.
m = The slope of the linear equation.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

GCMS ICAL/CCAL Data Review Checklist (Volatiles)

Method:_____ 5mL/10mL heated/unheated Instrument ID:_____
Analytical Batch ID:_____ Date Analyzed:_____
First Reviewer/Date:_____ Second Reviewer/Date:_____
Paragon Analytics Inc.

	First Review			Second Review			
Review QC Criteria	Y	N	NA	Y	N	NA	COMMENTS
Initial Calibration							
Tune ion ratio,criteria met?							
Minimum of five point calibration analyzed?							
Is there a standard at or below the RL for all compounds?							Check Program Spec's !
SPCC criteria met? (Ave. RF > 0.1 and 0.3)							
CCC criteria met? (RSD < 30%)							
Are average response factors used for quantitation?							
Are the RSD's <= 15% ?							
Are linear curve fits used for quantitation?							
Are all the corr. coef. >= 0.995 (R^2 = 0.990)							
Are quadratic curve fits used for quantitation?							
Minimum of six point calibration analyzed?							
Are all the CODs >= 0.990?							
Are isomers properly identified and integrated?							
Manual integrations documented before and after?							
Internal standard recoveries within 50-200% criteria?							
Initial Calibration Verification meet criteria? (+or- 25%)							Only 3 may exceed (up to 50%)
Are all target conc.'s verified in the acquisition method?							

What is the calibration range of the ICAL?	Internal Standard Response for mid-point std:
Exceptions to this range? **See Form 6**	IS1
(ketones 4x)	IS2
(m&p xylenes 2x)	IS3
(acrolein & acrylonitrile 10x)	
Additional comments:	

Date Analyzed:_____ Analytical Batch ID:_____
First Reviewer/Date:_____ Second Reviewer/Date:_____
Paragon Analytics Inc.

	First Review			Second Review			
Review QC Criteria	Y	N	NA	Y	N	NA	COMMENTS
Continuing Calibration							
Tune ion ratio criteria met?							
SPCC criteria met? (Ave. RF > 0.1 and 0.3)							
CCC criteria met? (D < 20%)							
Are additional client specified % D criteria met?							Check Program Specs!
Do Ave. RF values on the form 7 match values on form 6?							
Are isomers properly identified and integrated?							
Manual integrations documented before and after?							
Internal standard recoveries within 50-200% of ICAL?							

Additional comments:	Internal Standard Response for CCAL:
	IS1
	IS2
	IS3

GCMS ICAL/CCAL Data Review Checklist (Volatiles)

Recalculation Verification:

1.) Verify a calibration factor in the ICAL using the equation below.

Response factor $= (A_s \times C_{is})/(A_{is} \times C_s)$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_s = Concentration of the analyte.
C_{is} = Concentration of the internal standard.

Standard ID:_____
Analyte:_____

Standard ID:_____
Analyte:_____

2.) Verify the instrument concentration of a second source (ICV) compound using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Average response factor calibration:

$C_s = (A_s \times C_{is})/(A_{is} \times \overline{RF})$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_{is} = Concentration of the internal standard.

Lab Sample ID:_____
Analyte:_____

Linear calibration:

$y = mx + b$ or $A_s/A_{is} = m(C_s/C_{is}) + b$ or $C_s = [(A_s/A_{is}) - b]C_{is}/m$

$\overline{RF}$ = Average response factor from the ICAL.
C_s = Concentration of the analyte.
m = The slope of the linear equation.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Quadratic calibration: (Back calculate the peak area using the target concentration)

$y = ax^2 + bx + c$ or $A_s/A_{is} = a(C_s/C_{is})^2 + b(C_s/C_{is}) + c$ or $A_s = [a(C_s/C_{is})^2 + b(C_s/C_{is}) + c]*A_{is}$

a = quadratic term
b = linear term
c = constant term

Lab Sample ID:_____
Analyte:_____

GCMS ICAL/CCAL Data Review Checklist (Semi-Volatiles)

Method:_____Instrument ID:_____Date Analyzed:_____
Analytical Batch ID:_____
First Reviewer/Date:_____ Second Reviewer/Date:_____
Paragon Analytics Inc.

	First Review			Second Review			
Review QC Criteria	Y	N	NA	Y	N	NA	COMMENTS
Initial Calibration							
Tune ion ratio, tailing and degradation criteria met?							
Minimum of five point calibration analyzed?							
Is there a standard at or below the RL for all compounds?							
SPCC criteria met? (Ave. RF > 0.05)							
CCC criteria met? (RSD < 30%)							
Are average response factors used for quantition?							
Are all ARF RSD <15%?							
Are additional client specified % RSD criteria met?							
Are linear curve fits used for quantitaion?							
Are all the corr. coef. = 0.995 (R^2 = 0.990)							
Are quadratic curve fits used for quantitaion?							
Minimum of six point calibration analyzed?							
Are all the CODs = 0.990?							
Are isomers properly identified and integrated?							
Manual integrations documented before and after?							
Internal standard recoveries within 50-200% criteria?							
Initial Cal Verification within 25% for all compounds							Avg=

What is the calibration range of the ICAL?	ICAL files which required manual quant.	Internal Standard Response for mid-point std: SVSTD060:	ICAL R.T.
Exceptions to this range?		IS1	
		IS2	
		IS3	
		IS4	
		IS5	
		IS6	
Additional comments:			

Date Analyzed:_____ Analytical Batch ID:_____
First Reviewer/Date:_____ Second Reviewer/Date:_____
Paragon Analytics Inc.

	First Review			Second Review			
Review QC Criteria	Y	N	NA	Y	N	NA	COMMENTS
Continuing Calibration Verification							
Tune ion ratio, tailing and degradation criteria met?							
SPCC criteria met? (Ave. RF > 0.05)							
CCC criteria met? (D < 20%)							
Are there no more than 4 target compounds > 20%							
Are additional client specified % D criteria met?							
Do Ave. RF values on the form 7 match values on form 6?							
Are isomers properly identified and integrated?							
Manual integrations documented before and after?							File name:
Internal standard recoveries within 50-200% of ICAL?							

Additional comments:	Internal Standard Response for CCAL:	R.T.
	IS1	
	IS2	
	IS3	
	IS4	
	IS5	
	IS6	

GCMS ICAL/CCAL Data Review Checklist (Semi-Volatiles)

Recalculation Verification:

1.) Verify a calibration factor in the ICAL using the equation below.

Response factor $= (A_s \times C_{is})/(A_{is} \times C_s)$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_s = Concentration of the analyte.
C_{is} = Concentration of the internal standard.

Standard ID:_____ Standard ID:_____
Analyte:_____ Analyte:_____

2.) Verify the instrument concentration of a second source (ICV) compound using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Average response factor calibration:

$C_s = (A_s \times C_{is})/(A_{is} \times \overline{RF})$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_{is} = Concentration of the internal standard.

Lab Sample ID:_____
Analyte:_____

Linear calibration:

$y = mx + b$ or $A_s/A_{is} = m(C_s/C_{is}) + b$ or $C_s = [(A_s/A_{is}) - b]C_{is}/m$

$\overline{RF}$ = Average response factor from the ICAL.
C_s = Concentration of the analyte.
m = The slope of the linear equation.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Quadratic calibration: (Back calculate the peak area using the target concentration)

$y = ax^2 + bx + c$ or $A_s/A_{is} = a(C_s/C_{is})^2 + b(C_s/C_{is}) + c$ or $A_s = [a(C_s/C_{is})^2 + b(C_s/C_{is}) + c]*A_{is}$

a = quadratic term
b = linear term
c = constant term

Lab Sample ID:_____ Lab Sample ID:_____
Analyte:_____ Analyte:_____

GC/MS SV Analytical Batch Review Checklist

Analytical Batch ID:_____ Work orders:_____
Required Protocols:_____ Extraction Batches:_____
First Reviewer/Date:_____ Second Reviewer/Date:_____

Paragon Analytics Inc.

Analytical Review	First Review Y	First Review N	First Review NA	Second Review Y	Second Review N	Second Review NA
All ICAL criteria met? (See ICAL checklist)						
All ICV criteria met? (See ICAL checklist)						
All CCAL criteria met? (See ICAL checklist)						
All Client Specific Calibration Criteria Met? (All 8270C cal criteria must be met for sample analysis- Please note if additional criteria such as Lowered reporting limits have been considered)						
List projects which require TIC's?						
False Positives Deleted Prior to Pulling TIC's						
Analytical Holding time criteria met? (40 days from extraction, liquids and solids)						
Are All Injections within 12 hour Tune Time?						
Clean Instrument Blank?						
Internal Standard Recoveries within 50-200% criteria?						
Confirmed matrix? Y / N						
Confirmation file names to be included in raw data:						
Surrogate Recoveries within control limits?						
Confirmed matrix? Y / N (Low surrogate recoveries may indicate a loss of extract prior to analysis. Oftentimes, matrix can **only** be confirmed by RX. In isolated cases RA may confirm matrix.)						
Surrogates diluted below reporting limits:						
Confirmation file names to be included in raw data:						
All Method Blanks meet criteria? (All target analytes and TIC's below MDL?)						
Water / Soil / Other_____ EX_____						
Water / Soil / Other EX_____						
Water / Soil / Other_____ EX_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____ EX_____						
Water / Soil /Other_____ EX_____						
Water / Soil /Other_____ EX_____						

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GC/MS SV Analytical Batch Review Checklist

Analytical Review	Y	N		Y	N	
All MS/MSD criteria met? (All recoveries and RPDs in control?)	☐	☐		☐	☐	
MS/MSD MS/MSD						
Failed compounds okay in LCS/LCSD?	☐	☐		☐	☐	
Failed compounds detected in samples?	☐	☐		☐	☐	
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample	☐	☐		☐	☐	
Were reporting limits raised?	☐	☐		☐	☐	
Sample Df Dil. for Matrix / TC's / NTC's / TIC's Vi Vf						
Sample Df Dil. for Matrix / TC's / NTC's / TIC's Vi Vf						
Sample Df Dil. for Matrix / TC's / NTC's / TIC's Vi Vf						
Sample Df Dil. for Matrix / TC's / NTC's / TIC's Vi Vf						
Sample Df Dil. for Matrix / TC's / NTC's / TIC's Vi Vf						
Sample Df Dil. for Matrix / TC's / NTC's / TIC's Vi Vf						
Sample Df Dil. for Matrix / TC's / NTC's / TIC's Vi Vf						
Target Analytes Reported within Calibration Range?	☐	☐		☐	☐	
Manual Integrations are documented before and after?	☐	☐		☐	☐	
Are the LIMS run no.s correct?	☐	☐		☐	☐	
Recalculation Verification Performed?	☐	☐		☐	☐	
Please list samples not to be reported and a brief description why.						

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Average response factor calibration:

$C_s = (A_s \times C_{is})/(A_{is} \times RF)$

A_s = Peak area of the target analyte.
A_{is} = Peak area of the internal standard.
C_{is} = Concentration of the internal standard.
RF = Average response factor from the ICAL.

Lab Sample ID:_____________
Analyte:___________________

Linear calibration:

$A_s / A_{is} = m(C_s/C_{is}) + b$ **or** $C_s = [(A_s / A_{is}) - b]\, C_{is} / m$

C_s = Concentration of the analyte.
m = The slope of the linear equation.
b = The intercept of the linear equation.

Lab Sample ID:_____________
Analyte:___________________

Additional Comments:____

____

____

____

____

8330 Analytical Review Checklist
Paragon Analytics, Inc.

Work order(s):_____ Analytical Batch ID:_____

Instrument ID:_____ Date Analyzed:_____ Prep Batches Included:_____

Quant Column:_____

First Reviewer/Date:_____Second Reviewer/Date:_____

	First Review			Second Review		
Analytical Review	Y	N	NA	Y	N	NA
Extraction holding time criteria met? (7 days from collection liquids and 14 days solids)						
Analytical holding time criteria met? (40 days from extraction, liquids and solids)						
Any problems/observations during prep?						
If yes, refer to bench sheet						
All ICAL criteria met?						
All CCAL criteria met?						
All Method Blanks meet criteria? (All target analytes below MDL?)						
Water / Soil / Other_____EX_____						
Water / Soil / Other_____EX_____						
Water / Soil / Other_____EX_____						
All LSC/LCSD's meet criteria? (All recoveries and RPDs in control?)						
Water / Soil / Other_____EX_____						
Water / Soil /Other_____EX_____						
Water / Soil /Other_____EX_____						
All MS/MSD criteria met? (All recoveries and RPDs in control?)						
MS/MSD MS/MSD						
Are MS/MSD client specific?						
Failed compounds okay in LCS/LCSD?						
Failed compounds detected in samples?						
MS/MSD not analyzed due to insufficient sample / not requested / dilution of native sample						

8330 Analytical Review Checklist
Paragon Analytics, Inc.

Analytical Review	Y	N	NA	Y	N	NA
Surrogate Recoveries in control?						
Target Analytes reported within Calibration Range?						
Manual Integrations documented before and after?						

Analytical Review	Y	N	NA	Y	N	NA
Were sample dilutions made?						

Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments
Sample	Dilution factor	Matrix / Targets	Comments

Any samples to be re-analyzed in another batch?						

Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...
Sample	Confirm / Dilute / Other...

If a shaded box has been checked above, than corrective action must be taken.

Recalculation Verification:

Verify the instrument concentration using the curve fit equation from the initial calibration. Use the appropriate equation below depending upon the type of curve fit that was used.

Linear calibration:

$A = mC + b$ or $C = (A - b)/m$

A = The instrument response in area counts.
m = The slope of the linear equation.
C = The concentration present at the instrument.
b = The intercept of the linear equation.

Lab Sample ID:_____
Analyte:_____

Average response factor calibration:

$C = A/R_f$

C = The concentration present at the instrument.
A = The instrument response in area counts.
R_f = The average response factor from the initial calibration.

Lab Sample ID:_____
Analyte:_____

Total Organic Carbon Data Review Check Sheet

Analysis:

Method	Test Group	QCA	W.O #	CLIENT	RPT LEVEL	Rpt to MDL / RL	Matrix	Prep Batch ID	Anal. Batch ID	--REASONS FOR DILUTION-- CLN UP	R.DATA IN FILE	HIST DATA	PROTECT/ SCREEN	DIL INTO RANGE

Raw Data Review Checklist:

	1st Rev. Y(es) / N(o)	2nd Rev. Y(es) / N(o)	Comments
Calibrated on this date? (if no please specify calib ID)			
Is the **calibration curve** within the acceptance limits?			
Is the **MB** values below the RL?			
Is the **LCS** values within control?			
Is all **Matrix QC** within control?			
Are there **20 or less** samples per prep batch?			
Are there **15 or less** samples per CCV?			
Are sample within the established **hold times**?			
Did sample(s) require **filtration**			
Are samples **preserved** correctly?			

1st Review by:	Date:
2nd Review by:	Date:

Additional Comments:

i:Oprtns\Wtchm\Forms\Checklists\TOC

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 069 REVISION 8

TITLE: **MANAGING AND ARCHIVING CLIENT WORK ORDERS AND RECORDS, AND RETRIEVING ARCHIVED INFORMATION**

FORMS: **136**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9.8.06
QUALITY ASSURANCE MANAGER _____ DATE 9/8/06
LABORATORY MANAGER _____ DATE 9/8/06

HISTORY: Rev1, 1/17/93; Rev2, 4/9/96; Rev3, 7/15/99; Rev4, 1/26/00; Rev5, 8/15/02; Rev6, 5/4/04; Rev7, 11/10/05 (combined with SOP 332); Rev8, 9/11/06. re-released w/o revision 3/12/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) addresses the initiation, movement and archiving of client workorders. Management of raw data and other laboratory records, such as logbooks, is also discussed. Retrieval of archived information is addressed. All laboratory records must be retrievable and kept in a manner that prevents their loss or deterioration. Various controls are in place that limits access to laboratory records.

2. OVERVIEW

Workorder folders are initiated by Sample Receiving personnel, processed by Login personnel, reviewed and released by the appropriate Project Manager (PM), then routed to Reports Management, where they are retained until the completed data package reports are signed-in by the laboratories. Following review by the PM, the data package reports are paginated, as needed, scanned, sent to the client (as hardcopy and/or on CD), and invoiced. After approximately three months, the completed workorder folders (which have been imaged as the official record for retention) are transferred to a vendor for secure document destruction.

Where possible, laboratory raw data is captured electronically. Data package reports are compiled electronically (by direct import or by the compilation of images). Where laboratory benchsheets are not provided for by the Laboratory Information Management System (LIMS), logbook (SOP 303) information is scanned to create image files. Other records, such as PM logs, quality assurance (QA) records, etc., may also be imaged for retention. Once a hardcopy record has been imaged as the official record, and the image verified, the hardcopy originals may be destroyed confidentially (i.e., shredded).

Image archives are managed by the Information Systems (IS) Manager, and are backed-up per procedures described in SOP 1401.

Paragon's records are retained for a minimum of seven years. Clients will be notified, in

writing, before any final data reports are permanently destroyed.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Project Manager to assure that the client's data retention requirements are met by Paragon's archiving policies and procedures as described herein. As required by the client, the PM is also responsible for generating and reviewing the electronic data deliverable (EDD).

3.2 It is the responsibility of all staff who participate in records processes, to adhere to established standard operating procedures.

3.3 The QA Department is responsible for overseeing records generation, archiving, retrieval and retention procedures. The QA Department maintains the historical (pre-imaging) archive databases, and interfaces with the off-site storage and secure document destruction vendors.

4. PROCEDURES

4.1 WORKORDER INFORMATION

4.1.1 Workorder folders are initiated by Sample Receiving personnel as samples are received (SOP 202). The workorder folders are then forwarded to Login personnel, who enter the sample information into LIMS ~~(SOP 201)~~. 3/12/09 DAS

4.1.2 Following login, the workorder folder is given to the Project Manager for review. Corrections are made in LIMS as necessary, and, if not already done, the workorder is electronically dispatched/released. Sample Receiving personnel are contacted and directed to physically distribute the samples to the appropriate laboratories, if not already done.

4.1.3 The workorder folder is then routed to Reports Management, where the contents of the folder are scanned and posted to the network for laboratory reference. The workorder folder is then placed, sequentially, in designated hanging files.

4.1.4 As each laboratory's work is completed, reviewed (SOPs 052, 715) data package reports are "signed-in" to Reports Management. Reports Management staff track the receipt of each workorder component in LIMS. The workorder folder is retrieved from the hanging file and given to the Project Manager, along with the data package reports received.

4.1.5 The PM reviews the data package reports and interfaces with laboratory personnel as necessary, to resolve any discrepancies. The finalized reports are then given to Reports Management.

4.1.6 Reports Management personnel paginate the finalized data package reports, as needed, then scan them and post the images to the network.

Reports Management staff also generate data package cover letters and prepare the data package reports and/or CDs for shipment to the client.

4.1.7 After invoicing, the completed workorder folders are held in Reports Management in another designated file area for approximately three months, after which the files are purged (i.e., staged for the QA Department to obtain secure shredding).

4.2 EDD GENERATION AND RETENTION

4.2.1 Prior to project inception, the PM works with the IS Department to assure that the client's EDD requirements, if any, can be met.

4.2.2 After the laboratory analyses have been completed and the electronic data has been 'commit reviewed' in LIMS, the PM uses a specialized electronic application to generate the EDD. The compiled EDD is exported to a designated directory in LIMS.

4.2.3 The PM reviews/approves the EDD and electronically transmits the EDD to the client and/or works with Reports Management staff to copy and send the EDD on CD to the client. The network copy of the EDD is retained as an archived record.

4.3 IMAGED AND ELECTRONIC RECORDS

Archive images and electronic records are retained on Paragon's network for several months to provide easy 'read-only'access by laboratory personnel should questions arise. Images and designated electronic record directories are managed by the IS Manager and are backed-up daily and with the redundancy described in SOP 1401. If archived information is not readily available on the network, contact the IS and/or QA Manager for retrieval.

4.4 HISTORICAL HARDCOPY RECORDS

A database tracking system, managed by the QA Department, is used to manage Paragon records generated prior to current electronic imaging processes. These hardcopy records are maintained by an off-site vendor in a secure and environmentally-controlled atmosphere. Access to these records is limited. Should retrieval be required, a formal request to the QA Department (e-mail, Form 136) must be made.

5. REFERENCES

Current NELAC Standard.
Various client quality assurance guidance documents.

DOCUMENT REVISION HISTORY

9/11/06: Strengthened language regarding loss or deterioration of records, and limited access. Added DOCUMENT REVISION HISTORY. Attached Form.

Paragon Analytics

ARCHIVES REQUEST FORM

Date of Request _____

Requestor _____

Date Needed _____

WO Number(s) _____

Client Name(s) _____

Need Raw Data? _____ **If so, Analyses** _____

_____

Reference (Box) Number(s) _____

Comments _____

_____

Date Archive Request Fulfilled _____
(Was database properpy updated?) _____

Date Item(s) Returned to QA _____

Date Item(s) Returned to Archive _____
(Was database properpy updated?) _____

Form 136r4.doc (3/31/04)

Must Discard 30 Days from _____ (date printed)

See red font COC note, page 4. 4/1/09 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 103 REVISION 7

TITLE: QUALIFICATION AND USE OF SUBCONTRACT LABORATORIES

FORMS: 202 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ for DC DATE 8/13/07
QUALITY ASSURANCE MANAGER _____ DATE 8/12/07
LABORATORY MANAGER _____ DATE 8-13-07

HISTORY: NEW, 2/25/92; Rev1, 4/4/94; Rev2, 7/15/99; Rev3, 4/29/02; Rev4, 10/3/03; Rev5, 3/24/05; Rev6, 7/24/06; amended 9/13/06 (see DOCUMENT REVISION HISTORY); Rev7, 8/12/07.

1. SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to define the requirements for selecting and subcontracting another laboratory to perform analytical services for Paragon. Procedures for managing the subcontract laboratory relationship are defined, and procedures for shipping samples to the subcontract laboratory are discussed.

2. SUMMARY

Typically, the need to subcontract specific analyses is identified during bid response. Analyses may also need to be subcontracted in cases of emergency (e.g., Paragon instrument failure, unforeseen catastrophic event), etc. Based on applicable factors (e.g., type of analysis needed, sample matrix, required certifications, etc.), Paragon works with the client to identify suitable subcontract laboratories. The client selects the subcontract laboratory and Paragon's Project Manager (PM) makes the necessary arrangements with the other analytical facility. Paragon staff packages and ships the designated samples to the subcontract facility, observing chain-of-custody procedures and Department of Transportation (DOT) shipping requirements. Paragon's PM manages the subcontract facility relationship to ensure that all work is complete and satisfactory. Sample shipment paperwork and records of client communications pertaining to subcontracting are retained by the Paragon PM.

3. RESPONSIBILITIES

3.1 All staff involved with subcontract laboratory selection or packaging and shipping samples to a subcontracted facility are responsible for performing their task(s) in accordance with this SOP.

3.2 The Paragon PM is the point-of-contact with the client and is responsible for being aware of applicable client quality requirements and ensuring that these are requirements are met. Paragon Quality Assurance Department staff may be consulted as needed.

Paragon's PM is also the point-of-contact with the subcontracted laboratory. The PM is responsible for coordinating sample shipments with the subcontracted facility and with Paragon sample receiving and shipping staff. The PM is also responsible for coordinating, reviewing and reporting the subcontract data, for keeping the client informed should any issues arise, and for investigating and resolving those issues.

3.3 It is the responsibility of all personnel who work with samples involved with this process to note any anomalies or out-of-control events associated with sample handling. Corrective action must be taken and documented for any discrepancies noted.

4. PROCEDURE

4.1 IDENTIFYING THE NEED TO SUBCONTRACT ANALYSES

Paragon will request to subcontract analytical services when:

- Paragon is not able to perform the requested analyses.
- Instrument failure or excessive backlog prevents Paragon from performing the analyses in a timely manner.
- Any situation exists that would prevent the client's data quality objectives (DQOs) from being achieved.

4.2 DETERMINATION OF SUITABLE SUBCONTRACT LABORATORIES

4.2.1 Potential subcontract laboratories, including other DataChem facilities, will be identified using information obtained from professional journals, mass mailings, conferences, etc.

4.2.2 Laboratories may be initially pre-qualified by obtaining and reviewing relevant laboratory documentation, such as the laboratory's:

- Statement of Qualifications
- Quality Assurance Manual
- Certifications (e.g., State, Federal, radioactive materials license)
- recent Proficiency Test (PT) study results
- example hardcopy and/or electronic deliverables

4.2.3 A 'short list' of suitable subcontract facilities will be determined based on the specific client needs (e.g., type of analysis needed, sample matrix, required certifications, etc.). Further information (e.g., available capacity, cost, MDL information, etc.) pertinent to the client's requirements may be requested from the analytical laboratory and reviewed.

NOTE: In cases where Paragon was contracted to perform National Environmental Laboratory Accreditation Conference (NELAC) analyses, but must instead subcontract these analyses, the subcontract laboratory must also be NELAC-accredited for the analyses to be performed. Likewise, should Paragon need to subcontract DOD samples for analysis, DOD laboratory approval status is required for the subcontract laboratory for the analyses to be conducted. **Note also that the subcontract laboratory must receive project-specific approval from the DOD client before any samples are analyzed.**

4.3 FACILITY SELECTION / CLIENTAPPROVAL

Paragon's PM must receive permission from the client, in writing, prior to procuring and forwarding samples to the selected subcontract laboratory.

4.4 SUBCONTRACT LABORATORY AGREEMENT

At minimum, Paragon requires the terms of a subcontract agreement to include the following:

- Analytical method required
- Number and type of samples expected to be subcontracted
- Project-specific quality control requirements
- Deliverables required (hardcopy, electronic)
- Laboratory certification(s) required
- Price per analysis
- Turn around time required

Note that the client may request Paragon to conduct an on-site audit of the subcontracted facility.

4.5 CONTINUING QUALIFICATION

If the subcontract laboratory is routinely used to provide analytical services to Paragon, qualification will continue as long as the data provided is of known, documented, and appropriate quality.

4.6 PACKAGING AND SHIPPING SAMPLES

At the direction of the Paragon PM, Paragon staff packages and ships the designated samples to the subcontract facility. Chain-of-custody and Department of Transportation (DOT) shipping requirements must be observed.

4.6.1 A sample chain-of-custody (COC, Form 202) is prepared by the PM and given to the Sample Control Department. Note that some

subcontract laboratories provide their own forms to be used when submitting subcontracted work. In these instances, the subcontractor-supplied forms are used.

4.6.2 As appropriate to the matrices and analyses requested, the samples are held in a refrigeration unit (generally walk-in cooler RU #20) until the samples are packaged for shipment.

4.6.3 Sample Control staff gather the samples designated on the COC Form initiated by the PM, including any quality control samples, such as Trip Blanks. The samples are then packaged in an appropriate shipping container, including double-bagged ice or blue ice as required. Styrofoam peanuts and/or bubble wrap is used to cushion the samples, and fill-up the empty spaces inside the shipping container.

4.6.4 The COC is signed to release the samples to the commercial shipping carrier. The pink copy of the COC is retained by the laboratory and is forwarded to the PM for inclusion in the project's records. **(forward to Reports Management for inclusion in workorder image archive)** The white and yellow copies of the signed COC are placed inside the sample-shipping container.

For samples sent by commercial carrier, the sample-shipping container is sealed with strapping tape and chain-of-custody seals. Sample Control personnel release the prepared sample container to the commercial carrier.

NOTE: Where samples are hand-delivered to the subcontract laboratory, all pages of the COC are kept intact until the "Received By" signatures are obtained from the subcontract laboratory. The pink copy of the signed COC is returned to Paragon and forwarded to the PM for inclusion in the project's records.

4.7 MANAGEMENT OF SUBCONTRACT DATA

The Paragon PM is responsible for coordinating all subcontract data and ensuring that the deliverables received from the subcontracted facility are complete and correct. Should issues arise (e.g., quality of product, adherence to schedule, etc.), the PM shall ensure that the client is aware of these issues and shall keep the client apprised during the resolution process (if it is suspected that the subcontractor knowingly supplied deliverables of substandard quality, this also will be communicated to the client). Unless otherwise directed by the client, the Paragon PM will take the lead on corrective action investigation, assure that all issues are corrected completely, and that the final resolution satisfies all parties involved. The Paragon PM may issue a 'stop work' order or discontinue the use of services and/or payment until resolution can be successfully achieved.

The PM oversees the submission (reporting) of the subcontracted data to the client. Data that have been subcontracted must be clearly indicated as such in the client laboratory data package reports.

5. SAFETY AND HAZARDS

5.1 Some samples may be preserved with chemical preservatives. Appropriate cautions should be observed in the event of sample container breakage during processing.

5.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

6. REFERENCES

Current NELAC standard

Applicable client quality assurance documents

DOCUMENT REVISION HISTORY

7/24/06: Combined SOP 207 contents with SOP 103, added Form. Augmented RESPONSIBILITIES and PROCEDURE. Added DOCUMENT REVISION HISTORY.

9/13/06: Section 4.7 further augmented to strengthen investigation and correction, and to provide for discontinuance (suspension) until resolution achieved.

8/12/07: Laboratory DOD approval status and project-specific approval required when DOD samples need to be subcontracted, added to Section 4.2.3.

Paragon Analytics
A Division of DataChem Laboratories, Inc.

225 Commerce Drive Fort Collins, CO 80524
800-443-1511 or (970) 490-1511 (970) 490-1522 Fax

Accession Number (LAB ID) _____

Chain-of-Custody Date _____ Page ___ of ___

Originator: Retain pink copy!

Project Name/No.: _____ **Sampler(s):** _____ Turnaround (circle one): **Standard** or **Rush (Due** _____ **)** Dispose: **Date** _____ or **Return to Client**

Report To:
Phone:
Fax:
E-mail:
Company:
Address:

Circle method (right); provide additional information as needed (comments).

Sample ID	Date	Time *	Lab ID	Matrix	Preservative (indicate type... HCl, etc.)	No. of Containers	VOCs SW8260B	BTEX (only) SW8021B	SVOCs SW8270C	OC Pesticides SW8081A	PCBs SW8082	Herbicides SW8151A	Explosives SW8330	TCLP Organics SW1311 SW8260B 8270C 8081A 8151A	TCLP Metals SW1311 Hg SW6010B 7470	Total Metals by ICP Hg SW6010B 7470 7471 E200.7	Dissolved Metals by ICP Hg SW6010B 7470 E200.7	Total Metals by ICP/MS SW6020A E200.8	Dissolved Metals by ICP/MS SW6020A E200.8	Hexavalent Chromium SW7196A Alkaline Digest? Y / N	Inorganic Anions SW9056 E300.0 (specify in comments)	Solids: Total E160.3 TDS E160.1 TSS E160.2	pH SW9040B SW9045C	TPH SW8015B GRO DRO (circle one or both)	Gross Alpha / Beta SW9310 E900.0	Actinides by Paragon SOP Pu / U / Am / Th / Cm / ___	Tritium E906.0	Total Alpha-Emitting Radium SW9315 E903.0	Radium 226 E903.1	Radium 228 SW9320 E904.0	Strontium 90 (Total Radiosr) D5811-00	Gamma Isotopes E901.1	Radon 222 SM7510Rn			

* **Time Zone:** EST CST MST PST **Matrix Key:** O = oil, S = soil, NS = non-soil solid, W = water, L = liquid, E = extract, F = filter

Comments:

Form 202r6.xls (6/16/06)

Relinquished By: (1)	*Relinquished By:* (2)
Signature _____	Signature _____
Printed Name _____	Printed Name _____
Date _____ Time _____	Date _____ Time _____
Company _____	Company _____
Received By: (1)	*Received By:* (2)
Signature _____	Signature _____
Printed Name _____	Printed Name _____
Date _____ Time _____	Date _____ Time _____
Company _____	Company _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1100 REVISION 10

TITLE: **DETERMINATION OF TOTAL SUSPENDED SOLIDS (TSS or TOTAL NON-FILTERABLE RESIDUE) -- METHODS EPA 160.2 AND SM2540D**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/19/07
QUALITY ASSURANCE MANAGER _____ DATE 1/19/07
LABORATORY MANAGER _____ DATE 1-19-07

HISTORY: Rev0, PCN #224, 4/14/94; Rev1, PCN #490, 6/5/95; Rev2, 9/28/99; Rev3, 10/8/01; Rev4, 1/23/02; Rev5, 2/10/03; Rev6, 3/6/03; Rev7, 2/9/04 and 2/11/05 (re-released without revision), Rev8, 7/26/05; Rev9, 4/10/06; Rev10, 1/19/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- EPA Method 160.2 and Standard Method (SM) 2540D -- describe procedures for measuring Total Suspended Solids (TSS or Total Non-Filterable Residue), in drinking, surface, and saline waters and domestic and industrial wastes.

2. SUMMARY

An aliquot of well-mixed water sample is filtered through a tared pre-washed glass fiber filter under vacuum pressure. The residue retained by the fiber filter is dried to a constant weight in a drying oven maintained at 103-105°C. The weight of the dried residue (in mg) represents the TSS present in the sample aliquot.

NOTE: **The sample filtrate (i.e., the fluid that passes through the filter) may be used to determine Total Dissolved Solids (TDS) per SOP 1101.**

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or by the successful analysis of a proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard

criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for completeness, precision and accuracy is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 **It is very important that the samples be thoroughly mixed before each aliquot is withdrawn.** If a sample is allowed to stand, most of the sediment will usually begin to settle to the bottom of the container. Failure to obtain representative subsamples can bias results and cause variation between duplicate samples.

4.2 TSS results for samples high in dissolved solids, such as saline waters and brines, may be subject to high bias. Care must be taken to adequately wash the filter with deionized water to remove dissolved salts after the sample has passed through the filter.

4.3 **Too much residue will entrap water that will not be driven off during drying. A sample aliquot size that yields no more than 200mg residue must be used.**

4.4 **It is important to use the filtration material and apparatus and pre-washing and post-washing techniques and drying temperature as specified in this SOP because variations from these specifications are known to affect results.**

4.5 For TSS analysis, exclude large, floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

5. APPARATUS AND MATERIALS

5.1 Glass fiber filter, 47mm, Gelman™ A/E or Whatman™ grade 934AH or equivalent

5.2 Filter funnel assembly (funnel, glass-fritted filter base, funnel clamp, vacuum source, 1L vacuum flask)

5.3 Analytical balance, 0.0001g sensitivity

5.4 Personal computer (PC), connected to the in-house network and with BalanceLink™ software installed

5.5 BalanceLink™ hardware to connect the analytical balance to the computer

5.6 Graduated cylinders, 10-500mL

NOTE: Use only labware whose graduated volume has been previously verified to deliver within ±3% of the stated volume.

5.7 Weighing pans (sample boats), aluminum, disposable, 2in diameter

5.8 Forceps

5.9 Drying oven, set to maintain 103-105°C

5.10 Desiccator with color indicating desiccant

5.11 Wash bottle

6. REAGENTS

6.1 Deionized (DI) Water, obtained from the laboratory's deionized water system

6.2 Pottery clay, dried and ground to pass through a 120-mesh sieve. *Shelf Life = 5 years or until contamination is evident.*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples may be collected in either plastic or glass containers and should be collected according to an approved sampling plan.

7.2 Water samples must be kept cool (4-6°C) and should be analyzed as quickly as possible. Per Table 1 of Methods for the Chemical Analysis of Water and Wastes, 1983, a maximum holding time allowance of 7 days from date of collection is permitted.

8. PROCEDURE

8.1 FILTER PREPARATION

8.1.1 Label an aluminum weighing pan (sample boat) for each sample. Place a glass fiber filter into each sample boat. With each batch of twenty field samples or less processed as a unit, the following quality control (QC) samples must be prepared: one Method Bank (MB), one Laboratory Control Sample (LCS), one sample Duplicate (DUP).

8.1.2 Pre-wash filters by placing on filter assembly and passing 100mL of DI water through filter. Transfer filter to original weighing pan and place in oven at 103-105°C for approximately 1 hour. Place in desiccators and allow to cool for approximately 1 hour.

8.1.3 When available, it is most convenient and accurate to use the BalanceLink program that allows data from an analytical balance to be electronically entered into a spreadsheet datafile. To use this system, first open the appropriate template spreadsheet in Excel (e.g., i:\oprtns\wtchm\tss\template\tss1.xls); then open the BalanceLink™ program to create linkage between the computer and the analytical balance.

8.1.4 Redirect the electronic file to the year's directory, and rename the spreadsheet with a filename that uses a mmdd format. For example, if the preparation batch was performed on 2/14/04, the new filename would be i:\oprtns\wtchm\tss\ 2004\0214tss.xls. Enter pertinent information into the spreadsheet (e.g., date, analyst, sample IDs, sample volumes).

8.1.5 Using the computer's mouse, position the cursor on the "**Filter + Boat**" cell for the individual sample listed on the spreadsheet. For each sample, place the proper sample boat containing the fiber filter on the weighing pan of the analytical balance and close the door. Press the "**Print Scrn**" key on the PC keyboard. The weight in grams that appears on the computer screen, will be automatically entered into the spreadsheet.

NOTE: The analytical balance's calibration must be verified daily before use, per SOP 305.

A filter + boat weight must be obtained for each field and QC sample. Print out a copy of the spreadsheet to keep as a temporary hardcopy until the analyses are complete (this ensures that the information will be recoverable in the event of a power outage).

8.1.6 Store the boats and filters in a desiccator until used for sample processing.

8.2 SAMPLE PREPARATION

This test may be conducted simultaneously with the Total Dissolved Solids (TDS) component of SOP 1101. It is the residue trapped by the glass fiber filter during TDS filtrate preparation that can be used to test for TSS (so long as a tared glass fiber filter weight was obtained prior to filtering, and that the sample bottle was well shaken before an aliquot was taken). If using residue obtained during TDS preparation, proceed directly to Section 8.3.

8.2.1 Assemble the filtration apparatus (vacuum source, vacuum flask, filter base, filter, funnel and clamp). Select a previously identified and pre-weighed glass fiber filter and center it in the funnel. Turn on the vacuum. To ensure a good seal, pre-wet the filter with a small amount of DI water.

8.2.2 After mixing each sample thoroughly by shaking the sample bottle, measure an appropriate aliquot (see note below) into a graduated cylinder. *The graduated cylinder used must have been previously verified as capable of delivering ±3% of the stated volume.*

NOTE: For TSS measurement, two factors govern the aliquot volume used for a particular sample. These are: 1) the amount of non-filterable material in the sample, and 2) the required reporting limit for the analysis.

If the content of non-filterable solids in the sample is high, it may be necessary to decrease the aliquot volume to avoid overloading the filter. Total mg of TSS (non-filterable solids) must be limited to 200mg or less.

If the TSS content in the sample is low, the aliquot volume must be large enough to meet the required reporting limit. The standard reporting limit for TSS is 20mg/L, which requires an aliquot volume of 100mL. Some clients may request a lower reporting limit which will require a larger aliquot volume if the TSS content is low. Consult the LIMS program specifications for the required reporting limit.

8.2.3 For each sample, with the vacuum on, carefully pour the aliquot of sample contained in the graduated cylinder into the funnel so that the liquid is pulled through into the filtration flask. Use a wash bottle to rinse the graduated cylinder, the filter and the sides of the funnel twice with DI water. Allow the rinse water to pull through under vacuum.

8.2.4 Remove clamp and carefully remove funnel. Turn off the vacuum and use forceps to carefully transfer the filter + residue to the proper labeled, pre-weighed aluminum sample boat.

NOTE: Wash the filter assembly and glassware (e.g., funnel, graduated cylinder, vacuum flask) per SOP 334 - Glassware Cleaning Procedures and Maintenance of Glassware Used in The Organics and Inorganics Departments.

8.2.5 Repeat Steps 8.2.1 through 8.2.4 until all field and quality control samples are processed. Process 100mL DI water as a Method Blank. Select a field sample and process a second aliquot to serve as the DUP.

For the LCS, weigh out approximately 50mg (0.0500g) of dry pottery clay on the analytical balance. Use the PC's mouse to select the "Amt. Clay Weight for TSS Spike (g)" cell of the spreadsheet. Press the "Print Scrn" key on the PC keyboard. The weight in grams that appears on the computer screen, will automatically be entered into the spreadsheet. Quantitatively transfer the clay to a disposable beaker and add 100mL DI water; mix well. Process this clay-DI water slurry per Steps 8.2.1 through 8.2.4 to serve as the LCS.

8.3 SAMPLE DRYING AND WEIGHING

8.3.1 Place the boats + filters into a drying oven set to maintain 103-105ºC. Dry for at least one hour.

8.3.2 Remove the boats + dried filter residues from the oven and place in a desiccator. Allow to cool to room temperature.

8.3.3 Use the computer's mouse to select the appropriate "**Filter + Boat Residue**" cell on the spreadsheet. Weigh each boat + dried filter residue. For each, press the "**Print Scrn**" key on the PC keyboard to automatically enter the gross weight of the boat + dried filter residue into the spreadsheet. Repeat until all dried fiber filters have been weighed.

8.3.4 Replace the boats + dried filter residues in the 103-105ºC oven and heat for one hour. Cool the boats + dried filter residues (per Step 8.3.2) and weigh (per Step 8.3.3); repeating this Step (8.3.4) until a stable gross weight is obtained for each sample. A stable gross weight is achieved when the weight lost (upon further drying and cooling) is less than 4% of the previous weight recorded (particularly applicable in the case of high residue amounts), or when the weight change is less than ±0.5mg (particularly applicable in the case of low residue amounts), whichever has less statistical impact. In other words, the gross weight cannot be considered to be stable until it is determined that further drying and cooling does not significantly impact the reported value. **The gross weight must be measured at least twice for each sample.**

8.3.5 The spreadsheet will calculate the sample's Total Suspended Solids (TSS), which is equal to the final dried gross weight minus the tared boat + filter weight.

8.4 CALCULATIONS

8.4.1 If the weights were entered into the spreadsheet directly using BalanceLink™, the calculations will be performed automatically.

8.4.2 If the data were entered by hand, then the calculations must be performed manually. Use the following formula to calculate TSS results:

TSS (mg/L) = [(A - B) x 1000] x 1000/ sample volume (mL)

where:

A = final weight of boat + filter + residue (g)

B = tare weight of boat + filter (g)

9. QUALITY CONTROL (QC)

9.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), and laboratory duplicate (DUP). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

9.2 METHOD BLANKS

Method blanks (MB) are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed a method blank must be processed. For this procedure, the MB consists of 100mL DI water. The blank concentration found must be less than the reporting limit (usually 20mg/L).

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. Each time a batch of samples is analyzed, an LCS must be processed. A known amount of analyte is prepared and analyzed. For this method, 50mg of dry clay suspended in 100mL of DI water is used as the LCS. Results obtained are compared to results expected (see formula below), with the results expressed as percent recovery (%R).

$$\%R = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Target}}} \times 100$$

To be acceptable, the LCS recovery must be between 85% and 115% of the expected concentration.

9.4 LABORATORY DUPLICATE

A laboratory duplicate (DUP) is analyzed as a measure of the precision of the analytical results generated (see calculation below). Each time a batch of samples is

analyzed, a DUP must be processed. The precision between results for a sample and its duplicate is expressed as Relative Percent Difference (RPD). The RPD between a sample and its duplicate should not be greater than 15%.

$$RPD\ (\%) = \frac{|\ Result_x - Result_{Dup}\ |}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

10. DEVIATIONS FROM METHOD

Per Section 1.2 of Method EPA 160.2, the procedures described in this SOP are capable of determining total non-filterable residue (TSS) in the practical range of 4mg/L to 20,000mg/L. Paragon has established a standard reporting limit of 20mg/L for TSS (greater than the 4mg/L cited) based on the use of a standard 100mL sample aliquot volume. In order to capture the suggested minimum 1.0mg residue Section 7.2 of Method EPA 160.2 states, in effect, that the sample volumes should be increased. Note that Paragon does not vary sample aliquot size except where: (1) a client has specifically requested a reporting limit lower than 20mg/L (in this instance, a sample aliquot larger than 100mL is processed in situations where the client sample's TSS content is low); or (2) the client sample has high solids content which requires a sample aliquot of less than 100mL to limit the total mg of TSS to 200mg or less.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Aqueous residues shall be disposed of in the Aqueous Laboratory Waste satellite collection vessel.

11.2.2 Solid filtrate residues and any other solid residues shall be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

11.2.3 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Waste Management Officer will provide specific procedures and materials for these samples.

12. REFERENCES

12.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1983. Method 160.2, "Residue, Non-filterable".

12.2 A.P.H.A., A.W.W.A. and W.P.C.F., Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998. Method 2540D.

DOCUMENT REVISION HISTORY

2/9/04: Updated format.

2/11/05: Re-released without revision.

7/26/05: Added reference Program Specification directive in "Responsibilities".

4/10/06: Added DOCUMENT REVISION HISTORY.

1/19/07: Updated Section 3. Corrected text ('200mg maximum' rather than 'approximately'). Corrected Section 8 text (don't need to press 'Enter' key to commit value to spreadsheet).

Analytical Method: E 160.2; SM2540D	**Parameter:** Total Suspended Solids (TSS)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per each batch of ≤20 field samples	MB must not contain TSS at concentration greater than analyte reporting limit (RL)	Check all calculations. If no computation errors are found, prepare a fresh MB and analyze. Associated samples must also be reanalyzed.
Laboratory Control Sample (LCS)	One per batch of ≤20 field samples	Results obtained must agree between 85% and 115% of TSS content added	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.
Laboratory Duplicate (DUP)	One per batch of ≤20 field samples	RPD must be ≤15%	Check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1101 REVISION 10

TITLE: TOTAL SOLIDS, TOTAL DISSOLVED SOLIDS (TDS OR TOTAL FILTERABLE RESIDUE), AND TOTAL FIXED AND VOLATILE SOLIDS -- METHODS EPA 160.3, EPA 160.1, AND EPA 160.4 AND METHODS SM2540B, SM2540C, AND SM2540E

FORMS: 1116 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/19/07
QUALITY ASSURANCE MANAGER _____ DATE 1/19/07
LABORATORY MANAGER _____ DATE 1-19-07

HISTORY: Rev0, PCN #225, 4/14/94; Rev1, PCN #491, 5/30/95; Rev2, 9/28/99; Rev3, 10/8/01; Rev4, 1/23/02; Rev5, 2/10/03; Rev6, 3/6/03; Rev7, 2/9/04 and 3/25/05 (re-released without revision); Rev8, 7/26/05; Rev9, 4/10/06; Rev10, 1/19/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- Methods EPA 160.3, EPA 160.4, and EPA 160.1 and Standard Methods SM2540B, SM2540E, and SM2540C -- describe procedures for measuring Total Solids (TS), Total Fixed Solids (TFS), Total Volatile Solids (TVS), and Total Dissolved Solids (TDS or Total Filterable Residue) in drinking, surface, and saline waters and domestic and industrial wastes.

2. SUMMARY

For Total Solids (Total Residue) determination, an aliquot of a well-mixed water sample is added to a pre-weighed beaker and evaporated to dryness at 103-105°C. The residue dry weight (in mg) represents the TS present in the sample aliquot.

For the Total Dissolved Solids (TDS or Total Filterable Residue) test, an aliquot of water sample is filtered through a glass fiber filter using vacuum pressure. The filtrate captured by the flask is evaporated and dried at 180±2°C to a constant weight. The filtrate residue dry weight (in mg) represents the TDS present in the sample aliquot.

For Total Fixed and Volatile Solids (Total Fixed and Volatile Residue) determination, the residue remaining from the TS or TDS test is ignited in a muffle furnace at 550°C. The loss in weight after ignition is reported as Total Volatile Residue. The weight of residue remaining after ignition is reported as Total Fixed Residue.

The determination of TDS and TSS may be performed simultaneously. See SOP 1100 for determination for Total Suspended Solids (TSS or Total Non-Filterable Residue).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or by the successful analysis of a proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for completeness, precision and accuracy is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Residues from highly mineralized waters that contain significant concentrations of hygroscopic salts (e.g., calcium, magnesium, chloride, and/or sulfate) will require prolonged drying, desiccation, and rapid weighing to limit the exposure to the ambient humidity.

4.2 Samples containing high concentrations of bicarbonate require careful and possibly prolonged drying at 180°C to ensure that all the bicarbonate is converted to carbonate.

4.3 Too much residue in the beaker will crust over and entrap water that will not be driven off during drying. Therefore, a sample aliquot size that yields no more than 200mg must be used. Electrical conductivity screening is performed prior to preparation in order to minimize this interference.

4.4 For TS analysis, exclude large, floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that there inclusion is not desired on the final result.

4.5 Negative errors in the volatile or fixed solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids may be subject to considerable error. **Measure for suspected volatile components by another test (e.g., total organic carbon).**

5. APPARATUS AND MATERIALS

5.1 Glass fiber filter, 47mm (Gelman™ A/E or Whatman™ grade 934AH)

5.2 Filter funnel assembly (funnel, glass-fritted filter base, funnel clamp, vacuum source, 1L vacuum flask)

5.3 Disposable syringes, various sizes

5.4 Acrodisc™ 25mm, 1µm glass fiber syringe filter, Pall Life Sciences, PN4523T or equivalent

5.5 Analytical balance, capable of weighing to 0.0001g

5.6 Personal computer (PC), connected to the in-house network and with BalanceLink™ software installed.

5.7 BalanceLink™ hardware to connect the analytical balance to the computer

5.8 Graduated cylinders, 10-500mL

NOTE: Use only labware whose graduated volume has been previously verified to deliver within ± 3% of the stated volume.

5.9 Pyrex™ beakers, 150-250mL

5.10 Forceps and/or heat resistant oven gloves

5.11 Drying oven (forced air), set at less than 100°C (~ 95°C)

5.12 Drying oven (convection), set to maintain 103-105°C

5.13 Oven (convection), with temperature set to maintain 180±2°C

5.14 Muffle furnace, with temperature set to maintain 550±50ºC

5.15 Desiccator with color indicating desiccant

5.16 Pipets, variable Eppendorf or equivalent, capable of 0.50mL to 5.0mL

5.17 Pipette tips, 1mL - 5.0mL

5.18 Conductivity meter with electrode, capable of reading in TDS and/or µmhos

5.19 Wash bottle

6. REAGENTS

6.1 Deionized (DI) Water

6.2 Sodium Chloride (NaCl), JT Baker, 3628-01 or equivalent reagent grade

6.3 TDS Spiking Solution, 40mg/mL: Transfer 40.0g of pre-dried NaCl into a 1000mL volumetric flask. Dissolve the salt and bring to volume with DI water. (Different volumes may be used as long as the ratio stays the same.) Store in polypropylene container. *Shelf Life = 1 year.*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples may be collected in either plastic or glass containers and must be collected according to an approved sampling plan.

7.2 Water samples must be kept cool (4-6°C) and should be analyzed as quickly as possible. Per Table 1 of Methods for the Chemical Analysis of Water and Wastes, 1983, a maximum holding time allowance of 7 days from date of collection is permitted.

8. PROCEDURE

NOTE: Per Section 1.2 of Methods EPA 160.1 and EPA 160.3, these procedures are capable of determining TDS and TS residues in the practical range of 10mg/L to 20,000mg/L. Section 7.2.1 of Method EPA 160.3 (Total Solids) directs that the sample aliquot used should yield at least 25mg residue. Paragon has established a standard reporting limit of 20mg/L (greater than the 10mg/L cited) for TDS and TS, based on use of a 100mL sample aliquot volume. Note that where the client sample has high solids content, a smaller than 100mL sample aliquot may be processed in order to limit the solids to 200mg (maximum).

8.1 TOTAL SOLIDS

A conductivity meter can be used to screen a separate aliquot of sample in order to obtain information useful in determining appropriate sample size (record these screening readings in the Conductivity Screening Logbook, Form 1116). As a rule of thumb, if the conductivity measures below 2000µmhos, use the usual 100mL aliquot. Use a 25mL aliquot if the conductivity measures near to

5000µmhos, and a 10mL aliquot if the conductivity measures near to 10, 000µmhos. See **Table 1** below:

Table 1: GUIDELINES FOR SAMPLE ALIQUOT TO USE BASED ON CONDUCTIVITY SCREENING

Estimated Conductivity (umhos)	Estimated TDS (mg/L)	Volume For TDS Analysis (mL)	Max. Observed Wt. (mg)
0	0	100	0
</= 1300	< 1300	100	130
1301-3000	> 1300-3000	50	150
3001-6000	> 3000-6000	25	150
6001-12000	> 6000-12000	10	120
12001-30000	> 12000-30000	5	150
30001-50000	> 30000-50000	2	120
50001-150000	> 50000-150000	1	150

8.1.1 Label a 150-250mL Pyrex™ beaker for each sample. With each batch of twenty field samples or less processed as a unit, the following quality control (QC) samples must be prepared: one Method Bank (MB), one Laboratory Control Sample (LCS), and one sample Duplicate (DUP).

NOTE: If the sample(s) are to be subsequently tested for Total Volatile Solids (TVS), the beakers must first be numbered and conditioned in a muffle furnace at 550°C to ensure they are free of volatile organic residue and are at a constant weight. Cool and maintain the pre-conditioned beakers in a desiccator.

8.1.2 When available, it is most convenient and accurate to use the BalanceLink program that allows data from an analytical balance to be electronically entered into a spreadsheet datafile. To use this system, first open the appropriate template spreadsheet in Excel (e.g., i:\oprtns\wtchm\tds\ template\ts1.xls); then open the BalanceLink program to create linkage between the computer and the analytical balance.

8.1.3 Redirect the electronic file to the year's directory, and rename the spreadsheet with a filename that uses an mmdd format. For example, if the preparation batch were performed on 7/14/2005, the new filename would be i:\oprtns\wtchm\tds\ 2005\0714ts.xls. Enter pertinent information into the spreadsheet (e.g., date, analyst, sample IDs,

sample volumes).

8.1.4 Using the computer's mouse, position the cursor on the "**Empty Beaker Tare Weight (g)**" cell for the individual sample listed on the spreadsheet. For each sample, center the beaker on the weighing pan of the analytical balance and close the door. Press the "**Print Scrn**" key on the PC keyboard. The weight in grams that appears on the computer screen, will be automatically entered into the spreadsheet.

NOTE: The analytical balance's calibration must be verified per SOP 305 before use.

A tared empty beaker weight must be obtained for each field and QC sample. Print out a copy of the spreadsheet to keep as a temporary hardcopy until the analyses are complete (this ensures that the information will not be unrecoverable in the event of a power outage).

8.1.5 Using a graduated cylinder that is well rinsed with DI water between each use, add 100mL (or less) of well-mixed sample to the designated pre-weighed beaker. The graduated cylinder used must also have been previously verified as capable of delivering ±3% of the stated volume. Make sure the identity of the sample added, matches the sample identity labeled on the pre-weighed beaker.

8.1.6 Use 100mL DI water for the MB. Prepare a second aliquot of a selected field sample to serve as the DUP. For the LCS, use 100mL DI water into which 1.0mL of TDS spiking solution has been added (mix well before processing).

8.1.7 Pre-dry the sample beakers overnight in a forced-air oven set at less than 100°C (~ 95°C to prevent boiling and splattering of the sample). Allow the liquid to evaporate overnight.

8.1.8 After the water has evaporated, relocate the sample beakers to a convection oven (i.e., not forced-air), and continue drying at 103-105ºC for at least one hour.

8.1.9 Remove the sample beakers from the oven and place the beakers in a desiccator to cool for 1 or more hours.

8.1.10 Use the computer's mouse to select the appropriate "**Beaker + Residue Gross (g)**" cell on the spreadsheet. Place the corresponding dried sample beaker on the weighing pan of the analytical balance and close the door. Press the "**Print Scrn**" key on the PC keyboard to enter the

gross weight of dried sample into the selected cell of the spreadsheet. Repeat for each dried sample beaker.

8.1.11 Replace the dried sample beakers in the 103-105ºC convection oven and continue drying for about an hour. Cool (per Step 8.1.10) and weigh (per Step 8.1.11), repeating this Step (8.1.12) until a stable gross weight is obtained for each sample. A stable gross weight is achieved when the weight lost (upon further drying and cooling) is less than 4% of the previous weight recorded (particularly applicable in the case of high residue amounts), or when the weight change is less than ±0.5mg (particularly applicable in the case of low residue amounts), whichever has less statistical impact. In other words, the gross weight cannot be considered to be stable until it is determined that further drying and cooling does not significantly impact the reported value. The gross weight must be measured at least twice for each sample.

8.1.12 The spreadsheet will calculate the sample's Total Solids (TS), which is equal to the final dried gross weight minus the tared beaker weight.

8.1.13 If Total Fixed Solids (TFS) and Total Volatile Solids (TVS) are to be determined, proceed to Section 8.3.

8.2 TOTAL DISSOLVED SOLIDS (TDS; TOTAL FILTERABLE RESIDUE)
This test may be conducted simultaneously with SOP 1100 - Total Suspended Solids (TSS; Total Non-Filterable Residue). It is the filtrate from the TSS preparation that can be used directly to test for TDS.

8.2.1 A conductivity meter can be used to screen a separate aliquot of sample in order to obtain information useful in determining appropriate sample size (record these screening readings in the Conductivity Screening Logbook). As a rule of thumb, if the conductivity measures below 2000µmhos, use the usual 100mL aliquot. Use a 25mL aliquot if the conductivity measures near to 5000µmhos, and a 10mL aliquot if the conductivity measures near to 10,000µmhos. See **Table 1** above.

8.2.2 Label a 150-250mL Pyrex™ beaker for each sample. With each batch of twenty (20) or less field samples processed together as a unit, one MB, one LCS and a sample DUP must also be processed.

8.2.3 Open the appropriate template spreadsheet in Excel (e.g., i:\oprtns\wtchm\tds\template\tds1.xls); then open the BalanceLink program to create linkage between the computer and the analytical balance

8.2.4 Redirect the electronic file to the year's directory, and rename the spreadsheet with a filename that uses an mmdd format. For example, if the preparation batch were performed on 7/14/2005, the new filename would be i:\oprtns\wtchm\tds\2005\0714tds.xls.

Enter pertinent information into the spreadsheet (e.g., date, analyst, sample IDs, sample volumes).

8.2.5 Using the computer's mouse, position the cursor on the "**Beaker Weight**" cell for the individual sample listed on the spreadsheet. For each sample, center the beaker on the weighing pan of the analytical balance and close the door. Press the "**Print Scrn**" key on the PC keyboard. The weight in grams that appears on the computer screen, will be automatically entered into the spreadsheet.

NOTE: The analytical balance's calibration must be verified daily before use, per SOP 305.

A tared beaker weight must be obtained for each field and QC sample. Print out a copy of the spreadsheet to keep as a temporary hardcopy until the analyses are complete (this ensures that the information will not be unrecoverable in the event of a power outage).

8.2.6 Assemble the filtration apparatus (vacuum source, vacuum flask, funnel clamp, funnel, and filter base) and put a glass fiber filter in place. Turn on the vacuum. Pre-wet the filter using a small amount of DI water to ensure a good seal.

NOTE: If performing TDS only, a disposable syringe and Acrodisc™ 1μm glass fiber syringe filter may be used to filter the sample. If however, TSS will also be performed use the filtration apparatus discussed above.

NOTE: If the residue retained on the fiber filter is to be used to determine TSS, a tare weight of a pre-rinsed fiber filter must first be obtained (see Section 8.0 of SOP 1100).

8.2.7 If the filtrate from a previously prepared TSS sample is not available for use in conducting the TDS test, then prepare a filtered TDS sample by measuring-out an appropriate aliquot of sample in a graduated cylinder that has been well-rinsed with DI water between each use. The graduated cylinder used must also have been previously verified as capable of delivering ±3% of the stated volume.

8.2.8 With the vacuum on, carefully pour the aliquot of sample from the

graduated cylinder onto the fiber filter in the funnel, so that the liquid is pulled through the filter into a clean filtration flask. This pulled-through liquid (filtrate) is used to determine TDS. Rinse the graduated cylinder, the filter and the sides of the funnel twice with DI water wash bottle and allow the rinse water to pull through under vacuum.

8.2.9 Transfer the filtrate (i.e., the liquid contained in the filtration flask) to the proper pre-weighed beaker, being careful not to overfill the designated beaker. *Rinse the inside of the filtration flask well with a DI water wash bottle; add the rinsate to the pre-weighed beaker containing the sample filtrate.*

NOTE: If TSS is not to be determined, the glass fiber filter may be discarded. **Wash the filter assembly and glassware (e.g., funnel, graduated cylinder, vacuum flask assembly) per SOP 334 - Glassware Cleaning Procedures and Maintenance of Glassware Used in the Organics and Inorganics Departments.**

8.2.10 Reassemble the filter assembly and put another glass fiber filter in place, or if performing TDS only use the syringe and Acrodisc™ discussed above. Repeat Steps 8.2.6 and 8.2.7 until all field and quality control samples are processed. Process 100mL DI water as the Method Blank. Select a field sample and process a second aliquot to serve as the DUP. For the LCS, process 100mL DI water into which 1.0mL of TDS Spiking Solution has been added (mix well before processing).

8.2.11 Place the beakers + filtrate into a forced-air oven set at less than 100ºC (~ 95°C to prevent boiling and splattering of the sample). Allow the liquid to evaporate overnight.

8.2.12 After the water has evaporated, relocate the sample beakers to a convection oven set to maintain 180±2°C. Heat for at least one hour.

8.2.13 Remove the beakers containing the dried sample to a desiccator and allow beaker to cool to room temperature.

8.2.14 Use the computer's mouse to select the appropriate "**Beaker + Residue Gross (g)**" cell on the spreadsheet. When cool, weigh each beaker + dried sample. Press the "**Print Scrn**" key on the PC keyboard to enter the gross weight of the beaker + residue into the spreadsheet. Repeat until all dried samples have been weighed.

8.2.15 Replace the dried sample beakers in the 180±2 °C oven and heat for

one hour. Cool the dried sample beakers (per Step 8.2.13) and weigh (per Step 8.2.14), repeating this Step (8.2.15) until a stable gross weight is obtained for each sample. A stable gross weight is achieved when the weight lost (upon further drying and cooling) is less than 4% of the previous weight recorded (particularly applicable in the case of high residue amounts), or when the weight change is less than ±0.5mg (particularly applicable in the case of low residue amounts), whichever has less statistical impact. In other words, the gross weight cannot be considered to be stable until it is determined that further drying and cooling does not significantly impact the reported value. **The gross weight must be measured at least twice for each sample.**

8.2.16 The spreadsheet will calculate the sample's Total Dissolved Solids (TDS), which is equal to the final dried gross weight of filtrate minus the tared beaker weight.

8.2.17 If Total Fixed Solids (TFS) and Total Volatile Solids (TVS) are to be determined, proceed to Section 8.3.

8.3 TOTAL FIXED AND VOLATILE SOLIDS

8.3.1 Place the labeled beaker containing the dried TS or TDS sample residue into a pre-warmed muffle furnace set at 550±50ºC. Heat for 15-20 minutes.

8.3.2 Remove the beakers with muffled residue from the furnace and cool initially in air until most of the heat has dissipated. Then place the beakers with muffled residue in a desiccator until cooled to room temperature.

8.3.3 Use the computer's mouse to select the appropriate "**Beaker + Muffled Residue (g)**" cell on the spreadsheet. Place the corresponding sample beaker containing muffled residue on the weighing pan of the analytical balance and close the door. Press the "**Print Scrn**" key on the PC keyboard to enter the weight into the selected cell of the spreadsheet. Repeat for each sample beaker containing muffled residue. The loss of weight following ignition when muffled is reported as mg/L Total Volatile Solids (TVS). The weight of residue remaining after ignition is reported as mg/L Total Fixed Solids (TFS).

8.4 CALCULATIONS

8.4.1 If the weights were entered into the spreadsheet directly using BalanceLink™, the calculations will be performed automatically.

8.4.2 If the data are entered by hand, then the calculations must be performed manually. Use the following formula to calculate TS results:

TS (mg/L) = [(A - B) x 1000] x 1000 / sample volume (mL)

where:

A = final weight of beaker + residue (g)

B = tare weight of beaker (g)

8.4.3 Total volatile solids are calculated using the following formula:

TVS (mg/L) = [(A _ B) x 1000] x 1000 / sample volume (mL)

where:

A = weight of beaker + residue before ignition (g)

B = weight of beaker + residue after ignition (g)

8.4.4 Total fixed solids are determined by subtracting the amount of TVS from the amount of TS or TDS as shown below:

TFS (mg/L) = [(A _ C) x 1000] x 1000 / sample volume (mL)

where:

A = weight of beaker + residue before ignition (g)

C = weight of beaker (g)

8.4.5 Total dissolved solids are calculated using the following formula:

TDS (mg/L) = [(D - E) X 1000] x 1000 / sample volume (mL)

where:

D = weight of beaker + dried filtrate residue (g)

E = tare weight of beaker (g)

9. QUALITY CONTROL (QC)

9.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), and laboratory duplicate (DUP). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

9.2 METHOD BLANKS

Method blanks (MB) are analyzed to demonstrate that interferences from the analytical system and glassware are under control. Each time a batch of samples is analyzed, a MB must be processed. For this procedure, the MB consists of 100mL DI water. The blank concentration found cannot exceed the analyte reporting limit (usually 20mg/L).

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. Each time a batch of samples is analyzed, a LCS must be processed. A known amount of analyte is prepared and analyzed. For this method, 1.0mL of TDS spiking solution (40mg/mL) added to 100mL DI water is used as the LCS. Results obtained are compared to results expected, with the results expressed as percent recovery (%R), as shown below

$$\%R = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Target}}} \times 100$$

Based on procedures outlined in this SOP, a final concentration of 400mg/L is expected for the LCS. To be acceptable, the LCS recovery must be between 85% and 115% of the expected concentration (i.e., between 340 and 460mg/L).

9.4 LABORATORY DUPLICATE

A laboratory duplicate (DUP) is analyzed as a measure of the precision of the analytical results generated (see calculation below). Each time a batch of samples is analyzed, a DUP must be processed. The precision between results for a sample and its duplicate is expressed as Relative Percent Difference (RPD), and is calculated as follows:

$$\text{RPD (\%)} = \frac{| \text{Result}_x - \text{Result}_{\text{Dup}} |}{\frac{(\text{Result}_x + \text{Result}_{\text{Dup}})}{2}} \times 100$$

The RPD between a sample and its duplicate should not be greater than 15%.

10. DEVIATIONS FROM METHOD

10.1 Total Solids Methods EPA 160.3 (Section 7.1) and SM2540B (Section 3a); and Total Dissolved Solids Methods EPA 160.1 (Section 7.2) and SM2540C (Section 3b) discuss preconditioning the sample drying containers at 180±2°C before use. Paragon does not perform this pre-conditioning step because the laboratory uses Pyrex glass beakers (i.e., not ceramic containers).

10.2 Total Dissolved Solids Methods EPA 160.1 (Section 7.3) and SM2540C (Section 3d) call for the sample to be well mixed before processing. For samples with visibly settled solids, Paragon does not mix the sample before processing, unless

TSS analysis is also to be performed. Only the supernatant liquid is used for the TDS test.

10.3 As noted in Section 8.0 Procedure, Section 1.2 of Methods EPA 160.1 and EPA 160.3 state that these procedures are capable of determining TDS and TS residues in the practical range of 10mg/L to 20,000mg/L. Section 7.2.1 of Method EPA 160.3 (Total Solids) directs that the sample aliquot used should yield at least 25mg residue. Paragon has established a standard reporting limit of 20mg/L (greater than the 10mg/L cited) for TDS and TS, based on use of a 100mL sample aliquot volume. Note that Paragon does not vary sample aliquot size processed except where ~~(1) a client has specifically requested a reporting limit lower than 20mg/L (in this instance, a sample aliquot volume larger than 100mL is processed in situations where the client samples solids content is low); and~~ (2) the client sample has high solids content thus requiring that a smaller than 100mL sample aliquot volume be processed in order to limit the solids to about 200mg.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Aqueous residues shall be disposed of in the Aqueous Laboratory Waste satellite collection vessel.

11.2.2 Solid filtrate residues and any other solid residues shall be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

11.2.3 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Health and Safety Officer will provide specific procedures and materials for these samples.

12. REFERENCES

12.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1983. Method 160.3, "Total Residue";

Method 160.4, "Total Volatile Residue"; Method 160.1, "Total Residue, Filterable".

12.2 A.P.H.A., A.W.W.A. and W.P.C.F., Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998. Method 2540B, "Total Solids Dried at 103-105°C" Method 2540E, "Fixed and Volatile Solids Ignited at 550°C; Method 2540C, "Total Dissolved Solids Dried at 180°C".

DOCUMENT REVISION HISTORY

2/9/04: Updated format.

3/25/05: Re-released without revision.

7/26/05: Added reference Program Specification directive in "Responsibilities".

4/10/06: Added DOCUMENT REVISION HISTORY.

1/19/07: Updated Section 3. Corrected text ('200mg maximum' rather than 'approximately'). Corrected Section 8 text (don't need to press 'Enter' key to commit value to spreadsheet).

Analytical Method: EPA 160.3, 160.1, 160.4 and SM2540B, 2540C, 2540E	**Parameter:** Total Solids, Total Dissolved Solids (TDS), Total Fixed and Volatile Solids		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per each batch of ≤20 field samples	MB must not contain TS, TFS, TVS or TDS at a concentration greater than the analyte reporting limit (RL)	Check all calculations. If no computation errors are found, prepare a fresh MB and analyze. Associated samples must also be reanalyzed.
Laboratory Control Sample (LCS)	One per batch of ≤20 field samples	Results obtained must agree between 85% and 115% of solids content added	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.
Laboratory Duplicate (DUP)	One per batch of ≤20 field samples	RPD must be ≤15%	Check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers.

Paragon Analytics

FORM 1116

CONDUCTIVITY SCREENING WORKSHEET

Instrument ID: VWR Digital Conductivity Meter S/N A22036

Workorder ID / Sample No.		Estimated µS	Dilution(s)	Anion(s)	Date	Initials	Comments

Reviewed by / Date _____ **Form 1116r4.frm (6/29/04)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1104 REVISION 6

TITLE: POTENTIOMETRIC DETERMINATION OF (SIMPLE) FLUORIDE IN WATER AND SOIL USING AN ION SELECTIVE ELECTRODE -- METHODS EPA 340.2, SW9214 AND SM4500-F C

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER Steve Wortman DATE 7/21/08

QUALITY ASSURANCE MANAGER Deb Echerts DATE 7/20/08

LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: Rev0, PCN #463, 4/20/95; Rev1, 4/29/02; Rev2, 12/6/02; Rev3, 2/9/04 and 2/11/05 (re-released without revision); Rev4, 7/26/05; Rev5, 4/10/06; Rev6, 7/18/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- EPA 340.2, SW9214, and SM4500-F^- C -- describe the measurement of fluoride (F^-) in drinking, ground, and surface waters and domestic and industrial wastes by use of an ion selective electrode (ISE). *Note that the procedure outlined in this SOP is for the determination of simple fluoride, not total or dissolved fluoride, as the analysis is not preceded by a distillation step.* The introduction to Method 4500-F^- explains that distillation prior to analysis removes interfering ions thereby reducing measurement error. Method 4500-F^- provides for fluoride determination *without* distillation in cases where interfering ions are not present in excess of the tolerances of the method. The introduction to Method 340.2 states that distillation is required for CWA/NPDES monitoring, but is *not* required for SDWA monitoring. As provided for in Method SW9214, solid matrix samples may also be analyzed by this procedure by first creating an aqueous sample extract.

2. SUMMARY

Fluoride is determined potentiometrically using a fluoride combination ISE and a pH meter with an expanded millivolt (mV) scale. Total Ionic Strength Adjustment Buffer (TISAB) is mixed with standards and samples to adjust the test solution's ionic strength and buffer it to a pH of 5-5.5. The TISAB contains a chelating agent that breaks up metal-fluoride complexes. An electrode potential develops when the sensing element in the ISE (a lanthanum fluoride crystal) contacts the F^- ions contained in the test solution. This potential, which depends on the level of free F^- ions in solution, is measured against a constant reference potential with a mV meter. Calibration is performed by measuring a series of standards and plotting mV vs fluoride concentration using an electronic spreadsheet.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP

and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the workorder file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 The fluoride electrode is affected by temperature. It is important that all sample and standard solutions be at the same temperature (preferably ambient room temperature) when measurements are made with the electrode.

4.2 In solutions with a pH below 5, hydronium ions [H^+] complex a portion of the fluoride [F^-] ions, forming HF or HF_2^-, which cannot be detected by the electrode. For most solutions, adding TISAB will maintain a pH above 5.

4.3 Fluoride forms stable complexes with several polyvalent cations (e.g., Si^{+4}, Fe^{+3} and, most notably, Al^{+3}). The CDTA chelating agent contained in the TISAB will preferentially complex aluminum (Al) and iron (Fe) and release free fluoride (F^-). The TISAB solution is effective for sample solutions containing Al or Fe at concentrations >100mg/L.

4.4 The user should be aware of potential interferences from colloidal substances. If colloidal substances are apparent, then the samples may be filtered.

5. APPARATUS AND MATERIALS

5.1 Fluoride combination ISE, Orion Model 96-09 or equivalent (note that a reference electrode is contained within the body of the probe in a combination electrode)

5.2 Specific ion meter with expanded scale capable of reading to 0.1mV, Accumet 50 pH meter or equivalent

5.3 Magnetic stir plate

5.4 Magnetic stir bars, Micro (i.e., 1/2" length by 3/16" wide), Teflon™-coated

5.5 Disposable blood cell-counter vials, or equivalent, 20mL

5.6 Centrifuge tube, polypropylene, disposable, 50mL

5.7 Volumetric and pipette dispensers, Eppendorf™ or equivalent, capable of dispensing 0.01-5.0mL

5.8 Analytical balance, 0.0001g sensitivity, verified per SOP 305

5.9 Volumetric flask, 1000mL

5.10 TCLP tumbler for soil preparation

6. REAGENTS AND STANDARDS

NOTE: Only ACS grade or better chemicals may be used. Unless otherwise noted, reagents must be stored in polypropylene containers.

6.1 Deionized (DI) water. Obtained from the laboratory deionized water system.

6.2 Ottawa (Silica) Sand. EMD, SX0075-3 or equivalent. *Shelf Life = Indefinite.*

6.3 ISE Filling Solution: Purchased from Orion (Single Junction Reference Electrode Filling Solution, catalog # 90-00-01). *Shelf Life = Per expiration date stamped on bottle by manufacturer.*

6.4 Low-level TISAB Solution: In a 1L polypropylene bottle containing approximately 500mL of DI water and a magnetic stir bar, add 58g sodium chloride (NaCl), 57mL glacial acetic acid, and 4g of CDTA ($C_6H_{10}[N(CH_2CO_2H)_2]_2 \bullet H_2O$). Stir on a stir plate to mix and dissolve the components. Adjust to pH to 5.0-5.5 using 10N sodium hydroxide (NaOH). Dilute to 1L using DI water. *Shelf Life = 1 year.*

6.5 TISAB IV Solution: Used for samples containing high concentrations of Al and/or Fe. To 800mL of DI water in a 1L polypropylene bottle, add a magnetic stir bar, 230g of sodium tartrate ($Na_2C_4H_4O_6 \bullet 2H_2O$), 242g TRIS hydroxymethyl-aminomethane (a.k.a. THAM), and 84mL concentrated hydrochloric acid (HCl). Stir on a stir plate for 30-60 minutes to thoroughly mix and dissolve the components. Dilute to 1L using DI water. *Shelf Life = 1 year.*

6.6 Fluoride (F^-) Stock Solution, 10,000mg/L, (first source only): Made in-house from Sodium Fluoride (NaF) salt. In a 500mL volumetric flask containing approximately 250mL DI water, dissolve 11.0500g of anhydrous NaF salt then dilute to mark with DI water. The **first source** NaF stock solution is used to

prepare the 1000mg/L **first source** Fluoride solution. *Shelf life = 1 year from creation.*

6.7 Fluoride (F^-) Solution, 1000mg/L, (first and second sources): Purchased as a prepared solution or made in-house by dilution of the 10,000mg/L Fluoride Stock Solution, as follows - transfer 50.0mL of 10,000mg/L Fluoride Stock Solution into a 500mL volumetric flask and bring to mark using DI water. Store in refrigerator. *Shelf life = 1 year from creation or opening.*

6.8 Fluoride Calibration Standards (per **Table 1** below): Made in-house on each day of calibration by dilution of the first source 1000mg/L Fluoride Solution.

To prepare each calibration standard, pipet 10.0mL DI water into a 20mL vial. Before pipetting the appropriate aliquot of fluoride solution into the vial, first remove an equivalent volume of DI water from the vial using the pipet, so that the final volume contained in the vial is 10.0mL. Exception: 0.5mg/L calibration standard. Use an initial volume of 20.0mL DI water; remove water and add fluoride solution so that final volume is 20.0mL. (Remove 10mL before processing for analysis so that all standard volumes processed for analysis are 10mL).

TABLE 1: CALIBRATION STANDARD PREPARATION

VOLUME OF 1000mg/L FLUORIDE STANDARD USED (mL)	CONCENTRATION OF FINAL SOLUTION (ppm)	FINAL VOLUME OF CALIBRATION STANDARD (mL)
0.01	0.5	20
0.01	1.0	10
0.05	5.0	10
0.10	10.0	10
0.20	20.0	10

6.9 Initial Calibration Verification (ICV) Standard, 5.0mg/L F^-: Pipet 10.0mL of DI water into a 20mL capacity disposable vial. Using the pipet, withdraw 0.05mL of DI water and replace with 0.05mL **second source** 1000mg/L Fluoride solution.

NOTE: This standard solution is also used to prepare the aqueous LCS in the same manner.

6.10 Continuing Calibration Verification (CCV) Standard, 10.0 mg/L F^-: Pipet 10.0mL of DI water into a 20mL capacity disposable vial. Using the pipet, withdraw 0.10mL of DI water and replace with 0.10mL **first source** 1000mg/L Fluoride solution. **A CCV is analyzed after every 10 samples and at the end of every analytical sequence.**

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 All samples should be collected according to an approved sampling plan.

7.2 Per Section 6.0 of Method SW9214, samples must be collected in polyethylene containers.

7.3 No chemical preservation is required for aqueous or solid samples; samples should be chilled (4±2°C).

7.4 No maximum holding time allowance is established for solid samples. Aqueous samples should be analyzed within 28 days after collection.

8. SAMPLE PREPARATION

8.1 AQUEOUS EXTRACTION OF SOLID MATRIX SAMPLES AND ASSOCIATED QUALITY CONTROL (QC) SAMPLE PREPARATION

8.1.1 Weigh a 4.0g representative aliquot of moist sample into a labeled 50mL disposable polypropylene centrifuge tube.

8.1.2 Prepare a Method Blank (MB) by weighing 4.0g clean silica sand into a labeled 50mL disposable polypropylene centrifuge tube. One method blank must be prepared for each batch of twenty (or fewer) solid matrix environmental samples processed together as a unit.

8.1.3 Prepare a Blank Spike/Laboratory Control Sample (LCS) by weighing 4.0g clean silica sand into a labeled 50mL disposable polypropylene centrifuge tube. Add 0.40mL of 1000mg/L F^- solution (second source). One LCS must be prepared for each batch of twenty (or fewer) solid matrix environmental samples processed together as a unit. The concentration of the LCS is expected to be 100.0mg/kg F^-.

8.1.4 Prepare a Matrix Spike/Matrix Spike Duplicate (MS/MSD) set by selecting one sample representative of the batch and weighing additional 4.0g aliquots of sample into two labeled 50mL disposable polypropylene centrifuge tubes. Add 0.16mL of 1000mg/L Fluoride solution (first source) to each MS/MSD tube. One MS/MSD set must be prepared for each batch of twenty (or fewer) solid matrix environmental samples processed together as a unit. The concentration of the MS and MSD is expected to be 40.0mg/kg F^-.

8.1.5 To all of the above, add 40.0mL DI water.

8.1.6 Cap the prepared samples and shake for 1 hour on the TCLP tumbler.

8.1.7 Centrifuge the aqueous extracts for about 15 minutes at approximately 3500rpm.

8.1.8 If filtering is required due to presence of suspended material, then filter extract through a 0.45µm filter disk prior to analysis.

8.2 AQUEOUS FIELD AND ASSOCIATED QC SAMPLE PREPARATION

8.2.1 Aliquot 10mL of each aqueous sample or previously prepared solid sample extract (including associated QC samples) into a designated 20mL vial.

8.2.2 Prepare the aqueous Method Blank (MB) by aliquotting 10mL of DI water into a labeled 20mL vial. One method blank must be prepared for each batch of twenty (or fewer) aqueous matrix environmental samples processed together as a unit. This blank is also used as the Initial Calibration Blank (ICB); one ICB must be analyzed following the daily initial calibration. This blank is also used as the Continuing Calibration Blank (CCB). CCBs are analyzed following CCVs.

8.2.3 The ICV as discussed in Section 6.9 is used as the aqueous LCS.

8.2.4 Prepare an aqueous Matrix Spike/Matrix Spike Duplicate (MS/MSD) set by selecting one aqueous sample representative of the batch and aliquotting an additional 10.0mL aliquot of sample into each of two labeled 20mL vials. Add 0.04mL of 1000mg/L Fluoride solution (first source) to each MS/MSD vial. One MS/MSD set must be prepared for each batch of twenty (or fewer) aqueous matrix environmental samples processed together as a unit. The concentration of the MS and MSD is expected to be 4.0mg/L F^-.

8.2.5 If filtering is required due to presence of suspended material, then filter extract through a 0.45µm filter disk prior to analysis.

9. PROCEDURE

NOTE: While preparing samples and standards, condition the electrode by soaking (with stirring), in aliquots of low and high standard (with 10mL TISAB added).

9.1 Examine ISE and rinse outside with DI water. Add filling solution each day before use through filling hole. Shake electrode as you would shake down the fluid in a thermometer. The filling solution level should be at least one inch above the level of sample to ensure proper flow rate.

NOTE: If necessary, empty filling solution by pushing down of top of electrode and allowing it to drain completely. Rinse with deionized water and shake dry. Re-fill with fresh filling solution.

9.2 Connect electrode to meter and turn meter on by pressing “standby”. Switch to connected channel (Channel A) by pressing “channel”. Press “mV” to select mV mode. Press “expand” to display decimal place. Press “meas./monitor” to select measurement mode.

9.3 Prepare standards as indicated in Section 6 of this SOP; prepare samples as indicated in Section 8 of this SOP.

9.4 Add 10mL of TISAB IV reagent (i.e., 1:1 ratio with sample aliquot) and a stir bar to all sample and standard vials.

NOTE: Routinely, TISAB IV is used for F^- analysis. If necessary the Low-level TISAB buffer solution may be substituted.

Per Section 8.0 of Method 340.2, the amount of buffer may not be adequate for industrial waste samples. If the pH of the sample is >9, add 1N HCl to adjust to pH 8.3.

9.5 Analyze standards and samples per the following run sequence:

1. 0.5mg/L F^- calibration standard
2. 1.0mg/L F^- calibration standard
3. 5.0mg/L F^- calibration standard
4. 10.0mg/L F^- calibration standard
5. 20.0mg/L F^- calibration standard
6. ICV, 5.0mg/L F^- (second source)
7. ICB
8. Preparation (Method) Blank.
9. Laboratory Control Sample (LCS)
10-18. maximum of 8 Field Samples (including MS/MSD)
19. CCV
20. CCB
21-30. maximum of 10 Field Samples (including QC samples, as applicable)
31. CCV
32. CCB
33. repeat Steps 21 through 32

9.6 Select the lowest standard and place on the stir plate. Set the stir rate. Rinse the ISE with DI water and shake of the excess (DO NOT dry by wiping).

Place the electrode in the solution to be measured. Press “mV” to start the measurement. The monitor on the meter displays a “key” symbol and produces a slight “beep” when the reading has been reached. Do not record reading. Instead, press “mV” again, and repeat measurement (this ensures that no previous sample memory or drift occurs). Record the meter reading (in mV) in the LIMS template.

NOTE: Avoid stirring before immersing the electrode because air can become entrapped around the crystal and cause erroneous readings.

9.7 Repeat the step above until all standards and samples have been analyzed. Refer to QC Table at end of SOP for acceptance limits and associated corrective actions.

10. CALCULATIONS

10.1 COMPUTING THE STANDARD CURVE

Prepare a standard curve by plotting the observed mV reading versus log[F^-] for each calibration standard. This is most conveniently accomplished by using the spreadsheet template located in LIMS and renaming it as the appropriate analytical batch ID (example: FL060415-1A).

10.1.1 Enter the mV data obtained for each solution analyzed into the spreadsheet. Also, enter additional data as necessary (i.e., sample identification, volumes or weights, dilution, etc.)

10.1.2 Use the spreadsheet to perform a linear regression analysis between mV and log[F^-] for the calibration standards. The correlation coefficient (r^2) for the regression must be $\geq$0.995. Additionally, for the working concentration range of this procedure (i.e., 0.5-20mg/L), a plot of log[F^-] vs. electrode potential should be linear with a slope of about 59mV per unit change in log[F^-]. In other words, a ten-fold change in concentration should result in about a 59mV change in potential.

10.2 CALCULATING SAMPLE CONCENTRATION

10.2.1 The F^- concentration in water samples is calculated as follows:

$$\text{Concentration } (\mu g/mL) = A \times D$$

where:

A = 10^(mV*slope + intercept); where the slope and intercept are obtained from the linear regression equation

D = Dilution Factor (as applicable)

10.2.2 The F^- concentration in soil samples is calculated as follows:

$$\text{Concentration } (\mu g/g) = \frac{A \times D \times V}{W}$$

where:

A = 10^(mV*slope + intercept); where the slope and intercept are obtained from the linear regression equation

D = Dilution Factor (as applicable)

V = Extract Volume (40mL if this SOP is followed without deviation)

W = Dry weight of sample extracted; (4.0g * percent solids if this SOP is followed without deviation)

11. QUALITY CONTROL

11.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or fewer field samples associated with one unique set of batch QC samples that are processed together as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike and duplicate (MS/MSD). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

11.2 METHOD BLANKS

Method blanks (MBs) are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. For this procedure, the MB consists of 10.0mL of deionized water or 4.0g clean sand. Any analyte concentration found in the blank must be less than the analyte reporting limit.

11.3 LABORATORY CONTROL SAMPLE

The Laboratory Control Sample (LCS) is analyzed to measure the accuracy of the method. A known amount of analyte is spiked into an aliquot of representative clean matrix and analyzed. For this method, 10.0mL of DI water (representative of aqueous samples) and 4.0g clean sand (representative of solid samples) are used as the clean matrices.

LCS results obtained are compared to results expected using the equation presented below:

$$\text{Percent Recovery (\%R)} = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Expected}}} \times 100$$

where:

$\text{Conc}_{\text{Found}}$ = analyte concentration found in the LCS

$\text{Conc}_{\text{Expected}}$ = anticipated analyte concentration based on known amount spiked

To be acceptable, LCS recovery must be between 90% and 110% (aqueous matrix) and 85% and 115% (soil matrix) of the expected concentration..

11.4 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE

Matrix spikes (MSs) consist of representative field samples into which known concentrations of target analyte(s) are spiked. MSs are analyzed as a means of determining the effect of matrix on target analyte detection.

The matrix spike is prepared in duplicate (MSD) to serve as a laboratory duplicate, which is analyzed to measure the precision of the analysis.

Analyte recovery for the MS/MSD pair is calculated as shown below:

$$\%R = \frac{\text{Concentration}_{Found} - \text{Concentration}_{Sample}}{\text{Concentration}_{Target}} \times 100$$

where:

$Conc_{Found}$ = analyte concentration found in the MS or MSD
$Conc_{Sample}$ = analyte concentration found in the native field sample
$Conc_{Target}$ = analyte concentration anticipated based on known amount spiked

The advisory quality control limits for MS/MSD recovery are set at 85-115%.

Precision is evaluated as the Relative Percent Difference (RPD) between a sample and it's duplicate. RPD is calculated as shown below:

$$RPD\ (\%) = \frac{|\ Result_x - Result_{Dup}\ |}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

The RPD should be $\leq$15% to be accepted.

Advisory acceptance criteria for all spikes and duplicates should be met. If MS/MSD recovery or RPD criteria are not met, the result of the LCS analyses must be carefully considered. If the LCS results are acceptable, sample matrix interference is suspected and a notation n the narrative comments is made.

11.5 Note that performance of a method detection limit (MDL) study, is not applicable to this procedure.

12. DEVIATIONS FROM METHOD

12.1 Section 6.0 of Method 340.2 and Section 3.0 of SM4500-F C refer to distilled water for the preparation of standards and reagents. Paragon uses deionized (DI) water generated by the in-house laboratory deionization system. It has been demonstrated (through PT sample analysis, etc.), that Paragon's DI water is free of F^-, and meets the requirements of ASTM Type I and II water.

12.2 Paragon's stock and calibration standards are made in concentrations that differ somewhat from those described in Section 6.0 of Method 340.2 and Section 3.0 of SM4500-F C. Both Methods cite approximately 0.1 to 10mg/L F^- or greater (up to 1000mg/L) as the Method's operational range. Paragon standards bracket a range of approximately 0.5 to 20mg/L F^-.

12.3 The volume of reagents created or sample aliquots processed may differ from the amounts depicted in the Method references. Component ratios remain the same. These changes were implemented for waste minimization purposes.

12.4 Section 7.0 of Method SW9214 states that the ISE solution should be changed if the electrode has not been used for a week. Per manufacturer's instruction, Paragon checks the ISE and adds solution as needed before each use. The ISE solution is changed on an as needed basis.

12.5 Section 7.0 of Method SW9214 states that the ISE should be conditioned in a 10.0mg/L fluoride solution for 24 hours before each use. Paragon conditions the ISE prior to use using aliquots of low and high standard (or a range of standards), containing TISAB.

12.6 Section 8.5 of Method SW9214 states that the acceptance limits for matrix spiked recovery must be 75-125%, and if these criteria are not met, the sample must be analyzed using the method of standard additions. Paragon observes matrix spiked advisory limits of 85-115% and does not employ the method of standard additions.

12.7 As described in Method SW9214, solid matrix samples may also be analyzed by this procedure by first creating an aqueous sample extract. Section 8 of this SOP describes the solid preparation procedure. Paragon notes that Method EPA 340.2 is applicable to the measurement of fluoride in drinking, surface and saline waters, domestic and industrial wastes (Section 1.1).

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 SAFETY AND HAZARDS

13.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

13.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

13.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

13.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

13.1.5 All flammable compounds must be kept away from ignition sources.

13.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

13.1.7 Food and drink are prohibited in all lab areas.

13.2 WASTE DISPOSAL

13.2.1 The aqueous solutions generated by the analyses or the aqueous supernatant of solid samples shall be disposed of in the Aqueous Laboratory Waste.

13.2.2 The solid residues are to be disposed of the Contaminated Soils and Solids Waste.

13.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

13.2.4 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Waste Management Officer will provide specific procedures and materials for these samples.

14. REFERENCES

14.1 A.P.H.A., A.W.W.A. and W.P.C.F., 1989. Standard Methods for the Examination of Water and Wastewater, 18th edition, Revised 1992, "Method 4500-F- C. Ion-Selective Electrode Method".

14.2 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1974, Method 340.2, "Fluoride, Potentiometric, Ion Selective Electrode".

14.3 U.S. Environmental Protection Agency, SW846, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, Method 9214, "Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode". Revision 0, December 1996.

14.4 Orion Research, Inc. 1991. Instruction manual for Model 94-09, 96-09 fluoride/combination fluoride electrodes.

DOCUMENT REVISION HISTORY

2/9/04: Updated format.

7/26/05: Added reference Program Specification directive in "Responsibilities".

4/10/06: Added 10,000mg/L Fluoride Stock Solution to Section 6. Added DOCUMENT REVISION HISTORY.

7/18/08: Minor clerical corrections. TISAB shelf-life (6.5) changed from indefinite to 1yr. Nuance to 'measure twice' added to 9.6. MDL discussion clarified/updated.

Analytical Method: E 340.2; SW9214; SM4500-F C	**Parameter:** Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point (plus blank); first source	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria)	Correlation coefficient (r^2) for linear regression must be $\geq$0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification (ICV); second source	Once after each initial calibration; concentration different from CCV; at or below midpoint of curve	Response must agree within $\pm$10% of expected value	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV); first source	Run after every ten samples and to end any run sequence (must be followed by a CCB analysis); at or below midpoint of curve	Response must agree within $\pm$10% of expected value	Check that calculations and preparation are correct, evaluate/ correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Blanks: Method Blank (MB), Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	The MB may be run initially as part of the calibration curve, the ICB is run following the calibration curve. CCBs are run following the CCV (after every ten samples), and to close an analytical run sequence	Fluoride content of the blank must not exceed reporting limit (RL); RL usually 0.5mg/L F^-	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Laboratory Control Sample (LCS)	Matrix specific. One LCS must be prepared and analyzed per $\leq$20 environmental samples of similar matrix	Results must agree within $\pm$10% of expected value for aqueous sample analyses; within $\pm$15% for solid matrix extract analyses	Check all calculations. If no computation errors are found, prepare a fresh LCS and analyze. If criteria are still not met, system must be recalibrated and all samples associated with the failed LCS must be reanalyzed.
Matrix Spike (MS)	One per batch of $\leq$20 field samples	Recoveries should meet advisory limits of $\pm$15% of the expected values; client-specified criteria may apply	Compare with LCS results and check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike (laboratory) Duplicate	One per batch of $\leq$20 field samples of similar matrix	(See MS recovery criteria above) RPD advisory limit is $\leq$15; client-specified criteria may apply	(See MS recovery criteria above). For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1106 REVISION 7

TITLE: BICARBONATE, CARBONATE, HYDROXIDE AND TOTAL ALKALINITY BY TITRATION -- METHODS EPA 310.1 AND SM2320B

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER Steve Workman DATE 7/21/08

QUALITY ASSURANCE MANAGER Deb Zaheta DATE 7/20/08

LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: Rev0, PCN #286, 12/6/94; Rev1, 9/22/99; Rev2, 1/10/02; Rev3, 12/17/02; Rev4, 2/13/04 (format updated) and 3/25/05 (re-released without revision); Rev5, 7/26/05; Rev6, 4/10/06; Rev7, 7/18/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- USEPA Method 310.1 and Standard Method SM2320B -- are used to determine alkalinity in environmental water samples. By titrating to two endpoints (i.e., pH 8.3 and pH 4.5), the alkalinity can be speciated into bicarbonate (HCO_3^-), carbonate ($CO_3^=$), and hydroxide (OH^-). For each constituent, the results of the analysis are expressed as mg $CaCO_3$/L. These procedures are suitable for determining all concentration ranges of alkalinity, however, sample size used should be evaluated to avoid requiring titration volumes greater than 100mL.

2. SUMMARY

The alkalinity of a water sample is its quantitative capacity to neutralize a strong acid to a designated pH. The measured alkalinity, therefore, depends on the endpoint pH used. For most surface waters, alkalinity is primarily a function of bicarbonate (HCO_3^-), carbonate ($CO_3^=$), and hydroxide (OH^-) content. The concentration of these constituents can be calculated when the sample is titrated to two endpoints, pH 8.3 and pH 4.5.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or by the successful analysis of a proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy and completeness and is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

NOTE: ***The sample may not be altered in any way to remove interferences.***

4.1 Soaps, oily matter, suspended solids, or precipitates may cause a sluggish response with the pH meter or make colored indicators difficult to see. It may be necessary to allow additional time between titrant additions to let the electrode come to equilibrium.

4.2 Substances, such as salts of weak acids, present in large amounts may cause interferences in the electrometric pH measurements.

4.3 Samples with high concentrations of mineral acids (e.g., mine wastes and associated receiving waters), should be analyzed by alternative methods (such as ASTM D-1067).

5. APPARATUS AND MATERIALS

5.1 Beakers, Pyrex™, 150mL

NOTE: *An appropriate beaker size which keeps the air space above the solution to a minimum should be used.*

5.2 Pipettes, plastic transfer

5.3 Volumetric flasks, Class A, 500mL and 1L

5.4 Top loading balance capable of reading to 0.01g, and verified per SOP 305

5.5 Accumet pH/mV Meter 50, or equivalent, capable of reading to ± 0.05 pH units

5.6 pH electrode, glass, combination style with reference electrode contained within probe body

5.7 Magnetic stir plate

5.8 Magnetic stir bars, Teflon-coated

5.9 Adjustable Eppendorf™ Pippette (or equivalent), capable of delivering 1.0mL; *operate observing requirements contained in SOP 321*.

6. REAGENTS

6.1 Deionized (DI) water.

6.2 pH Buffers (4.01, 7.00, 10.01): Orion 910104, 910107, 910110 or equivalents (first source); RICCA Chemical Co. #1551-16 or equivalent (second source). Store in polypropylene. *Shelf life = 1 year.*

6.3 Phenolphthalein Indicator Solution: VWR, Cat. No. VW3341-2 or equivalent. Store in polypropylene. *Shelf life = 1 year.*

6.4 Bromocresol Green Indicator Solution: EM Science, 2800 or equivalent. Dissolve 0.5g of bromocresol green sodium salt in 500mL of DI water. Store in polypropylene. *Shelf life = 1 year.*

6.5 Hydrochloric Acid (HCl), 0.1N: JT Baker, 9530-33 (concentrated) or equivalent. Purchased from a commercial vendor or made in-house by diluting 8.3mL of concentrated HCl to 1L with DI water. Store in polypropylene. *Shelf life = 1 year or until degradation is evident.*

6.6 Hydrochloric Acid (HCl), 0.02N: Purchased from a commercial vendor or made in-house by diluting 200mL of 0.1N HCl to 1L with DI water. Standardization of this solution is carried out for each usage by titrating against the standard base (i.e., THAM). Store in polypropylene. *Shelf life = 1 year or until degradation is evident (i.e., same a parent, above).*

6.7 Tris(hydroxymethyl)aminomethane (THAM), 0.20N: JT Baker, 4099-06 or equivalent. Dry about 15g primary standard THAM at about 100°C for 1-2 hours and cool in a desiccator. Transfer 12.114g of the dried THAM to a 500mL volumetric flask. Add 200-300mL of DI water to the flask and swirl to dissolve the salt. Fill to the mark with DI water and mix thoroughly. Store in polypropylene. *Shelf life = 1 year.*

6.8 Sodium Carbonate Standard Solution (Na_2CO_3), 0.20N: JT Baker, 3604-01 or equivalent. Dry about 10g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Transfer 5.300g of the dried Na_2CO_3 to a 500mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in polypropylene. *Shelf life = 1 year.*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples may be collected in either plastic or glass containers and must be collected according to an approved sampling plan. The sample containers should be filled as full as possible to minimize headspace.

7.2 Water samples should be kept refrigerated (0-6°C) from the time of collection until analysis. The samples must be analyzed within 14 days after collection.

8. PROCEDURE

8.1 STANDARDIZATION OF TITRANT

8.1.1 Calibrate the pH meter according to manufacturer's instructions by using pH buffers 4.01, 7.00 and 10.01. On the Accumet 50 pH meter, push "standardize" on the meter and select choice #2, "clear existing standards". Place the probe in first pH buffer, push "standardize" and select choice #1, "update or add standard". Enter buffer value and push "ENTER". Let the probe sit in the buffer solution for 1-2 minutes, then push enter. Repeat these steps for next two buffers concentrations. Discard the buffer aliquots after each day's use.

8.1.2 Pipette 1.00mL of 0.20N THAM into a 150mL beaker containing 100mL DI water. Add a stir bar, and approximately 2mL bromocresol green indicator. Place the beaker + contents on the laboratory balance and tare the balance.

8.1.3 Place the beaker + contents on a stir plate. Adjust the stir plate control so that the beaker's contents mixes slowly.

8.1.4 Place the pH probe in the beaker. Using the pH meter and color indicator as reference points, titrate to a pH of 4.5 by adding 0.02N HCl dropwise. When the color of the solution turns from blue to green, the endpoint has been reached. Place the beaker + titrated contents on the balance and record the weight of the titrant used on the LIMS benchsheet.

8.1.5 Repeat Steps (8.1.2 - 8.1.4) twice more for a total of three standardization replicates. The average of the standardization results will be calculated to determine the titrant's concentration.

NOTE: Because people see colors/interpret endpoints differently, Paragon policy is that the same analyst who standardizes the acid, analyzes the samples.

8.2 TITRATION OF SAMPLES

NOTE: Allow all samples to come to room temperature before preparation and analysis.

8.2.1 Place a 150mL beaker containing a stir bar on the top loading balance. Tare the balance. Gravimetrically pipet a 100mL aliquot of sample (or less if a smaller sample size is required) into the beaker. Record the sample volume on the benchsheet. If less than a 100mL aliquot of sample is used, bring to a final gravimetric volume of 100mL with DI water.

8.2.2 With the beaker + contents still on the balance, add 1-2 drops of phenolphthalein solution. If the pH of the beaker's contents is greater than 8.3, the contents will turn pink in color. Re-tare the balance.

NOTE: If no pink color appears initially upon the addition of phenolphthalein (swirl beaker to mix contents), add approximately 2mL bromocresol green indicator solution. Re-tare the balance and proceed to Step 8.2.5.

8.2.3 Move the sample beaker to the stir plate and submerge the pH probe in the sample solution. Adjust the stir control so that the beaker's contents mix slowly.

8.2.4 Add 0.02N HCl dropwise to the prepared sample beaker until the solution turns clear and the pH meter reads 8.3. Place the beaker with titrated sample on the top loading balance and record the amount of titrant used on the bench sheet. Add approximately 2mL bromocresol green indicator solution; re-tare the balance.

8.2.5 Place the beaker + contents containing the bromocresol green indicator on the stir plate; submerge the pH probe in the sample solution. Titrate by adding 0.02N HCl dropwise until the color of the sample solution turns from blue to green and pH meter reads 4.5.

8.2.6 Move the beaker and titrated contents to the top loading balance and record the amount of titrant used on the bench sheet.

NOTE: Rinse the pH probe with DI water between each sample solution processed.

8.2.7 Laboratory Duplicate (DUP): Select one sample per batch of 20 or less field samples processed as a unit, and prepare a second aliquot of that sample to serve as the laboratory duplicate. Process as described in Steps 8.2.1 through 8.2.6 above.

8.2.8 Initial Calibration Verification (ICV); Laboratory Control Sample (LCS); Continuing Calibration Verification (CCV): Prepare this check sample by transferring 1.00mL of 0.20N sodium carbonate standard solution to a 150mL beaker containing a stir bar; dilute to 100mL with DI water. Titrate as described in Steps 8.2.1 through 8.2.6.

The ICV aliquot is analyzed at the beginning of each day's analysis following standardization of the HCl titrant. One LCS is to be analyzed per batch of 20 or less field samples processed as a unit. If more than twenty field and quality control (QC) samples are analyzed, the analysis of one CCV must follow.

8.2.9 Blanks - Initial Calibration Blank (ICB); Method Blank (MB); Continuing Calibration Blank (CCB): Aliquot 100mL of DI water into a 150mL beaker. Prepare and titrate as described in Steps 8.2.1 through 8.2.6.

Blanks are run to demonstrate that interferences from the analytical system, glassware and reagents are under control. Analyze one blank (ICB) following the ICV. Analyze one blank per batch of twenty or less field samples processed as a unit (MB). A CCB must follow each CCV analyzed.

NOTE: When reporting laboratory quality control sample results, report as Total Alkalinity.

8.2.10 ANALYTICAL RUN SEQUENCE
The alkalinity determinations should be run in the following sequence:

1. ICV
2. ICB
3. MB
4. LCS
5. DUP
6. 17 field samples

If more than 17 field samples are analyzed, the sequence must continue as follows:

7. CCV
8. CCB
9. - 11. three more field samples (from same batch)

If a second batch of samples is to be analyzed, the sequence repeats beginning with a MB, LCS, DUP, 14 field samples, CCV/CCB, etc.

8.3 CALCULATIONS

8.3.1 CALCULATION OF HCL TITRANT

$$C_{HCl} = \frac{(C_{THAM})(V_{THAM})}{V_{HCl}}$$

where:

C_{HCl} = concentration of HCl titrant, N or eq/L
C_{THAM} = concentration of THAM standard, N or eq/L; (equals 0.20N if preparation is followed without deviation)
V_{THAM} = volume (mL) of THAM standard titrated; (equals 1.0mL if SOP is followed without deviation)
V_{HCl} = volume (mL) of HCl titrant required to reach endpoint

Therefore:

$$C_{HCl} = \frac{(0.20\ N)(1.0mL)}{V_{HCl}}$$

Average the results of the three replicate standardizations to calculate the HCl titrant concentration.

8.3.2 CALCULATION OF ALKALINITY

$$C_{Alk} = \frac{(C_{HCl})(V_{HCl}) \times 50{,}000}{(V_S)}$$

where:

C_{Alk} = concentration of alkalinity (in sample), mg $CaCO_3$/L
C_{HCl} = concentration of HCl titrant, N or eq/L
V_{HCl} = volume (mL) of HCl titrant required to reach endpoint
V_S = volume (mL) of sample titrated
50,000 = conversion factor (eq/L to mg $CaCO_3$/L)

8.3.3 To speciate the alkalinity in terms of bicarbonate (HCO_3^-), carbonate ($CO_3^{=}$) and hydroxide (OH^-), the following relationships are used:

Result of Titration (as $CaCO_3$)	Hydroxide Alkalinity (as $CaCO_3$)	Carbonate Alkalinity (as $CaCO_3$)	Bicarbonate Alkalinity (as $CaCO_3$)
P = 0	0	0	T
P < 1/2T	0	2P	T-2P
P = 1/2T	0	2P	0
P > 1/2T	2P-T	2(T-P)	0
P = T	T	0	0

where:

P = volume of acid required to reach phenolphthalein endpoint
T = total volume of acid required to reach bromocresol green endpoint

$$[HCO_3^-] = \frac{(T - 2P)(C_{HCl}) \times 50{,}000}{(V_S)}$$

$$[CO_3^{=}] = \frac{(2P)(C_{HCl}) \times 50{,}000}{(V_S)} \quad \textit{when } P \leq 1/2\ T$$

$$[CO_3^{=}] = \frac{2(T-P)(C_{HCl}) \times 50{,}000}{(V_S)} \quad \textit{when } P > 1/2\ T$$

$$[OH^-] = \frac{(2P - T)(C_{HCl}) \times 50{,}000}{(V_S)} \quad \textit{when } P > 1/2\ T$$

$$[OH^-] = \frac{(T)(C_{HCl}) \times 50{,}000}{(V_S)} \quad \textit{when } P = T$$

NOTE: In all cases, the concentration is reported as mg $CaCO_3$/L.

9. QUALITY CONTROL (QC)

9.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or less field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB; *or initial calibration blank, ICB or continuing calibration blank, CCB*), laboratory duplicate (DUP) and laboratory control sample (LCS; *or initial calibration verification standard, ICV or continuing calibration verification standard, CCV*). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

9.2 BLANKS

Blanks are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank (MB) should be processed. Three types of blanks exist for this procedure - MB, initial calibration blank (ICB) and continuing calibration blank (CCB). The ICB is run following the ICV. A CCB must be run following each CCV analyzed. All blanks consist of 100mL DI water. The blank concentration found must be less than the reporting limit (usually 5mg $CaCO_3$/L).

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. It consists of an aliquot of clean matrix (in this instance, 100mL DI water), into which a known amount of analyte is spiked (see Step 8.2.8). For this method, the same spike process is used to create the Initial Calibration Verification (ICV) standard and the Continuing Calibration Verification (CCV). The ICV aliquot is analyzed at the beginning of each day's analysis following standardization of the HCl titrant. One LCS is to be analyzed per batch of 20 or less field samples processed as a unit. If more than twenty field and QC samples are analyzed, the analysis of one CCV must follow (refer to Step 8.2.10 - Analytical Run Sequence).

Results obtained for these check samples are compared to results expected. The mathematical evaluation is expressed as percent recovery, %R, calculated as follows:

$$\%R = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Target}}} \times 100$$

To be acceptable, percent recovery must be between 85% and 115% of the expected concentration.

9.4 LABORATORY DUPLICATE

A second aliquot of one sample per batch of twenty (20) or less field samples processed as a unit is prepared and analyzed as a laboratory duplicate. The laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. The duplicate results are compared mathematically (shown below), with the precision expressed as Relative Percent Difference (RPD)

$$\text{RPD (\%)} = \frac{|\ \text{Result}_x - \text{Result}_{Dup}\ |}{\frac{(\text{Result}_x + \text{Result}_{Dup})}{2}} \times 100$$

For this procedure, the RPD should not be greater than 15%.

10. DEVIATIONS FROM METHOD

10.1 Section 5.1 of Method EPA 310.1 and Section 3a of Method SM2320B describe the creation of 0.05N sodium carbonate (Na_2CO_3) standard solution. This SOP provides for a sodium carbonate standard solution that is approximately 4 times stronger (0.20N).

10.2 As described in Section 5.2 of Method E310.1 and Section 3b of Method SM2320B, Paragon does not boil the sodium carbonate (Na_2CO_3) standard solution aliquot during standardization of the 0.1N and 0.02N HCl standard acid solutions. Further, Paragon standardizes the 0.02N HCl with THAM, as described in Section 8.1 of this SOP. The successful completion of proficiency testing (PT) studies has demonstrated that these practices do not affect the accuracy of the pH results generated.

10.3 As described in Section 6.3.2 of Method E310.1 and in the General Discussion of Method SM2320B, for low alkalinities (those less than 20mg $CaCO_3$/L), Paragon does not determine the equivalence endpoint by continuing the titration of the 4.5 pH endpoint to determine the amount of standard acid required to reduce pH by exactly 0.30 pH units.

10.4 Both Method E310.1 and SM2320B recommend analysis as soon as possible. Paragon strives to analyze all alkalinity samples as soon as possible after receipt, however, a 14-day from date of collection maximum holding time allowance is allowed (per Table 1 of Methods for Chemical Analysis of Water and Wastes, citation source for Method E310.1).

10.5 In contrast to Section 4b of SM2320B (generation of a potentiometric titration curve), Paragon uses a series of pH buffers (4.01, 7.00 and 10.01) to standardize the pH meter.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire

extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The aqueous solution left over from the titration shall be disposed of in the Aqueous Laboratory Waste satellite collection vessel.

11.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

11.2.3 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Health and Safety Officer will provide specific procedures and materials for these samples.

12. REFERENCES

12.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1983. Method 310.1, "Alkalinity (Titrimetric, pH 4.5)".

12.2 A.P.H.A., A.W.W.A. and W.P.C.F., Standard Methods for the Examination of Water and Wastewater, 20th edition, pp 2:26-29, 1998. Method 2320B, "Alkalinity".

12.3 Elementary Quantitative Analysis, Theory and Practice, W. J. Blaedel and V. W.

Meloche, 2nd edition, 1963, Harper & Row, New York, p. 794.

DOCUMENT REVISION HISTORY

2/13/04: Updated format.

7/26/05: Added reference Program Specification directive in "Responsibilities".

4/10/06: Added DOCUMENT REVISION HISTORY.

7/18/08: Minor clerical corrections. Policy note added to 8.1.

Analytical Method: E310.1; SM2320B	**Parameter:** Alkalinity		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Calibration: Analyte content is determined by direct concentration (obtained by calculation from titration) The titrant is standardized each day of use.	Daily; each day of use	Titrant must calculate to be between 0.18-0.22 N	If titrant does not meet concentration criteria; prepare fresh and standardize via three replicate analyses.
Initial Calibration Verification (ICV); run within the established range of the method	Daily; each day of use	Results for the ICV must agree within ±15% of the expected (true) value	If ICV criterion not met, check for preparatory and calculation errors; remake and reanalyze. If ICV criterion is still not met, prepare titrant fresh and standardize via three replicate analyses. Reanalyze ICV.
Continuing Calibration Verification (CCV); run within the established range of the method	Run to bracket each batch of environmental samples processed	Results for the CCV must agree within ±15% of the expected (true) value	If CCV criterion not met, check for preparatory and calculation errors; remake and reanalyze. All samples run since the last acceptable CCV must also be reanalyzed.
Blanks: Method Blank (MB), Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB)	One MB per each batch of ≤20 field samples and each time a reagent is changed. One ICB run immediately following ICV. One CCB run following each CCV analysis	No blank's alkalinity may exceed the reporting limit (RL); RL usually 5mg $CaCO_3$/L	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All associated samples must also be reanalyzed.
Laboratory Control Sample (LCS)	One per batch of ≤20 field samples	Results obtained must agree between 85% and 115% of expected (known) alkalinity concentration	Check calculations and preparation for documentable errors. If no errors are found, remake and reanalyze. All associated samples must also be reanalyzed.
Laboratory Duplicate (DUP)	One per batch of ≤20 field samples	RPD must be ≤15%	Check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1110 REVISION 12

TITLE: **DETERMINATION OF TOTAL AND AMENABLE CYANIDE (DISTILLATION) -- METHODS SW9010B, SW9013, SW9014, EPA 335.1, EPA 335.2 AND CLP INORGANIC SOW (ILMO4.0)**

DETERMINATION OF WEAK AND DISSOCIABLE CYANIDE – METHOD SM4500-CN I

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/19/07
QUALITY ASSURANCE MANAGER _____ DATE 1/19/07
LABORATORY MANAGER _____ DATE 1-19-07

HISTORY: Rev0, 3/27/96; Rev1, 8/15/97; Rev2, 3/3/00; Rev3, 1/10/02; Rev4, 3/2/02; Rev5, 12/18/02; Rev6, 2/9/04; Rev7, 4/21/04; Rev8, 5/21/04; Rev9, 8/25/04; Rev10, 4/10/06; Rev11, 7/5/06; Rev12, 1/19/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- SW9010B, SW9013, SW9014; EPA 335.1, EPA 335.2; the CLP Inorganic SOW ILMO4.0; and SM4500-CN I -- describe procedures to extract and quantify cyanide in waters, soils, and various wastes and waste leachates. Cyanide that is present either as soluble salts or in complexed forms is detected.

Total cyanide, total cyanide extractable from solids and oils, cyanide amenable to chlorination, and/or weak and dissociable cyanide can be determined by the procedures outlined in this SOP. These procedures are written to address trace analyses (cyanide concentrations <1000ppm), but may also be used to determine minor (1000-10,000ppm) and major (>10,000ppm) concentrations of cyanide by adapting the sample preparation techniques (e.g., employment of sample dilution) or determinative techniques (e.g., use of the titration procedure provided for in Methods EPA 335.2, SW9010B and SW9014, in lieu of colorimetric development, where cyanide concentrations are significant).

Procedures presented in the CLP Inorganic SOW ILMO4.0 are based on total cyanide Method EPA 335.2. The CLP Inorganic SOW also provides for the direct analysis (i.e., without extraction) of solid matrix samples. The extraction procedure for total cyanides in solid or oil matrices contained in this SOP references Method SW9013. The reflux-distillation preparation for liquid samples or extracts described by this SOP references Methods SW9010B and EPA 335.2. The spectrophotometric determination of cyanide described herein references Methods SW9010B, SW9014 and EPA 335.2.

Procedures for the determination of cyanide amenable to chlorination contained in this SOP reference Methods SW9010B and EPA 335.1. The procedures for the determination

of weak and dissociable cyanide described by this SOP reference Method SM4500-CN I.

2. SUMMARY

Cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation process conducted under acidic conditions. The released cyanide is absorbed in a scrubber containing sodium hydroxide (NaOH) solution. It is critical that the amount of sodium hydroxide solution in the scrubber is the same for all standards and samples processed. The amount of cyanide contained in this basic scrubber solution is then determined colorimetrically. The colorimetric reaction involves the formation of cyanogen chloride (CNCl) by reaction with chloramine-T. It is essential that the same amount of chloramine-T is added to all standards and samples processed. Then pyridine-barbituric acid is added as a color development reagent. The colored complex is detected by measuring absorbance at 578nm with a spectrophotometer. Methods SW9010B, SW9014 and EPA 335.2 alternately provide for the use of pyridine-pyrazolone (instead of pyridine-barbituric acid) as the color development reagent. If pyridine-pyrazolone is used, the time required for color development is longer (40 minutes rather than 8 minutes) and the samples must be read at 620nm (rather than 578nm).

To determine cyanide amenable to chlorination, two sample aliquots (one carried through a chlorination process, and one that is not) are processed. The amount of cyanide amenable to chlorination is determined by calculation (i.e., amount CN present in unchlorinated aliquot - amount CN remaining in chlorinated aliquot).

Liquid samples or extracts for determination of weak and dissociable cyanide are prepared by distillation under less acidic conditions than those established for total and amenable cyanide determination. Different preparatory reagents are also used. Colorimetric reaction, development and reading are the same as with total and amenable cyanide determination.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the preparation and analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, and/or the successful analysis of a proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon’s standard

criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or qualified designee. Initialing and dating the file indicate that this review for precision, accuracy and completeness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these methods to note any anomalies or out-of-control events associated with the handling, preparation or analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Oxidizing agents such as chlorine decompose most cyanides. Interference from chlorine can be removed by adding an excess of sodium arsenite ($NaAsO_2$) to the sample prior to preservation and storage. Sodium arsenite reduces the chlorine to chloride, which does not interfere. Alternatively, an excess of ascorbic acid may be used to remove the residual chlorine.

4.2 Sulfides interfere by producing hydrogen sulfide (H_2S) during distillation. Sulfide interference can be removed by adding an excess of bismuth nitrate [$Bi(NO_3)_3$] to the sample before distillation (to precipitate the sulfide). Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation, should be treated by the addition of bismuth nitrate.

4.3 Nitrate and nitrite at levels higher than 10mg/L may react with some organic compounds to generate hydrogen cyanide (HCN) yielding high results. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds, once formed, will decompose under test conditions to generate HCN. The possibility of interference from nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation.

4.4 Thiocyanate has been reported to be an interference when present at very high levels. Concentrations of 10mg/L were not found to interfere.

4.5 Where titration (rather that colorimetric development) is used as the determinative step, fatty acids, detergents, surfactants, and other compounds may interfere. When these substances are present in large concentrations, foaming may occur during distillation, thus making the endpoint of the titration difficult to detect.

Section 6.8 of Method SW9010B and Section 5.3 of Method EPA 335.2 describe procedures for the removal of these interferent substances.

4.6 Some unidentified organic chemicals may oxidize or form breakdown products during chlorination, yielding higher results for cyanide *after* chlorination than before chlorination. This may lead to a negative value for cyanides amenable to chlorination after distillation for some wastes (e.g., steel industry, petroleum refining, pulp and paper processing). Method 4500CN I (Dissociable Cyanide) is recommended where these interferences occur.

4.7 Some metal-cyanide complexes may be sensitive to ultraviolet light. Sample processing under incandescent light is recommended to prevent photodecomposition.

5. APPARATUS AND MATERIALS

5.1 Midi-Dist™ cyanide distillation system, Model 110-10R or equivalent, containing Midi glassware (e.g., reflux impingers, tubes and cold fingers; absorption impingers and tubes), all connective tubing, a flow meter and a heating block

5.2 vacuum source for operation of the Midi-Dist™ system

5.3 water source for operation of the Midi-Dist™ system

5.4 spectrophotometer, Sequoia-Turner, Model 340 or equivalent

5.5 cuvettes, optically matching, 1 inch diameter, Bausch & Lomb or equivalent

5.6 cuvette stand

5.7 analytical balance, capable of weighing to 0.0001 gram

5.8 top-loading balance, capable of weighing to 0.01 gram

5.9 volumetric flasks, glass, Class A, 100mL, 500mL and 1L sizes

5.10 magnetic stir plate

5.11 magnetic stir bars, Teflon™-coated

5.12 pipets, variable Eppendorf™ or equivalent and disposable pipet tips

5.13 pipets, plastic, disposable

5.14 beakers, glass, 250mL

5.15 beakers, plastic, disposable, 100mL

5.16 pH paper, narrow-range (acidic) and narrow-range (basic), or wide-range (0-14)

5.17 indicator paper, KI-starch

5.18 test paper, lead acetate

5.19 centrifuge tubes, 50 and 250mLs, disposable (used in the extraction of cyanide from solid and oil matrices)

5.20 centrifuge, capable of producing 3500rpm rotation

5.21 tumbler, rotary

5.22 filtration apparatus (vacuum pump, funnel, filter discs or glass wool)

6. REAGENTS AND STANDARDS

6.1 reagent water, laboratory deionized (DI)

6.2 clean silica sand

6.3 ascorbic acid, reagent grade, fine powder

6.4 Sodium hydroxide solution, 10N: Used for sample preservation and pH adjustment during sample preparation. Dissolve 40g NaOH in a final volume of 100mL using DI water. Shelf Life = 1 year.

6.5 Calcium hypochlorite solution, 0.35M: Used in determining cyanide amenable to chlorination. Use DI water to dissolve 5g $Ca(OCl)_2$ and bring to full volume in a 100mL Class A volumetric flask. **Store in an amber bottle; shake well before using**. Shelf Life = 1 month.

6.6 Magnesium chloride solution, 2.5M, 51% (w/v): Used as an anti-foaming agent during distillation. Obtained from a commercial vendor or made in-house by dissolving 510g $MgCl_2 \bullet 6H_2O$ in DI water and bringing to full volume in a 1L Class A volumetric flask. Shelf Life = 1 year.

6.7 Bismuth nitrate solution, 0.062M: Used prior to distillation to remove sulfide interferences. Dissolve 30g $Bi(NO_3)_3$ in 100mL of DI water. Add 250mL glacial acetic acid, stir. Bring to full volume in a 1L Class A volumetric flask. Shelf Life = 1 year.

6.8 Sulfamic acid solution, 0.4N: Used for the removal of nitrate/nitrite interferences. Use DI water to dissolve 40g NH_2SO_3H and bring to full volume in a 1L Class A volumetric flask. Shelf Life = 1 year.

6.9 Sodium hydroxide solution, 0.25N: Used as the scrubber solution and scrubber solution diluent; also used to prepare the working calibration standards. Dissolve 10g NaOH in a final volume of 1L using DI water. Shelf Life = 1 year.

6.10 Sulfuric acid solution 18N, 50% (v/v): Used to establish acidic conditions for distillation. Carefully add 100mL concentrated H_2SO_4 to 100mL DI water. Shelf Life = 1 year.

6.11 Sodium phosphate monobasic buffer solution, 1M: Dissolve 138g of $NaH_2PO_4 \bullet H_2O$ in 1L of DI water. ***Refrigerate.*** Shelf Life = 1 year.

6.12 Standard silver nitrate titrant, 0.0192N: Obtained from a commercial vendor or prepared in-house. Use DI water to dissolve 3.2647g dried $AgNO_3$ and bring to full volume in a 1L Class A volumetric flask. Shelf Life = 1 year.

6.13 p-Dimethylaminobenzalrhodanine indicator, reagent grade: Obtained from a commercial vendor or made in-house by dissolving 0.020g p-dimethylamino-benzalrhodanine in a final volume of 100mL acetone (spectral grade). Shelf Life = 1 year.

6.14 Stock potassium cyanide standard, 1000mg/L CN: Use 0.25N NaOH solution to dissolve 0.2504g potassium cyanide (KCN) salt and bring to final volume in a 100mL Class A volumetric flask. ***Refrigerate.*** Shelf Life = 1 year.

NOTE: ***Two stock solutions (one each) are prepared from two independent sources of KCN salt (i.e., "first source" and "second source").***

The concentration of each of the stock potassium cyanide standard solutions (i.e., **first source** and **second source**) must be verified when made. Use the standardization procedure following to verify the stock solutions (*Note: this titration standardization procedure is detailed in SM4500-CN D)*:

6.14.1 Transfer 10.0mL of potassium cyanide stock standard to a 250mL beaker. Dilute to about 100mL using DI water.

6.14.2 Add a few drops of the p-dimethylaminobenzalrhodanine indicator solution.

6.14.3 Add a clean magnetic stir bar to the beaker and place the beaker + contents on the analytical balance; tare the balance.

6.14.4 Put the beaker + contents on a magnetic stir plate. Begin agitation.

6.14.5 Titrate with 0.0192N $AgNO_3$, adding dropwise, to the first change in color (i.e., from yellow to salmon). Reweigh the beaker + contents and record the weight change in the appropriate logbook (weight change equals amount of titrant added).

6.14.6 Titrate three replicate aliquots for each stock standard and average the results for each.

6.14.7 An aliquot of DI water (DI water blank) is also titrated according to the procedure described above.

6.14.8 Use the average result obtained for each stock standard to calculate the CN concentration as follows:

$$\text{mg } CN^- / L = \frac{(A - B) \times 1000^*}{C}$$

where:

A = mL standard 0.0192N $AgNO_3$ required for aliquot of stock

B = mL standard 0.0192N $AgNO_3$ required for DI water blank

C = mL CN- stock standard titrated**

* NOTE: 1.0mL 0.0192N $AgNO_3$ = 1.0mg CN^-

** (C = 10.0mL, if this SOP is followed without deviation)

6.14.9 The titration verification must yield results within ±2% (i.e., between 980 and 1020mg/L CN) in order for the stock standards to be acceptable. If this criterion is not met, the stock standards must be remade.

6.15 Intermediate potassium cyanide standard solution, 10mg/L: Add 1.00mL of 1000mg/L cyanide stock solution to 99.00mL of 0.25N NaOH. ***Store in a refrigerator (4±2°C).*** *Shelf Life = 3 months.*

NOTE: ***Prepare intermediate potassium cyanide standards from both of the first and second source stock KCN standard solutions. The first source 10mg/L intermediate potassium cyanide standard solution is used to spike the MS/MSD samples and to create the low and high distillation check standards. The second source 10mg/L intermediate potassium cyanide standard solution is used to prepare the ICV standard.***

6.16 See Section 8 for directions for making the daily working calibration standards.

6.17 Chloramine-T solution: Dissolve 1g of chloramine-T in 100mL of DI water. *Prepare fresh each day of use.* ***Refrigerate until ready to use****.*

6.18 Pyridine-barbituric acid solution: Place 7.5g of barbituric acid in a graduated container (i.e., marked at 125mL) and add a minimal amount of DI water necessary to wash the sides of the flask and wet the barbituric acid. Add 37.5mL of pyridine and mix. Add 7.5mL of concentrated HCl, mix and cool to room temperature. Dilute to 125mL with DI water and mix. ***Store in an amber glass bottle and refrigerate.*** *This reagent is stable for about 6 months; if a precipitate forms on the bottom of the container, discard and prepare fresh reagent*

6.19 Methyl red indicator: Used in the determination of weak and dissociable cyanide. Dissolve 0.10g methyl red sodium salt in 100mL of DI water. Shelf Life = 1 year.

6.20 Acetic acid solution, 1:9: Used in the determination of weak and dissociable cyanide. Mix 1 volume of glacial acetic acid with 9 volumes of DI water. Shelf Life = 1 year.

6.21 Acetate buffer: Used in the determination of weak and dissociable cyanide. Dissolve 41.0g sodium acetate trihydrate ($NaC_2H_3O_2 \bullet 3H_2O$) in 50mL DI water. Add glacial acetic acid (approximately 50mL) to yield a solution of pH 4.5. Shelf Life = 1 year.

6.22 Zinc acetate solution, 100g/L: Used in the determination of weak and dissociable cyanide. In a 100mL volumetric flask, dissolve 10g zinc acetate, $Zn(C_2H_3O_2) \bullet H_2O$, and bring to full volume with DI water. Shelf Life = 1 year.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIME

7.1 All samples should be collected according to an approved sampling plan.

7.2 Plastic or glass containers may be used.

7.3 Oxidizing agents, such as chlorine, decompose most cyanide forms. To determine whether oxidizing agents are present, test a drop of sample with KI-starch indicator paper. A blue color indicates the need for treatment. To treat, add 0.1N sodium arsenite ($NaAsO_2$) solution, a few mL at a time, until a drop of sample produces no color on the KI-starch indicator paper. Add an additional 5mL of the 0.1N $NaAsO_2$ solution per each liter of sample. Ascorbic acid can be used as an alternative, although it is not as effective as sodium arsenite. Add a few crystals of ascorbic acid at a time (gently swirl after each addition), until a drop of sample produces no color on KI-starch indicator paper. Then add an additional 0.5g of ascorbic acid powder per each liter of sample volume.

7.4 Aqueous samples must be preserved by adding 2mL of 10N NaOH per L of sample volume (Method EPA 335.2) or sufficient 50% NaOH solution (Methods SW9010B and SM4500-CN B) until the pH of the sample is equal to or greater than 12 at the time of collection.

Carbonate in high concentration may affect the distillation procedure by causing the violent release of carbon dioxide with excessive foaming when reflux-distilled under acid conditions, thereby causing the pH of the absorption solution to be reduced. Calcium hydroxide (CaOH) should be used in lieu of NaOH to preserve samples suspected to contain significant carbonate amounts.

7.5 Samples should be kept cool (i.e., 4±2°C).

7.6 To meet Paragon holding time requirements, analyses must be completed within 14 days of sample collection.

8. PROCEDURE

8.1 EXTRACTION PROCEDURE FOR SOLID SAMPLES - Method SW9013

8.1.1 EXCEPTIONS

8.1.1.1 If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when agitated but mixes so that the solids are entirely suspended, then the sample may be analyzed directly (per Method SW9010B) without an extraction step.

8.1.1.2 The sample may be analyzed directly (without extraction) per Method SW9010B if it is known to contain 50µg/g cyanide or greater. Direct preparation for analysis can be accomplished by placing 1g of sample in the distillation flask and diluting to 50mL with 0.25NaOH.

8.1.2 Samples that contain free water may be filtered and separated into aqueous and solid components. The non-aqueous component may then be extracted and an aliquot of the extract combined with an aliquot of the filtrate in proportion to the composition of the sample (see Method SW9013, Section 7.0 for details). Alternately, the components may be analyzed separately with cyanide concentrations reported for each component.

8.1.3 The solid sample preparation procedure outlined below must be followed for clients requesting SW9013 - Cyanide Extraction Procedure for Solids and Oils. If Method SW9013 preparation for solid samples is not specified, the direct analysis alternative procedure (i.e., 1.0g sample added directly to the Midi-Dist™ apparatus as provided for in the Section 7.0 of the CLP SOW ILMO4.0) may be followed.

8.1.3.1 Place 10g of representative solid sample into a clean, labeled 250mL disposable centrifuge tube.

8.1.3.2 Prepare a method blank (MB) by placing 10g clean sand into a clean, labeled 250mL disposable centrifuge tube.

8.1.3.3 Add 195mL DI water and 5mL of 10N NaOH to each centrifuge tube.

NOTE: If heavy grease is present, 20mL of reagent grade n-hexane may be substituted for 20mL DI water in order to prevent an emulsion from forming.

8.1.3.4 Cap tube and shake for 1 minute. Check pH using indicator paper.

8.1.3.5 If pH <12, add 10N NaOH dropwise until pH is at least 12. Recap tube and shake for 1 minute. Check pH. Repeat this step as necessary until pH does not drop.

8.1.3.6 Place sample tubes into a 2L plastic jar(s) so that they can be placed onto the rotary tumbler. Extract by tumbling for 16 hours.

8.1.3.7 Centrifuge tubes at 3500rpm for 15 minutes or filter the extract using the vacuum pump, buchner funnel and glass fiber filter setup.

8.1.3.8 Proceed with pretreatment for cyanides amenable to chlorination (Section 8.3) or proceed with the distillation and analysis of weak and dissociable cyanide (Section 8.5) or proceed directly with total cyanide analysis (Section 8.4), as applicable.

8.2 VERIFICATION OF AQUEOUS SAMPLE pH

Test the pH of each aqueous field sample by using a clean disposable transfer pipet to place a drop of aliquot onto a piece of pH test paper. Compare the paper's color to the pH packet's color standard chart and determine the sample's pH. Record result on LIMS benchsheet. The sample pH must be 12 or greater. If not, consult with the Project Manager for client direction as to how to proceed.

8.3 PRETREATMENT FOR CYANIDE AMENABLE TO CHLORINATION

8.3.1 Because cyanides amenable to chlorination is determined by subtracting the sample's total cyanides result from the amenable cyanides result, two identical sample aliquots are required to determine cyanides amenable to chlorination. Prepare two 50mL sample aliquots (or sample aliquots diluted to 50mL with DI water), into two labeled 100mL disposable beakers. *Only one of the sample aliquots is subjected to alkaline chlorination.*

A chlorinated batch <u>duplicate</u> (DUP) must also be prepared. Choose one sample per batch of twenty and prepare another 50mL aliquot for alkaline chlorination for that sample.

8.3.2 Dispense 50mL of DI water into a labeled 100mL disposable beaker to serve as the <u>method blank</u> (MB).

<u>NOTE</u>: ***The following procedures must be performed under incandescent light only because $K_3[Fe(CN)_6]$ may decompose under fluorescent light causing a false positive response for cyanide amenable to chlorination. For this reason and because of the possibility of toxic***

gases being evolved, this procedure must be performed in a fume hood.

8.3.3 Place a Teflon™-coated magnetic stir bar into each beaker to be subjected to alkaline chlorination, put the beakers on a stir plate and begin gentle agitation.

8.3.4 Add calcium hypochlorite solution dropwise (while maintaining a pH between 11 and 12 by adding 10N NaOH dropwise) until an excess of chlorine is present -- indicated by KI-starch paper turning blue upon testing. Maintain an excess of chlorine for one hour while gently agitating the sample continuously. Periodically test for excess chlorine with KI-starch paper and add additional calcium hypochlorite as necessary.

Also, periodically test pH using pH test paper to ensure that a pH between 11 and 12 is maintained; add 10N NaOH dropwise as necessary.

8.3.5 After one hour, add 0.05g portions of ascorbic acid until the KI-starch paper shows no residual chlorine (i.e., does not turn blue). Add 0.05g of excess ascorbic acid to ensure the presence of excess reducing agent.

8.3.6 Distill each chlorinated sample aliquot (along with the other aliquot of sample that was not subjected to alkaline chlorination) per Section 8.3 below.

Following spectrophotometric determination, the difference of cyanide content in the unchlorinated sample aliquot minus that of the chlorinated sample aliquot is the amount of cyanide amenable to chlorination for that sample.

8.4 DISTILLATION (TOTAL AND AMENABLE CYANIDE)

8.4.1 One method blank and one sample duplicate were prepared per each batch of twenty samples subjected to alkaline chlorination.

One sample duplicate must also be prepared for total cyanides by CLP SOW ILMO4.0. Select one sample per batch of twenty and dispense an additional aliquot to serve as the sample duplicate.

One method blank and one matrix spike/matrix spike duplicate (MS/MSD) set must be prepared for each batch of twenty samples to be distilled for total cyanide analysis. Sample volume permitting, select one sample per batch of twenty (aqueous or solid samples) and dispense two additional sample aliquots to serve as the basis for the

MS/MSD set. For solid samples not specified to be prepared by Method SW9013, weigh two 1.0g sample aliquots into two cyanide reflux tubes and add 0.25N NaOH to the 50mL marking for each to serve as the basis for the MS/MSD set.

To create a method blank for solid samples not specified to be prepared by Method SW9013 and/or solid samples processed via CLP SOW ILMO4.0, place 1.0g clean sand into a separate labeled cyanide reflux tube and fill with 0.25N NaOH to the 50mL marking.

8.4.2 Sample aliquots are tested for interferences and treated as needed. Sample aliquots are then distilled, followed by color development and measurement using a spectrophotometer.

8.4.2.1 Sulfide Test To test for the presence of sulfide interfering compounds in the sample, use a clean disposable transfer pipet to place a drop of sample on a piece of lead acetate paper. If the paper's color turns black, the presence of sulfide interference is indicated and the sample needs to be treated. Record the sulfide test result on the LIMS benchsheet.

For each sample yielding positive sulfide interference test results, add 1mL of 0.062M bismuth nitrate solution to each dispensed aliquot. Add a Teflon™-coated magnetic stir bar to the beakers, transfer to a stir plate, and carefully mix for about three minutes. Repeat the lead acetate paper test.

Add additional bismuth nitrate solution, mix and repeat the lead acetate paper test as necessary until all sulfide interferences are removed.

8.4.2.2 Oxidizing Agent Test To test for the presence of oxidizing agents in the sample, use a clean disposable transfer pipet to place a drop of sample on a piece of KI-starch indicator paper. A blue color indicates the presence of oxidizing agent interference and the need for sample treatment. Record the oxidizing agent test result on the LIMS benchsheet.

For each sample yielding positive oxidizing agent interference test results, add 0.05g ascorbic acid to each dispensed aliquot. Add a Teflon™-coated magnetic stir bar to the beakers, transfer to a stir plate, and carefully mix for about three minutes. Repeat the KI-starch indicator paper test.

Add 0.05g increments of ascorbic acid and repeat the KI-starch indicator paper test as necessary until a drop of aliquot produces no color on the KI-starch indicator paper. Then add an excess of 0.05g of additional ascorbic acid.

8.4.3 Place each prepared sample aliquot, including chlorinated sample aliquots, method blanks, duplicates and MS/MSDs, into separate, labeled cyanide reflux tubes.

8.4.4 Spike all the MS/MSD aliquots with 0.5mL of **first source** 10mg/L intermediate potassium cyanide standard solution. Expected concentrations for the MS/MSD samples is 0.10mg/L CN (aqueous samples), 5.0mg/Kg CN (solid samples)

8.4.5 Paragon prepares both high and low distilled standards with each batch of cyanide samples processed as a check of the effectiveness of the distillation procedure. Concentrations of these distilled standards are compared to similar values on the calibration curve to ensure that the distillation technique is reliable.

Prepare the aqueous and Method SW9013 extract low (0.2mg/L) and high (0.4mg/L) distillation standards (which also serve as the laboratory control samples, LCSs) by pipetting 1.0mL and 2.0mL of the **first source** 10mg/L intermediate potassium cyanide standard solution, respectively, into separate, labeled cyanide reflux tubes. Dilute to the 50mL mark with 0.25N NaOH.

To create the low (5.0mg/Kg CN) and high (20.0mg/Kg CN) distillation standards for solid matrices prepared by CLP SOW ILMO4.0, add 1.0mL and 2.0mL of the first source 10mg/L intermediate potassium cyanide standard solution to two separate 1.0g aliquots of clean sand placed into separate, labeled cyanide reflux tubes. Dilute to the 50mL mark with 0.25N NaOH.

NOTE: Additional distilled quality control samples (e.g., independent calibration verification standard, ICV) may be required based on client request. A distilled ICV is required by CLP SOW ILMO4.0 protocol.

To prepare the ICV for distillation, pipet 0.5mL of **second source** 10mg/L intermediate potassium cyanide standard solution into a labeled cyanide reflux tube and dilute to the 50mL mark with 0.25N NaOH. The expected concentration of this ICV standard is 0.10mg/L CN.

In addition to the distilled ICV, CLP SOW ILMO4.0 protocol requires that a reference soil sample with certified CN^- concentration be analyzed with each sample batch. A 1.0g aliquot of this reference soil (brought to the 50mL mark with 0.25N NaOH) is distilled and analyzed.

8.4.6 To all prepared aqueous sample or aqueous extract aliquots, add 1.0g of clean Ottawa sand. The clean sand is used in lieu of Teflon™ boiling chips; on-going successful Performance Testing (PT) analysis results show no adverse impact to method performance. The sand is not reused. No ottawa sand needs to be added to prepared field or quality control samples already containing 1.0g of soil or ottawa sand.

8.4.7 Add 50mL of 0.25N NaOH to each gas absorber tube.

8.4.8 Connect the reflux impingers, absorption impingers and cold fingers. Recheck all fittings.

8.4.9 Turn on the cooling water and adjust the flow rate indicated on the flow meter to 60GPH across the Midi-Dist™ unit.

8.4.10 Turn on the vacuum and adjust the valve until the level of bubbles in the gas absorber tube at each station is about 12cm above the 50mL mark.

8.4.11 If a sample is known or suspected to contain nitrate or nitrite, or if the sample aliquot was treated with bismuth nitrate to remove sulfide interferences, add 5mL of 0.4N sulfamic acid through the air inlet tube. Allow to mix for about three minutes.

8.4.12 Use a pre-calibrated repeat pipettor to slowly inject 5mL of 50% (v/v) H_2SO_4 solution through each air inlet. Wait approximately 5 minutes while the acid mixes with the sample.

Sufficient acid must be added to bring the sample solution pH to <2. Very basic or highly buffered samples may require additional acid.

Add an additional 3mL of 50% (v/v) H_2SO_4 solution or check the pH if the sample aliquot's pH is suspect.

8.4.13 To control excessive foaming during distillation, add 51% MgCl2 solution to the sample through the air inlet, as needed.

8.4.14 Turn on the heating block (red switch). This will heat the block to 123-125°C. Adjust the timer to 105 minutes. The timer will automatically turn off the block heater.

8.4.15 After the heaters have turned off, allow the unit to cool 15 minutes (continue the vacuum).

8.4.16 Lift the fritted absorber impinger from the absorption tube. Disconnect the absorber-to-reflux connection. Disconnect the absorption impinger from the vacuum. Repeat for all Midi-Dist™ stations.

8.4.17 Turn off the vacuum valve.

8.4.18 Seal the absorber tubes and store at 4±2 °C until colorimetric development and analysis. Make sure each tube is properly labeled with sample identity.

8.4.19 Disconnect the Midi-Dist™ glassware and clean the distillation apparatus per the manufacturer's instructions.

8.5 DISTILLATION (WEAK AND DISSOCIABLE CYANIDE) - METHOD SM 4500-CN I

The distillation for weak and dissociable cyanide is carried out under *slightly* acidic (pH 4.5 - 6.0) conditions. Preparative steps such as checking pH, checking for interferences, preparation of quality control samples, staging aliquots in CN reflux tubes, and other set-up procedures are conducted as described in the previous Sections. Continue by following the distillation procedure outlined in Section 8.4 above with the following exceptions:

8.5.1 Do not add sulfamic acid solution because NO_2^- and NO_3^- do not interfere.

8.5.2 Do not add H_2SO_4 or $MgCl_2$, instead, add 1mL each of the acetate buffer and zinc acetate solutions, followed by 2-3 drops of methyl red indicator.

8.5.3 Rinse the air inlet tube with DI water and allow the air to mix the reflux tube's contents. If the solution is not pink, add 1:9 acetic acid dropwise through the air inlet tube until a pink color persists.

8.5.4 Complete the distillation as described in Section 8.4 above, with the exception that the pH of the samples do not need to be checked following distillation.

8.6 MANUAL SPECTROPHOTOMETRIC DETERMINATION

A series of calibration standards are prepared then developed colorimetrically. Absorbance at 578nm is read on a spectrophotometer. A standard curve is then calculated by plotting the absorbance for each standard vs. the standard's concentration.

8.6.1 Standard Curve Use 0.25N NaOH to prepare the calibration standards (made each day of use) in optically matching 1-inch diameter spectrophotometer cuvettes as described in the chart below.

Standard Concentration (mg/L)	Volume of 10 mg/L Intermediate Standard (mL)	Final Volume[ii] (mL)
0	0	10
0.01	0.010	10
0.05	0.050	10
0.10	0.10	10
0.20 (CCV)[i]	0.20	10
0.30	0.30	10
0.40	0.40	10
0.50	0.50	10
0.10 (ICV)[iii]	0.10	10

[i] From first source 10mg/L intermediate potassium cyanide standard solution.

[ii] Note that calibration standards are prepared directly in 1-inch, optically matched cuvettes.

[iii] From second source 10mg/L intermediate potassium cyanide standard solution.

8.6.2 Standard Curve for Samples Containing Sulfide Per all method references, the method of standard additions (MSA) must be used for the analysis of all samples that suffer from matrix interferences (e.g., samples that contain sulfides). MSA is not required where interferences have been successfully removed during pretreatment. Details regarding MSA performance are provided in Method SW9014 (Section 7.4) and Method EPA 335.2 (Section 8.9).

8.6.3 Color Development and Absorbance Measurements

NOTE: The steps below *must* be performed in a fume hood.

8.6.3.1 For each distilled sample, pipet 10mL of scrubber solution (contained in the sealed absorber tube) into a pre-labeled 1-inch diameter, optically matched spectrophotometer cuvette.

8.6.3.2 Color development and absorbance measurements are performed in the following sequence:

1. 0.00 mg/L cal std

2. 0.01 mg/L cal std
3. 0.05 mg/L cal std
4. 0.10 mg/L cal std
5. 0.20 mg/L cal std
6. 0.30 mg/L cal std
7. 0.40 mg/L cal std
8. 0.50 mg/L cal std
9. ICV
10. ICB (calibration blank)
11. Preparation blank (distilled method blank)
12. LCS (distilled standards low and high; followed by the known reference material)
13. MS
14. MSD
15. Chlorinated amenable cyanide sample duplicate

16-22 up to six field samples.

23. CCV (0.20 mg/L calibration standard, 1st Source)
24. CCB (calibration blank)
25. up to ten more field or QC samples, then CCV, CCB (repeated until all samples are analyzed)

NOTE: No more than ten field or QC samples may be analyzed between the ICV/ICB and first CCV/CCB set, or between successive CCV/CCB sets. A CCV/CCB set must close out the run sequence.

8.6.3.3 Add 3.0mL of 1M NaH_2PO_4 buffer solution to each cuvette.

NOTE: After this solution is added, the cyanide in the sample is no longer stable and the color development steps must be continued without delay.

8.6.3.4 Add 1.0mL of chloramine-T reagent to each cuvette and mix well.

8.6.3.5 After 1 to 2 minutes, add 1.0mL of pyridine-barbituric acid and 5.0mL of DI water; mix well immediately.

NOTE: All spectrophotometer checks must be performed per manufacturer's instructions prior to use.

8.6.3.6 After the red color has fully developed (usually about 8 to 15 minutes), read absorbance at 578nm using the spectrophotometer. Establish an instrument range from 0 to 100 % T or 0.00 to 2.000 absorbance.

8.6.4 Plotting the Standard Curve Prepare the standard curve by plotting the absorbance of each standard versus the standard's cyanide concentration (mg/L). This may be done using a spreadsheet program on a personal computer. Proceed with standard curve evaluation and calculations as described in the following Section.

8.7 CALCULATIONS

Perform a linear regression analysis of the plotted standard curve. The regression equation for the standard curve must have a correlation coefficient (r^2) that is $\geq$ 0.995. If this criterion is not met, check the standards preparation data, plotting and computation for errors. If no errors are found, the calibration standards can be rerun. If the criterion is still not met, the analysis must be halted, new calibration standards prepared, and a new calibration curve generated.

8.7.1 Calculate the cyanide concentration in aqueous samples as follows:

$$\text{Concentration of CN (mg/L)} = A \times D$$

where:

A = mg/L of CN in distillate as determined from the regression analysis

D = dilution factor (if dilution was necessary to produce a response within the calibration range)

8.7.2 Calculate the cyanide concentration in solid samples as follows:

$$\text{Concentration of CN (mg/Kg)} = \frac{A \times D \times V}{W \times E}$$

where:

A = mg/L of CN in distillate as determined from the regression analysis

D = dilution factor (if dilution was necessary to produce a response within the calibration range)

V = volume of distillate solution (liters); if this SOP is followed exactly, V = 0.050 L

W = wet sample weight (g)

E = correction factor for moisture content (i.e., % solids/ 100, as determined per SOP 642)

8.7.3 Once the concentration of total cyanide and amenable cyanide have been determined via the calculations shown above, the concentration of cyanide amenable to chlorination can be determined as follows:

Concentration CN Amenable to Chlorination	=	Concentration of Total CN (Unchlorinated aliquot)	-	Concentration of Total CN (Chlorinated aliquot)

9. QUALITY CONTROL (QC)

9.1 BLANKS

One preparation (i.e., method blank) per type of matrix analyzed must be carried through the entire preparation, reflux-distillation and analytical processes to determine if any contamination or memory effects are occurring. For this procedure, the preparation blank consists of DI water only (aqueous samples) or DI water + clean sand (solid matrix samples not processed by Method SW9013 extraction). A clean sand (+ 50mL DI water) solid matrix method blank is prepared and processed during the Method SW9013 extraction procedure. No blank may yield positive results greater than the analyte reporting limit (usually 0.01mg/L CN; 0.50mg/Kg CN). If this criterion is exceeded, the analyst should determine the cause of the problem, correct it and reanalyze the sample batch.

9.2 SPIKE RECOVERIES

Laboratory control samples (LCSs) consist of clean matrices (i.e., DI water or clean sand), which are spiked with a known amount of target compound. In some cases (e.g., CLP SOW ILMO4.0), pre-spiked reference samples are commercially available for use. LCS analyses are performed to evaluate the accuracy of the analytical system.

Matrix spike (MS) samples consist of additional sample aliquots, which are spiked with a known amount of target compound. MS analyses are performed to determine the effect of sample matrix interferences.

Spiked samples are evaluated based on percent recovery (%R), which is a calculation of the amount of target analyte yielded vs. the amount of target analyte anticipated. The following equation is used to calculate spike recovery:

$$\%R = \frac{Concentration_{Found} - Concentration_{Aliquot}}{Concentration_{Anticipated}} \times 100$$

where:

$Conc_{Found}$ = amount of target analyte yielded by the spiked analysis

$Conc_{Aliquot}$ = amount of target analyte found in the *unspiked* aliquot (i.e., "zero" for clean LCS matrix aliquots; or concentration of target analyte calculated to be present in the unspiked sample matrix aliquot)

$Conc_{Anticipated}$ = amount of target analyte expected to be yielded based on known amount spiked

The spiked LCS results should agree within ±15% of the anticipated value for aqueous samples (i.e., 85-115 % recovery), and within vendor-specified limits for solid reference samples. *Note that other acceptance criteria may be applicable as requested by the client.* The advisory control limits for the matrix spiked analyses are set at 75-125% recovery.

If established spike recovery quality control criteria are not met, check all calculations and spike preparations for errors. If no errors are found, the sample batch must be reanalyzed for LCS exceedances. Narrate if sample matrix interference is suspected as the cause of MS (or MSD) exceedance.

9.3 DUPLICATE PRECISION

A sample duplicate is prepared for amenable cyanide determinations and for cyanide analyses per CLP SOW ILMO4.0 protocol. Also, generally the matrix spike sample is prepared and analyzed in duplicate. Duplicates are analyzed to measure analytical precision. Precision is evaluated in terms of Relative Percent Difference (RPD), which is calculated as follows:

$$RPD\ (\%) = \frac{|\ Result_{Sample} - Result_{Dup}\ |}{\frac{(Result_{Sample} + Result_{Dup})}{2}} \times 100$$

Generally, an RPD of ≤20 is set as the quality control limit. This RPD limit is not applicable for matrix spiked duplicates whose native (i.e., unspiked) concentration of target analyte is greater than 5X the analyte's reporting limit.

If the RPD quality control criterion is not met, check all calculations and spike preparations for errors. Consult with the Department, Project and Quality Assurance Managers if the RPD criterion is not met for duplicates. Narrate if sample matrix interference is suspected as the cause of the RPD limit not being met for an MS/MSD set.

9.4 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall be conducted in the manner prescribed by the method (e.g., per defined spike levels, etc.) and shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study shall be performed as needed and at a minimum, annually.

10. DEVIATIONS FROM METHODS

10.1 Note that Paragon utilizes a Midi-Dist™ apparatus for distillation in lieu of a round bottom flask setup.

10.2 Section 7.7 of Method SW9013 describes the use of 50% NaOH (added in 5mL increments as needed) to maintain a pH of 12 or greater during the extraction of cyanide in solid and oil matrices. Instead, this SOP prescribes the addition of 10N NaOH dropwise to achieve adequate pH adjustment.

10.3 Section 4.1 of Method EPA 335.1 and Section 7.1.2 of Method SW9010B describe the use of 1.25N NaOH to maintain a pH between 11 and 12 during the chlorination process for cyanides amenable to chlorination. Instead, this SOP prescribes the addition of 10N NaOH dropwise to achieve adequate pH adjustment.

10.4 Section 7.1.4 of Method SW9010B discusses the use of sodium arsenite to remove all residual chlorine after the amenable cyanide chlorination process. As described in Section 4.3 of Method EPA 335.1, Paragon uses ascorbic acid to neutralize all residual chlorine generated in the amenable cyanide chlorination process.

10.5 Section 8.0 of Method EPA 335.2 and Section 7.2.1 of Method SW9010B indicate that 1.25N NaOH is to be used as the reflux scrubber solution. Paragon utilizes 0.25N NaOH as the reflux scrubber solution. Successful Proficiency Test (PT) sample studies show that this practice does not impair sample results.

10.6 Per Section 8.8 of Method EPA 335.2, 1.25N NaOH is used in the creation of working cyanide standards; 1N NaOH is used in the creation of working cyanide standards per Sections 5.3.7 of Method SW9014. Paragon uses 0.25N NaOH to create the working cyanide standard solutions. This provides for the same matrix as the distillates that are trapped in 0.25N NaOH.

10.7 To remove sulfide interferences, Section 8.2 of Method EPA 335.2 describes the addition of lead acetate to the reflux scrubber and Section 4.2 of the CLP SOW ILMO4.0 discusses the use of powdered cadmium carbonate. Per Method SW9010B (Sections 3.3 and 7.2.3), this SOP prescribes the use of 0.062M bismuth nitrate solution to remove sulfide interferences.

10.8 The referenced methods discuss addition of sulfamic acid powder to the sample prior to distillation for the removal of nitrate/nitrite interferences. To provide for better delivery into the Midi-Dist™ system, Paragon uses a 0.4N sulfamic acid solution instead.

10.9 The referenced methods describe the use of Teflon™ boiling chips during the distillation process. Paragon uses 1.0g of clean silica sand in lieu of boiling chips. On-going successful Performance Testing (PT) performance has shown no adverse impact to method performance.

10.10 Section 8.7.1 of Method EPA 335.2 and Section 7.2.2 of Method SW9014 cite the addition of 2mL chloramine-T reagent and 5mL pyridine-barbituric reagent during the color development process (Paragon uses 1mL each because smaller volumes are developed colorimetrically). Also, Section 7.2.2 of Method SW9014 discusses using KI-starch paper to test for excess chlorine following the addition of the 2mL chloramine-T reagent, with additional increments of 0.5mL chloramine-T added until chlorine residual is achieved and with a final excess of 0.5mL chloramine-T added. Paragon does not test for chlorine residual. The generation of successful Proficiency Test (PT) sample results have shown that these practices do not adversely affect sample results.

10.11 Section 8.8.2 of Method EPA 335.2 and Section 8.6 of Method SW9010B recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. Both method references state that if the distilled standards do not agree within ±10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding. It is Paragon's policy (per Section 8.3 of Method SW9010B and Section 7.2.2.1 of the CLP SOW ILMO4.0), that the distilled check standards must yield values within ±15% of the expected value. It is Paragon's interpretation that the conflicting criterion given in Method SW9010B (Section 8.6 vs Section 8.3) be resolved in favor of the looser ±15% criterion.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples),

handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

11.1.5 The cyanide standard solution preparations, distillations, and color development processes shall be handled/conducted only in a properly functioning fume hood.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The basic scrubber solution and all remnants from the color development process shall be disposed of in the Aqueous Laboratory Waste Satellite collection vessel.

11.2.2 The acidified distillate remnants shall be disposed of in the Acidic Aqueous Laboratory Waste Satellite collection vessel.

11.2.3 Any solid residues are to be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

11.2.4 All empty solvent bottles or reagent are to be disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

11.2.5 Certain clients may require the return of their sample remainders. The Waste Compliance Officer will provide specific procedures and materials for these handling these sample remainders where return to the client applies.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 5, Method 9010B, “Total and Amenable Cyanide: Distillation”, Revision 2, December 1996.

12.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 5, Method 9013, "Cyanide Extraction Procedure for Solids and Oils", Revision 0, July 1992.

12.3 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 5, Method 9014, "Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide", Revision 0, December 1996.

12.4 US EPA, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, Method 335.1, "Cyanides, Amenable to Chlorination", 1974.

12.5 US EPA, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, Method 335.2, "Cyanide, Total (Titrimetric, Spectrophotometric)", 1980.

12.6 US EPA, EPA-540/R95/121, Contract Laboratory Program (CLP), Statement of Work (SOW) for Inorganics Analysis, Multi-media, Multi-concentration, ILMO 4.0.

12.7 Standard Methods for the Examination of Water and Wastewater, 17th Edition, Chapter 4, Method 4500-CN I, "Weak and Dissociable Cyanide", 1989.

DOCUMENT REVISION HISTORY

2/9/04: Updated format.

8/25/04: Separated out Drinking Water procedures and added reference Program Specification directive in "Responsibilities".

4/10/06: Updated controlled form benchsheet references to LIMS. Added DOCUMENT REVISION HISTORY.

7/5/06: Augmented "Interferences" to address difficulties with amenable cyanide analysis in soils.

1/19/07: Section 6 changes: Shelf-life of magnesium chloride solution changed from 5yrs to 1 year; stock potassium cyanide standard needs standardized only when made. Section 8 changes: Since it is not required by any referenced method, the directive to check pH after distillation has been removed.

Analytical Method: SW 9010B, 9013, 9014; E 335.1, 335.2; OLMO4.0; SM4500-CN I	**Parameter:** Total and Amenable Cyanide by Distillation; Weak and Dissociable Cyanide		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 7-point (plus blank)	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria)	Correlation coefficient (r^2) for linear regression must be $\geq$ 0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze calibration standards. If quality control acceptance criterion still not met, analyses cannot proceed; a new suite of calibration standards must be prepared and analyzed. Analyses cannot proceed until an acceptable initial calibration curve is generated.
Independent Calibration Verification (ICV); second source standard; at or below midpoint	Once after each initial calibration	Results must agree within $\pm$15% of corresponding value generated by the initial calibration	If QC criterion not met, prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV); first source; at or below midpoint	Run to bracket a set of 10 analyses, and to end any run sequence (must be followed by a CCB analysis)	Response must agree within $\pm$15% of corresponding value generated by the initial calibration	Check for preparation and calculation errors; evaluate/correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Blanks: Method (Preparation, MB) Also run as an Initial Calibration Blank (ICB) and Continuing Calibration Blanks (CCBs)	One method blank per batch of twenty or less environmental samples processed. ICB run immediately following calibration curve. CCB run following the CCV to bracket a set of ten analyses and to close a run sequence	CN content of the blank must be less than the analyte reporting limit (RL); RL usually 0.01mg/L CN; 0.50mg/Kg CN	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Distilled LCS (low and high distillation check standards)	One low and one high prepared and analyzed per batch of $\leq$ 20 field samples	Distilled LCS result must agree within ±15% of non-distilled ICV result	Check data for preparation or calculation errors. If no errors are found, the distillation of these standards and all associated samples in the batch must be repeated.
Distilled ICV; second source ICV subjected to reflux-distillation (run per CLP protocol and by client	Once per analytical run sequence	Distilled ICV result must agree within ±15% of non-distilled ICV result (see Section 10.0 - Deviations, of	If QC criterion not met, check for preparation errors or instrument malfunction. If distilled low and high LCS criteria also not met,

Analytical Method: SW 9010B, 9013, 9014; E 335.1, 335.2; OLMO4.0; SM4500-CN I	**Parameter:** Total and Amenable Cyanide by Distillation; Weak and Dissociable Cyanide		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
request); at or below midpoint		this SOP)	repeat distillation for all samples in batch.
Matrix Spike (MS) and Matrix Spike Duplicate (MSD)	One set prepared and analyzed per batch of ≤20 field samples	Recoveries should meet control limits of 75-125 % RPD between duplicates should be ≤20	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative.
Sample Duplicate (DUP)	One prepared and analyzed per batch of ≤20 field samples.	RPD should be ≤20	For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers (narrate if sample matrix interferences are suspected as the cause of the RPD limit not being met for an MS/MSD set).
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL) and per procedures prescribed by the method	As needed; at a minimum annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with the system. Repeat the MDL study. If criteria still not met, discuss with QA Manager (RL may be adjusted if required).

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1112 REVISION 5

TITLE: **DETERMINATION OF REACTIVE CYANIDE AND SULFIDE -- EPA METHOD SW846 CHAPTER 7**

FORMS: **NONE**

APPROVED BY:
TECHNICAL MANAGER Steve Workman DATE 4/12/06
QUALITY ASSURANCE MANAGER Deb Schenk DATE 4/11/06
LABORATORY MANAGER K Gillis DATE 4-12-06

HISTORY: Rev0, 6/2/97; Rev1, 4/6/01; Rev2, 8/15/02; Rev3, 2/13/04 and 3/25/05 (re-released without revision); Rev4, 7/26/05; Rev5, 4/10/06.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- USEPA SW846 Chapter 7 -- describe the determination of reactive cyanide and sulfide in solid and aqueous wastes. The data user should note that the USEPA has formally withdrawn their guidance and requirements for the performance of this method, as it is likely to underestimate the sample's potential to liberate free cyanide and sulfide under waste management conditions. No alternative procedure is being supported. Paragon informs our clients of this context in our reactivity data package case narratives.

2. SUMMARY

An aliquot of waste contained within a closed gas generation system is acidified to a low pH. Hydrocyanic acid (HCN) and hydrogen sulfide (H_2S) are released as gases from the acidified waste and are trapped in a basic scrubber solution. The amount of cyanide trapped by the scrubber solution is developed colorimetrically and measured by manual spectrophotometric determination (Method SW 9014 referenced). The amount of sulfide trapped by the scrubber solution is quantified by an iodometric titration (Method SW 9034 referenced).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training

review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/ analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these methods to note any anomalies or out-of-control events associated wit the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Interferences are undetermined.

5. APPARATUS AND MATERIALS

5.1 GAS GENERATION AND TRAPPING SYSTEM

5.1.1 flasks, round bottom, three-neck with 24/40 ground glass joints, 500mL

5.1.2 gas scrubbers made from a 250mL side-arm flask and a one-hole stopper. A piece of plastic tubing that extends nearly to the bottom of the flask when the stopper is in place is inserted through the stopper. The other end of the plastic tubing connects to one neck of the round bottom flask by an elbowed gas inlet adapter with 24/40 ground glass joint.

5.1.3 addition funnels, 250mL, equipped with a pressure equalizing tube, and a stopcock valve possessing a 24/40 ground glass joint and Teflon™ sleeve. Connects to one neck of the round bottom flask.

5.1.4 nitrogen gas provided via two-stage regulation and with an in-line needle valve for controlling gas flow. Connected to addition funnel by an elbowed gas inlet adapter possessing a 24/40 ground glass joint.

5.1.5 gas flow meter

5.1.6 magnetic stir plates and 1.5" egg-shaped stir bars (Teflon™ coated)

5.1.7 top-loading (capable of weighing to 0.1g) and analytical (capable of weighing to 0.0001g) balances

5.1.8 volumetric graduated cylinders, 100, 250, 500mL and 1L sizes

5.1.9 beakers with lids, plastic, disposable, 100mL

5.1.10 ground glass stoppers, 20/40; connects to one neck of round bottom flask

5.1.11 volumetric flasks, glass, Class A, 100 and 500mL sizes

5.1.12 pressure clips for ground glass connections and round bottom holders

5.2 CYANIDE DETERMINATION EQUIPMENT

5.2.1 Sequoia-Turner, Model 340 spectrophotometer or equivalent

5.2.2 cuvettes, optically matched, 1-inch diameter, Bausch & Lomb or equivalent

5.2.3 pipets, variable, Eppendorf™ or equivalent, with disposable dispensing tips

5.2.4 vortex mixer

5.3 SULFIDE DETERMINATION EQUIPMENT

5.3.1 magnetic stir plate and magnetic stir bars (Teflon™ coated).

5.3.2 pH paper, narrow-range acidic or wide range (0-14), EMD, Cat. 1.09580 and Cat. 1.09590 or equivalents, or pH meter, Corning Model 320 or equivalent

5.3.3 top loading balance, capable of weighing to 0.01g

5.3.4 pipets, variable, Eppendorf™ or equivalent with disposable dispensing tips

5.3.5 beakers, Pyrex™, 150mL

6. REAGENTS

6.1 Deionized (DI) water, laboratory-generated.

6.2 Nitrogen gas, 0.99% or greater purity.

6.3 Sulfuric Acid, (H_2SO_4) Solution, 18N, 50% (v/v): EMD, SX1247-2 or equivalent. Carefully add 100mL concentrated H_2SO_4 to 100mL DI water (volume may differ as long as 1:1 ratio remains the same). *Shelf Life = 1 year.*

6.4 Sulfuric Acid (H_2SO_4) Solution, 0.01N: Add 1.0mL of 50% H_2SO_4 to DI water and dilute to 1800mL. Stopper and invert carefully several times to mix. *Shelf life = 1 year.*

6.5 Sodium Hydroxide (NaOH), 0.25N: JT Baker, 3722-07 or equivalent. Dissolve 10g NaOH in DI water and dilute to 1L. *Shelf life = 1 year.*

6.6 p-Dimethylaminobenzalrhodanine Indicator, reagent grade: Obtained from a commercial vendor or made in-house by dissolving 0.020g p-dimethylaminobenzal rhodanine (JT Baker, J431-02 or equivalent) in a final volume of 100mL acetone (spectral grade). *Shelf Life = 1 year.*

6.7 Standard Silver Nitrate ($AgNO_3$) Titrant, 0.0192N: Obtained from a commercial vendor or prepared in-house (JT Baker, J431-02 or equivalent). Use DI water to dissolve 3.2647g dried $AgNO_3$ and bring to full volume in a 1L Class A volumetric flask. *Shelf Life = 1 year.*

6.8 Sulfide Spiking Solution, approximately 4000mg/L sulfide: Dissolve 15.0g $Na_2S \bullet 9H_2O$ (GFS Chemicals, Item No. 1040 or equivalent) in DI water and bring to 200mL volume. Store in a refrigerator (4±2°C). *Shelf life = 1 year.*

6.9 The salt used in preparing the sulfide spiking solution is very hygroscopic and cannot be used as a primary standard. Therefore, an aliquot of sulfide spiking solution must be analyzed in order to determine the exact concentration of the prepared sulfide LCS. Standardize the sulfide spiking solution daily as needed as follows:

6.9.1 Place a 0.50mL aliquot of the sulfide spiking solution into a beaker and dilute to approximately 100mL using DI water. Add 2mL of 6N HCl, then add an additional 2mL 6N HCl.

6.9.2 Place the beaker on a balance and tare the balance. Add approximately 15mL of standardized standard iodine solution. The beaker's contents should be yellow. Record the weight change caused by the addition of the standard iodine solution. Add 2-4 drops of starch indicator. The beaker's contents should be dark blue. Tare the balance.

6.9.3 Titrate with standardized sodium thiosulfate solution. Continue to add sodium thiosulfate dropwise until the beaker's contents become clear. Record the total volume of sodium thiosulfate titrant used.

6.9.4 Compute the value as follows:

$$\text{Reactive Sulfide (mg/L)} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{S}$$

where:

A = normality of the iodine solution
B = volume of iodine solution used (mL)

C = normality of the sodium thiosulfate solution
D = volume of sodium thiosulfate used (mL)
S = volume of Sulfide Spiking Solution

6.10 Sodium Phosphate Monobasic (NaH_2PO_4) Solution (sodium dihydrogenphosphate solution), 1M: Dissolve 138g of $NaH_2PO_4 \bullet H_2O$ (GFS Chemicals, Item No. 735 or equivalent) in 1L of DI water. Store in a refrigerator (4 ± 2°C). *Shelf Life = 1 year.*

6.11 Chloramine-T solution: Dissolve 1g of chloramine-T (Mallinckrodt, 0614-58 or equivalent) in 100mL of DI water. *Refrigerate until ready to use; prepare fresh each day of use.*

6.12 Potassium Iodide, KI, reagent grade: JT Baker, 3162-01 or equivalent. *Shelf-life = 5 years.*

6.13 Hydrochloric Acid (HCl), 6N: JT Baker, 9530-33 or equivalent. Dilute 500mL concentrated HCl to 1L. *Shelf life = 1 year.*

6.14 Starch Indicator, 2 %: VWR, Cat. No. VW3638-2 or equivalent. *Shelf-life = 1 year or as stated by manufacturer.*

6.15 Standard Potassium Biiodate ($KH(IO_3)_2$) Solution, 0.025N: Dissolve 0.4062g of $KH(IO_3)_2$ salt (EM Science, PX1351-2 or equivalent) in 500mL of DI water. Store in polypropylene. *Shelf-life = 1 year.*

6.16 Sodium Thiosulfate ($Na_2S_2O_3$) Solution, approximately 0.025N: Dissolve 3.95g of $Na_2S_2O_3$ anhydrous (EM Science, SX0820-1 or equivalent) and 0.4gof NaOH in 1L of deionized water. Store in polypropylene. *Shelf-life = 1 year.*
Standardize against $KH(IO_3)_2$ once before use, as directed below:

6.16.1 Place 10.00mL standard potassium biiodate ($KH(IO_3)_2$) solution in a 200mL beaker.

6.16.2 Dilute to about 100mL with DI water.

6.16.3 Add approximately 2g of potassium iodide (KI) pellets.

6.16.4 Add 4-5 drops of 50% sulfuric acid (H_2SO_4).

6.16.5 Add 2-3 drops of starch indicator.

6.16.6 Tare the beaker + contents on a top loading balance.

6.16.7 Titrate with standard potassium biiodate solution on stirplate until the solution turns from blue to colorless.

6.16.8 Record the amount of titrant used.

6.16.9 Repeat three times and compute the average of the three replicates calculated as follows:

sodium thiosulfate conc (eq/L) = (0.025) *(10.00) / (V)

where:

V = volume of sodium thiosulfate required to reach endpoint

0.025 = normality of potassium biiodate solution titrated

10.00 = volume of potassium biiodate solution titrated

6.17 Pyridine-barbituric Acid Solution: Place 7.5g of barbituric acid in a graduated container (i.e., marked at 250mL) and add a minimal amount of DI water necessary to wash the sides of the flask and wet the barbituric acid. Add 37.5mL of pyridine and mix. Add 7.5mL of concentrated HCl, mix and cool to room temperature. Dilute to 180mL with DI water and mix. ***Store in an amber glass bottle and refrigerate. This reagent is stable for approximately 6 months.*** If a precipitate forms on the bottom of the container, discard and prepare fresh reagent.

6.18 Standard Iodine (I_2) Solution: Dissolve 25g of Potassium Iodide, KI (reagent grade) in 800mL of deionized water. Add 3.2g of iodine crystals and dissolve. Dilute to 1L with deionized water. Store in polypropylene. *Shelf-life = 1 year.* **Standardize against $Na_2S_2O_3$ daily before use as follows:**

6.18.1 Add approximately 100mL of deionized water and a stir bar to a clean plastic container.

6.18.2 Place the container + contents on a stir plate and cautiously add approximately 2.0mL of 6N HCL.

6.18.3 Place the container + contents on a top loading balance and tare the balance. Add approximately 2.5mL of standard iodine solution and record the weight to the nearest 0.01g in the laboratory logbook.

6.18.4 Add 2-3 drops of starch indicator and tare the balance again.

6.18.5 Place the container on a magnetic stir plate and titrate to a colorless endpoint using the standardized sodium thiosulfate solution.

6.18.6 Place the container and contents back on the balance and record the weight of the titrant used

6.18.7 Repeat three times and compute the average value, calculated as follows:

Iodine conc (eq/L) = (CTh) * (VTh) / (VI)

where:

CTh = concentration (eq/L) of sodium thiosulfate

VTh = volume of sodium thiosulfate required to reach endpoint

VI = volume of iodine solution titrated

7. PRIMARY AND INTERMEDIATE CYANIDE STANDARDS

7.1 Cyanide Stock Solutions, 1000mg/L cyanide, (first and second source): Dissolve 0.2504g Potassium Cyanide (KCN) salt into 100mL of 0.25N NaOH. **Store in a refrigerator (4 ± 2°C).** *Shelf life = 1 year.*

NOTE: Two stock solutions (one each) are prepared from two independent sources of KCN salt (i.e., "first source" and "second source").

7.2 Verify the concentration of each of the potassium cyanide stock solutions (i.e., first source and second source) when made, as follows:

NOTE: As referenced in Section 5.4.2 of SW846 9014, this titration standardization procedure is detailed in SM 4500-CN D.

7.2.1 Transfer 10.0mL of potassium cyanide stock solution to a 250mL beaker.

7.2.2 Dilute to about 100mL using DI water.

7.2.3 Add a few drops of the p-dimethylaminobenzalrhodanine indicator solution.

7.2.4 Add a clean magnetic stir bar to the beaker. Place the beaker + contents on the analytical balance and tare the balance.

7.2.5 Put the beaker + contents on a magnetic stir plate. Begin agitation.

7.2.6 Titrate with 0.0192N $AgNO_3$, adding dropwise, to the first change in color (i.e., from yellow to salmon). Reweigh the beaker + contents and record the weight change (weight change equals amount of titrant added).

7.2.7 Titrate three replicate aliquots for each stock solution and average the results for each.

7.2.8 An aliquot of DI water (DI water blank) is also titrated according to the procedure described above.

7.2.9 Use the average result obtained for each stock solution to calculate the CN concentration as follows:

$$\text{mg } CN^- / L = \frac{(A - B) \times 1000^*}{C}$$

where:

A = mL standard 0.0192N $AgNO_3$ required for aliquot of stock

B = mL standard 0.0192N $AgNO_3$ required for DI water blank

C = mL CN^- stock standard titrated**

* NOTE: 1.0mL 0.0192N $AgNO_3$ = 1.0mg CN^-

** C = 10.0mL, if this SOP is followed without deviation

7.2.10 The titration verification must yield results within ±2% (i.e., between 980 and 1020mg/L CN) in order for the stock solutions to be acceptable. If this criterion is not met, the stock solutions must be remade.

7.3 Intermediate Potassium Cyanide Standard solutions, 10mg/L: Dilute 5mL of 1000mg/L cyanide stock solution to 500mL with 0.25N NaOH. *Shelf Life = 3 months.* Store in a refrigerator (4±2°C).

NOTE: Prepare intermediate potassium cyanide standards from both of the first and second source stock CN standard solutions.

8. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

8.1 All samples must be collected according to an approved sampling plan.

8.2 Samples containing, or suspected to contain sulfide or a combination of sulfide and cyanide wastes, should be collected with minimum aeration and the containers filled completely, without headspace, and capped.

8.3 It is suggested that samples containing cyanide and/or sulfide wastes be tested as soon as possible.

8.4 Water samples can be preserved for reactive cyanide analysis by adjusting the sample to pH>12 using a strong base. Water samples can be preserved for the analysis of reactive sulfide by adding zinc acetate, and adjusting the sample pH to >9. It should be noted that the addition of preservatives dilutes the sample, increases the ionic strength, and possibly changes other physical or chemical characteristics of the waste. These changes may affect the rate of release of HCN or H_2S.

8.5 Samples should be stored under refrigeration in the dark until analysis.

9. PROCEDURE

9.1 GAS GENERATION AND TRAPPING

NOTE: Due to the evolution of hazardous gases, this procedure must be carried out under a ventilated fume hood.

9.1.1 Prepare one Method Blank (MB = 10.0g deionized water), one cyanide Laboratory Control Sample (LCS-CN = 10.0g of 1000ppm first source cyanide stock solution), one Sulfide Laboratory Control Sample (LCS-S = 5.0g of sulfide spiking solution, to a final weight of 10.0g with deionized water), and one sample duplicate (DUP) for each batch of 20 or less environmental samples.

9.1.2 Add 10.0g of sample to a round bottom flask.

9.1.3 Add 100mL of 0.25N NaOH to the side arm flask scrubber apparatus and assemble with stopper and tubes.

9.1.4 Add an egg-shaped stirbar to each flask and place the flask on a stir plate. Attach scrubber apparatus. Connect 250mL addition funnel with cock valve in off position and fill with 0.01N H_2SO_4. Place gas inlet tube in top of addition funnel. Place glass stopper in third opening of flask and attach pressure clips to ground glass connections in order to fully close system.

9.1.5 Turn on nitrogen gas and adjust the flow of nitrogen using the needle valve. Check the flow rate using a flow meter attached to the scrubber outlet. The flow rate should be about 60mL/min.

9.1.6 With the nitrogen flowing, add 250mL of 0.01N H_2SO_4 by opening the cock valve on the addition funnel. Begin stirring while the acid is being added. Adjust stir rate to achieve adequate stirring (the stirring should not be fast enough to create a vortex; the stirring speed must remain constant throughout the gas evolution process). Start the 30-minute gas generation period.

9.1.7 After 30 minutes, discontinue the nitrogen flow and disconnect the scrubber. Disassemble the apparatus in reverse order of set up. Transfer the trap solutions to labeled 100mL disposable beakers.

9.1.8 Determine the amounts of reactive cyanide and sulfide trapped in the scrubber solution as discussed in the following sections.

9.2 DETERMINATION OF CYANIDE IN THE SCRUBBER SOLUTION

9.2.1 CYANIDE CALIBRATION STANDARDS

Use 0.25N NaOH to prepare the cyanide calibration standards in optically matching 1-inch diameter spectrophotometer cuvettes as described below. *Calibration standards are made daily for each day of analysis*:

Standard Concentration (mg/L)	Volume of 10mg/L Intermediate Standard (first source) (mL)	Final Volume (mL)
0	0	10
0.01	0.010	10
0.05	0.050	10
0.10	0.10	10
0.20	0.20	10
0.30	0.30	10
0.40	0.40	10
0.50	0.50	10
0.10 (ICV)[i]	0.10	10

[i] From second source 10mg/L Intermediate Potassium Cyanide Standard Solution. ICV concentration is 0.10mg/L CN.

9.2.2 CYANIDE COLOR DEVELOPMENT AND ABSORBANCE MEASUREMENTS

- The steps below must be performed in a fume hood.
- Perform the color development and absorbance measurements in the following sequence:

(1) 0.00mg/L cal std
(2) 0.01mg/L cal std
(3) 0.05mg/L cal std
(4) 0.10mg/L cal std
(5) 0.20mg/L cal std
(6) 0.30mg/L cal std
(7) 0.40mg/L cal std
(8) 0.50mg/L cal std
(9) ICV (2nd Source; 0.10mg/L)
(10) ICB (calibration blank)
(11) Preparation blank (prepared method blank)

(12) LCS-CN

(13) DUP

(14-20) up to seven field samples

(21) CCV (0.20mg/L calibration standard, 1st Source)

(22) CCB (calibration blank)

(23-32) up to ten more field or QC samples, then CCV, CCB (repeated until all samples are analyzed)

- No more than ten field or QC samples may be analyzed between the ICV/ICB and first CCV/CCB set, or between successive CCV/CCB sets. A CCV/CCB set must close out the run sequence.
- Place a 10mL aliquot (in 0.25N NaOH matrix) of each prepared sample into a separate 1-inch diameter, optically matched spectrophotometer cuvette.

  NOTE: The LCS scrubber solutions will need to be diluted 40 fold prior to color development. This is accomplished by placing a 0.25mL aliquot of the LCS scrubber solution into a cuvette, and diluting it to 10mL with 0.25N NaOH.

- Add 3.0mL of 1M NaH_2PO_4 solution to each cuvette containing standard or prepared sample.

  NOTE: After this solution is added, the cyanide in the sample is no longer stable and the color development steps must be continued without delay.

- Add 1.0mL of chloramine-T reagent to each cuvette and mix well using the vortex mixer.
- After 1 to 2 minutes, add 1.0mL of pyridine-barbituric acid reagent and 5.0mL of DI water and mix well immediately.
- After the red color has fully developed (usually about 8 to 15 minutes), read absorbance at 578nm using the spectrophotometer. Establish an instrument range from 0 to 100 %T or 0.000 to 2.000 absorbance.

  NOTE: All spectrophotometer checks must be performed per manufacturer's instructions prior to use.

9.2.3 CYANIDE STANDARD CURVE PREPARATION

Prepare a standard curve by plotting the absorbance of each standard (on a scale of 0.00 to 2.00 units) versus the standard's cyanide concentration (on a scale of 0 to 500µg/L). Perform a linear regression analysis (Note: A spreadsheet program on a personal computer may be used for plotting and regression analysis.) The linear regression correlation coefficient must be ≥0.995 for the calibration curve to be accepted.

9.2.4 DETERMINATION OF REACTIVE CYANIDE SAMPLE CONCENTRATIONS

Determine the concentration of reactive cyanide in each sample as follows:

$$\text{Reactive CN (mg/Kg)} = \frac{(A) \times (D) \times (V)}{W}$$

where:

A = µg/L CN in scrubber solution, determined from regression analysis

D = dilution factor if dilution was required to produce a response within the calibrated range

V = volume of scrubber solution (L); if this SOP is followed exactly, V = 0.200 LW = sample weight (g)

9.3 DETERMINATION OF SULFIDE IN THE SCRUBBER SOLUTION

The amount of scrubber solution available to be analyzed by gravimetric titration for reactive sulfide must be accurately known. Usually 90mL of scrubber solution is available since 10mL of the 100mL total scrubber solution is used for the cyanide analysis. Determine the amount of reactive sulfide in each scrubber solution as follows:

9.3.2 Transfer an aliquot (usually 90mL) of the scrubber solution into a beaker of suitable size. Add a clean Teflon-coated magnetic star bar and place the beaker on a magnetic stir plate.

9.3.3 The scrubber solution must be acidified to a pH of 2 prior to proceeding with the titrimetric determination. Using pH electrode or pH test strips, add 2mL of 6N HCl to the trap solution and check the pH. Continue adding 6N HCl until the pH drops to below 2. Pipet an additional 2mL of 6N HCl into the trap solution.

9.3.4 Place the beaker of adjusted pH solution on the balance and tare. Add

standard iodine solution to the beaker in 2.0mL increments until a yellow color persists. Record the total volume (in mL) of the standard iodine solution added. Add 2-4 drops of starch indicator solution. The color should now be blue-black. Re-tare the balance.

9.3.5 Add Standard Sodium Thiosulfate Solution dropwise until the blue-black color disappears and the sample turns clear. Record the weight change caused by the addition of titrant.

9.3.6 Calculate the concentration of reactive sulfide in the sample as follows (Note: A spreadsheet program on a personal computer may be used for calculating concentrations):

$$\text{Reactive Sulfide (mg/Kg)} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{W \times \frac{V}{T}}$$

where:

A = normality of the iodine solution

B = volume of iodine used (mL)

C = normality of the sodium thiosulfate solution

D = volume of sodium thiosulfate used (mL)

W = sample weight (g)

V = volume of scrubber solution titrated

T = total volume of scrubber solution

10. QUALITY CONTROL (QC)

10.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or less field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory duplicate (DUP) and laboratory control sample (LCS). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

10.2 BLANKS

Blanks are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank (MB) must be processed. All blanks (including initial calibration blanks and continuing calibration blanks, as applicable), must be free of positive analyte results greater than the analyte reporting limit.

10.3 LABORATORY CONTROL SAMPLE
The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. The results obtained are compared to results expected. Acceptance criteria are based on client's requirements and are often quite wide (e.g., 0%-200%).

10.4 LABORATORY SAMPLE DUPLICATE
The laboratory sample duplicate is analyzed as a measure of the precision of the analytical results generated. For this procedure, the Relative Percent Difference (RPD) between a sample and its duplicate should not be greater than 20%. RPD is calculated as shown below:

$$\text{RPD (\%)} = \frac{|\text{Result}_x - \text{Result}_{Dup}|}{\frac{(\text{Result}_x + \text{Result}_{Dup})}{2}} \times 100$$

Advisory acceptance criteria for all duplicates should be met. If RPD criteria are not met, check calculations. Narrate if sample inhomogeniety is suspected.

10.5 METHOD DETECTION LIMIT STUDY
Not Required. *Reactive* cyanide is a process defined parameter, and as such no viable verification standard exists. The LCS employed here is a check of cyanide *measurement* capability and does not reflect the presence of cyanide in a potentially reactive state (i.e., MDL not relevant because preparatory extraction steps cannot be captured).

11. DEVIATIONS FROM METHOD

11.1 Section 5.4 of SW-846 Chapter 7 Reactive Cyanide discusses a check sample called a cyanide reference solution (made from KCN and KOH and standardized against $AgNO_3$). Paragon uses the cyanide stock solution (made from KCN and NaOH) to create the laboratory control (check) sample. This cyanide stock solution is standardized against $AgNO_3$.

11.2 Paragon creates a stronger sulfide reference solution (sulfide spiking solution) than that specified in Section 5.4 of SW-846 Chapter 7 Reactive Sulfide. The method directs that 4.02g of $Na_2S{\bullet}9H_2O$ is dissolved in and brought to a 1L final volume with reagent water. Paragon uses 15g of $Na_2S{\bullet}9H_2O$ brought to 200mL using DI water.

11.3 Section 7.1 of the SW-846 Chapter 7 Reactive Cyanide and Sulfide procedures direct that 50mL of 0.25N NaOH solution plus a sufficient amount of organic-free reagent water for adequate depth be used as the scrubber solution. Paragon uses 100mL of undiluted 0.25N NaOH for an adequate depth of scrubber solution.

11.4 Section 8 of the SW-846 Chapter 7 Reactive Cyanide and Sulfide procedures depict calculations to determine the *rate* of release of HCN or H_2S gas. Paragon measures the *amount* of HCN or H_2S gas released.

11.5 Paragon does not perform matrix spike analyses for reactive cyanide or reactive sulfide. These QC analyses are not stipulated in SW846 Chapter 7.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

12.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

12.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.5 All flammable compounds must be kept away from ignition sources.

12.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name; NFPA Health, Flammability, and Reactivity ratings, and date.

12.1.7 Food and drink are prohibited in all lab areas.

12.2 WASTE DISPOSAL

12.2.1 Solid residues shall be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

12.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

12.2.3 Certain clients may require that the samples and residues from their analyses be returned to them. The Waste Compliance Officer will address these sample returns.

13. REFERENCES

U.S. Environmental Protection Agency, SW846, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods. Chapter 7, "Reactive Cyanide and Sulfide," Revision 3, 1996.

DOCUMENT REVISION HISTORY

7/26/05: Added reference Program Specification directive in "Responsibilities".
4/10/06: Discussed in "Introduction" EPA's withdrawal of this method guidance. Added DOCUMENT REVISION HISTORY.

Analytical Method: EPA SW846, Chapter 7	**Parameter:** Reactive Cyanide and Sulfide in Wastes		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration - minimum 5-point plus blank (cyanide)	As needed (i.e., at on-set of analyses or repeated when continuing calibration does not meet criteria)	Correlation coefficient (r^2) for linear regression must be $\geq$0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification - ICV (cyanide)	Once after each initial calibration	Response must agree within ±15% of initial calibration	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Method Blank (MB) Initial Calibration Blank - ICB and Continuing Calibration Blank – CCB (cyanide)	The MB may be run initially as part of the calibration curve (as applicable). (cyanide) The ICB is run following the calibration curve. CCBs are run following the CCV (after every ten samples), and to close an analytical run sequence	Analyte content of the blank must not exceed the analyte reporting limit (RL)	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Continuing Calibration Verification - CCV (cyanide)	Run after every ten samples and to end any run sequence (must be followed by a CCB analysis)	Response must agree within ±15% of initial calibration	Check that calculations and preparation are correct, evaluate/ correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Laboratory Control Sample (LCS)	One LCS must be run per 20 environmental samples processed	No acceptance limits have been established for the reactive cyanide or sulfide LCSs.	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.
Laboratory Duplicate (DUP)	One sample DUP must be run per batch of 20 or less environmental samples processed	RPD between the sample and its duplicate should be $\leq$20.	For RPDs outside of QC limit, check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

Text clarification re: calibration curve fit made to Deviations 11.1 and SOP Table. 10/22/08 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1113 REVISION 11

TITLE: DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY -- METHODS EPA 300.0 AND SW9056

FORMS: 1116 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER Steve Workman DATE 3/7/08

QUALITY ASSURANCE MANAGER [signature] DATE 3/7/08

LABORATORY MANAGER [signature] DATE 3-7-08

HISTORY: Rev0, 7/29/97; Rev1, 7/28/99; Rev2, 4/6/01; Rev3, 1/23/02; Rev4, 3/2/02; Rev5, 4/17/02; Rev6, 12/16/02; Rev7, 4/22/04; Rev8, 3/10//05; Rev9, 4/10/06; Rev10, 8/11/07; Rev11, 3/6/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- Methods EPA 300.0 and SW9056 -- are used to determine the concentration of selected ions in environmental water samples and in aqueous extracts of environmental solid samples. An Ion Chromatograph (IC) is used to separate and detect the anions. Paragon typically uses this procedure to determine the following anions: Chloride (Cl^-), Bromide (Br^-), Fluoride (F^-), Nitrate (NO_3^-), Nitrite (NO_2^-), Sulfate ($SO_4^{=}$), and Orthophosphate (PO_4^{3-}).

2. SUMMARY

The anions are separated and measured using an analytical system consisting of an autosampler, pump, and an IC containing ion exchange columns, a suppressor device, and a conductivity detector.

Small volumes of sample (typically 5mL) are injected via the autosampler into the IC to flush and fill the 25µL sample loop. The contents of the filled sample loop are then injected into a bicarbonate-carbonate eluent stream, which is pumped through a series of two ion exchange columns. The anions of interest are separated by the two ion exchange columns and then carried by the eluent stream through a third (suppressor) column. The suppressor column reduces the anions to their acid form, and also reduces the background conductivity of the eluent. Next, the eluent stream passes through a conductivity detector, and its signals are captured and maintained by a microprocessor (PC). The anions are identified based on retention times and are quantitated using an external standard calibration method.

Solid samples must first be extracted using deionized (DI) water prior to determination.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the ability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or by the successful analysis of a proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the workorder file indicate that this review for precision, accuracy and completeness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving these methods to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Samples that contain particles larger than 0.45µm and reagent solutions that contain particles larger than 0.20µm require filtration to prevent damage to instrument columns and flow systems.

4.2 Constituents that elute at retention times close to the retention times of analytes may interfere. Sample spiking with the analyte of interest can be used to solve most interference problems associated with retention times.

4.3 Large concentrations of an anion can cause interference by causing poor resolution or by overloading the capacity of the column. Sample dilution can be used to solve most interference problems associated with column overloading.

4.4 Several of the anions (NO_3^-, Cl^-, $SO_4^{=}$) are commonly found in the laboratory in concentrated acids and can easily cause contamination. Clean glassware and reagents are critical in order to prevent the occurrence of a noisy baseline or contamination of samples.

5. APPARATUS AND MATERIALS

5.1 Dionex DX-120 Ion Chromatograph (IC), or equivalent, equipped with an autosampler, eluent pump and conductivity detector

5.2 Dionex AS-14 or AS-14A anion exchange analytical columns with AG-14 or AG-14A guard columns, or equivalents

5.3 Anion ASRS-Ultra self-regenerating suppressor column, 4mm, or equivalent

5.4 Dionex *PeakNet* software, or equivalent

5.5 Dionex auto sampler vials ("PolyVials") with filter caps, 5mL, with appropriate 6-vial cassette holder

5.6 centrifuge tubes, polypropylene, disposable, 50mL

5.7 filter disks, 0.45 and 0.7µm

5.8 insertion tool for the PolyVial filter caps

5.9 Eppendorf™ adjustable pipettor, or equivalent, operated per SOP 321 requirements

5.10 volumetric flasks, various sizes, Class A

5.11 analytical balance, capable of weighing to 0.0001g, verified per SOP 305

5.12 conductivity meter

5.13 TCLP-type rotary tumbler

5.14 PolyVials, disposable, 10mL with caps

5.15 vortex mixer

6. REAGENTS – Only reagent grade or better chemicals may be used!

6.1 Deionized (DI) water, obtained from the laboratory's deionized water system

6.2 Helium (He) compressed gas, high purity grade or better

6.3 Eluent Solution Concentrate, 0.1M $NaHCO_3$ + 0.35M Na_2CO_3 (for AS-14/ AG-14): Dissolve 8.4g of sodium bicarbonate ($NaHCO_3$) and 37.1g sodium carbonate (Na_2CO_3) in DI water and dilute using DI water to 1000mL final volume. *Store at room temperature. Shelf Life = 1 year.*

0.1M $NaHCO_3$ + 0.8M Na_2CO_3 (for AS-14A/ AG-14A): Dissolve 8.4g of Sodium bicarbonate ($NaHCO_3$) and 84.8g sodium carbonate (Na_2CO_3) in DI water and dilute using DI water to 1000mL final volume. *Store at room temperature. Shelf Life = 1 year.*

6.4 Eluent Working Solution: Dilute the eluent concentrate solution 100-fold using DI water. Usually, 10mL of concentrate is diluted to a final volume of 1L. *Make fresh daily. Store at room temperature.*

7. STANDARDS

Two Stock Solutions (i.e., "first source" and "second source") are required for each analyte to create the necessary calibration and spiking solutions. Standard and spiking solutions may be prepared in-house from ACS reagent grade materials or can be purchased as certified solutions from a commercial vendor. Paragon's Standards and Solutions database is used to document and manage all standards in use at Paragon. **All anion standards are to be kept refrigerated at 4±2°C and Nitrite standards have shelf life of one month.** *Consult the Standards and Solutions database for the concentrations and traceability of the Nitrite (NO_2^-) and anion (Cl^-, Br^-, F^-, NO_3^-, $SO_4^=$, PO_4^{3-}) standards and solutions used in this procedure.*

8. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

8.1 Samples should be collected according to an approved sampling plan.

8.2 Samples should be collected in clean plastic or glass bottles. The volume collected should be sufficient to provide a representative sample and to allow for the analysis of quality control samples (i.e., matrix spike and duplicate).

8.3 Samples requiring analysis of nitrate, nitrite, and orthophosphate must be kept cool (4±2°C) and must be analyzed within 48 hours of collection.

8.4 Samples requiring analysis of bromide, chloride, fluoride and sulfate should be kept cool (4±2°C) and must be analyzed within 28 days of collection.

9. PROCEDURE

9.1 PREPARATION OF CALIBRATION STANDARDS

Calibration standards (see compositions below) are prepared by diluting the first source anion intermediate standard at five different levels using eluent working solution as the diluent. An eluent working solution blank is used as the 6th calibration point.

ANION CALIBRATION STANDARDS (mg/L)

Analyte Standard	#1 1000X	#2 100X	#3 25X	#4 10X	#5 5X
F^-	0.05	0.5	2	5	10
Cl^-	0.1	1	4	10	20
Br^-	0.1	1	4	10	20
NO_2^- as N	0.05	0.5	2	5	10
NO_3^- as N	0.1	1	4	10	20
PO_4^{3-} as P	0.1	1.0	4	10	20
$SO_4^=$	0.5	5	20	50	100

Calibration standard #4 (first source) is also used as the continuing calibration verification (CCV) standard. The "second source" intermediate anion standard is used to prepare the independent calibration verification (ICV) standard. With the exception of Nitrite, the ICV is made at concentrations half that of the CCV (concentration of Nitrite is 2.0mg/L).

9.2 SYSTEM START-UP AND SHUT-DOWN

9.2.1 Turn on gas and set He regulator to 2psi.

9.2.2 Turn on power by depressing the white button on the front of the instrument.

9.2.3 From the "Main Menu" window in *PeakNet*, click on the "**PEAKNET RUN**" icon. In the Peak Net Run window, select the "**DIRECT CONTROL**" icon. In the Direct Control window, click to start the pump, eluent pressure and SRS/cell.

9.2.4 The eluent flow rate should be set at 1.20mL/min for AS-14 or 1.00mL/min for AS-14A column/guard column. Check this manually by using a graduated cylinder to collect eluent from the waste line and calculate the flow rate from the volume expelled over the time period collected.

9.2.5 Allow the pressure to stabilize for about 30 minutes before starting an analytical sequence.

9.2.6 To shut down system, turn off the pump, eluent pressure and SRS/cell from the "**DIRECT CONTROL**" window. Turn off power (white button on main panel) and close gas tank valve OR:

<u>NOTE</u>: Turn on and off by pressing Local/Remote on front panel to highlight Local and manually press pump, eluent pressure and SRS/ cell.

9.3 EXTRACTION OF SOLID SAMPLES

9.3.1 Weigh 4.0g of sample into a 50mL polypropylene centrifuge tube. Add 40mL DI water.

9.3.2 Mix the suspension thoroughly and tumble using a rotary tumbler (TCLP-type) for about 60 minutes.

9.3.3 Centrifuge the resulting slurry for about 15 minutes.

9.3.4 Filter the supernatant as necessary using a 0.7μm filter disk and/or a 0.45μm filter disk.

9.4 SCREENING AQUEOUS SAMPLES AND SOLID SAMPLE EXTRACTS

Samples should be screened prior to analysis using a conductivity meter. Record screening results in logbook (Form 1116). The electrical conductivity of an aqueous solution is directly related to the concentration of total dissolved solids (TDS). The type of meter used is capable of converting conductivity to estimated TDS in mg/L.

9.4.1 It may be necessary to dilute a sample/extract prior to injection into the IC in order to protect the instrument and provide for sample analysis within the instrument's calibrated linear range. Samples/extracts should be diluted with eluent working solution as necessary so that solutions injected into the instrument do not exceed 1000mg/L estimated TDS (the sample screening information is used to determine the extent of dilution required). Visual appearance of the sample/extract, historical data, or additional information provided by the client may also provide information used to determine the extent of dilution needed.

NOTE: Use a small amount of eluent concentrate instead of eluent working solution as diluent when needed, to ensure that <1% volume change is effected overall.

9.4.2 Prepare aliquots of each pre-filtered sample or extract for analysis in 5mL Dionex vials; dilute as necessary per discussion above. Place filter caps half way down on vials and vortex. Use insertion tool to push cap down fully on vials. Load vials into cassettes for the autosampler.

9.5 SEQUENCE SET-UP

9.5.1 Analytical sequences are set-up using the *PeakNet* Chromatography Software. A new "**SCHEDULE**" is created for each day. Typically this schedule is renamed from the previous day's schedule and then edited to create the new schedule. Sample, sample type, method, and data file must be filled out correctly to save properly.

9.5.2 Each day's data are stored in a new subdirectory named for the day, using a yymmdd format (e.g., 050214). A typical daily analytical sequence is shown below:

1 - 6	calibration standards (when ICAL is performed)
7	ICV
8	ICB
9	MB
10	LCS
11 – 18	8 samples, may include MS/MSD

19 CCV
20 CCB

An analytical sequence can continue indefinitely by repeating Steps 9 – 20, so long as the quality control criteria are met. No more than 10 samples/extracts (including QC samples) may be analyzed between calibration verifications (i.e., CCV, CCB set). One Method Blank, one LCS, and one MS/MSD pair must be analyzed per twenty environmental samples of like matrix. A CCV, CCB set must close the analytical sequence. A CCV, CCB is used to initiate analysis when an ICAL is not performed.

At the end of the sequence, the autosampler stops, but the eluent pressure and SRS/cell pump will continue to run until stopped manually; unless stop method (Stop.met) is placed at the end of the schedule in the method column.

9.6 PEAKNET METHOD

A "**METHOD**" is created in *PeakNet* when calibration is needed. The method is a subprogram, which controls the events that take place throughout the analytical sequence (trigger autosampler, operate injection valve, start and end data acquisition, etc.) The method contains the integration parameters that are used in processing the raw data. The method also contains a table with the calibration curves and retention time windows for each analyte. This table is updated each time a new calibration is established. However, retention times may be updated as necessary using the information obtained from the first calibration verification check run that day.

9.7 DATA ACQUISITION AND PROCESSING

9.7.1 AUTOSAMPLER OPERATION

- Place cassette on autosampler facing inward.
- Press **"**Hold/Run**"** button (on autosampler) to advance cassette to injection port.
- Then press "Load" (on autosampler).
- After the autosampler "Load" button light begins to blink, click on the "Start" icon in the *PeakNet* "**RUN**" window.

Usually, a new injection is made every 10 minutes. Each chromatogram is stored in a separate file. Filenames are automatically given to each chromatogram based on information that is entered when the sequence is created (i.e., a filename prefix, and a value for the counter). The filename prefix is the date of acquisition, and the counter is set to add one for each injection (e.g., 060209_005.dxd designates the 5th injection made on February 9th).

9.7.2 Data processing (integration, peak identification, quantitation) is performed after the chromatograms have been acquired. It is important to review the integration to ensure that baselines are drawn correctly. In cases where it is necessary to modify a baseline, the raw data must include printouts of the chromatogram before and after the baseline correction (refer to SOP 939 for further directives). Only values that fall between the lowest and highest calibration standards are reported. Samples yielding results that exceed the highest standards should be diluted and reanalyzed. Results are reported in mg/L. Report NO_2^- as N, NO_3^- as N, and PO_4^{3-} as P.

9.8 RUN LOG

A record of each day's analyses is entered into the instrument "**SCHEDULE**". The following information is recorded:

- Date of analysis
- Analyst's initials
- Solution ID (including any dilutions)
- Filename
- Schedule ID

9.9 MAINTENANCE AND TROUBLESHOOTING

9.9.1 A maintenance logbook is used to record all information concerning instrument maintenance. The logbook documents all repairs and symptoms of problems.

9.9.2 The fritted disks (sometimes called "bed supports") at the ends of the guard and analytical columns should be changed periodically. The system backpressure will gradually increase over a period of many days or weeks as the fritted disks become clogged with small particles.

9.9.3 In blanks (ICBs, CCBs, MBs), small peaks may be observed in the retention time windows for various anions after analyzing samples high in dissolved salts. This problem is most frequently encountered with orthophosphate. Carryover effect can be addressed via the following:

- Carryover may be lessened or prevented by setting up the autosampler to pass an aliquot of eluent working solution through the sample loop between sample injections. To accomplish this, a vial of eluent working solution is placed between each vial containing a sample or standard in the autosampler. The autosampler recognizes the added vial to be a "rinse vial" because the filter cap is pushed down to the first position using the special insertion tool.

- The sample loop and the tubing that carries the sample solution from the autosampler to the IC can be cleaned with 0.1N HCl using a syringe with a luer lock connector. All traces of HCl must be removed from the system by rinsing the line thoroughly with DI water before analyzing samples.

9.9.4 The guard column will need to be replaced more frequently than the analytical column. Generally, the guard column is replaced about three times for each analytical column that is used over approximately a 1-year period. Overlap of peak retention times is a sign that the analytical column needs replacing.

10. QUALITY CONTROL (QC)

10.1 DEFINITION OF ANALYSIS BATCH

An analysis batch is defined as a group of twenty (20) or less field samples of like matrix that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike and duplicate (MS/MSD). All QC samples must be carried through all stages of the sample preparation and measurement steps.

10.2 METHOD BLANKS

Method blanks (MBs) are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. The blank concentration found must be less than the analyte reporting limit.

10.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) should contain all the analytes of interest and is analyzed to measure the accuracy of the method. To be acceptable, the LCS recovery must be between 90% and 110% of the expected concentration for each analyte of interest for aqueous samples, and between 85% and 115% of the expected concentration for each analyte of interest for solid sample extracts.

10.4 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE

Matrix spikes (MS) consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection. The matrix spike duplicate (MSD) serves as a laboratory duplicate analysis. All of the analytes of interest should be spiked. Analyte recovery for matrix spikes is calculated as shown below:

$$\text{MS \% Recovery} = \frac{(C_{found} - C_{native})}{C_{added}} \times 100$$

where:

C_{found} = analyte concentration found in the spiked sample
C_{native} = native analyte concentration found in the unspiked sample
C_{added} = spike added analyte concentration

The quality control acceptance limits for MS/MSD recovery vary (consult LIMS Program Specifications).

The MSD is analyzed as a measure of the precision of the analytical results generated. The Relative Percent Difference (RPD) between a sample and its duplicate should not be greater than 20% (or as specified by client criteria). RPD is calculated as shown below:

$$RPD = \frac{| Result_x - Result_{Dup} |}{(Result_x + Result_{Dup}) / 2} \times 100$$

Acceptance criteria for all spikes and duplicates should be met. If MS/MSD recovery or RPD criteria are not met, results of the laboratory control sample analyses must be carefully considered. If LCS results are acceptable, sample matrix interference is suspected and a notation in the narrative comments is made.

10.5 LINEARITY STUDY

A linearity study must be performed at minimum, every six months, or whenever there is a significant change in operator, background, or instrument response. The study must consist of a blank and a minimum of three standards. The range of the linearity study is generally broader than that defined as the linear calibration range, since the purpose of the linearity study is to verify the instrument's overall capabilities. All verification results must agree within ±10% of expected values.

10.6 RETENTION TIME WINDOW (RTW) STUDY

Analyte retention time window studies are conducted periodically, at minimum upon column change out. An analyte RTW study is performed by noting the variations in analyte retention times yielded in the various concentrations of standards run across the course of a day. The analyte RTW study is typically accomplished when initial calibrations are performed. The width of the RTW is established for each analyte based on three times the standard deviation of the analyte retention times noted during the study. Subsequent CCVs are evaluated against these established times and windows, and are acceptable if the RT has not drifted more than 10%. The CCV RT may be used to re-center the window, so long as the 10% drift criterion has been met. If the 10% drift criterion is exceeded, a new ICAL is performed. RTWs are used to identify target analytes,

11.1 Section 7.3.3 of Method SW846 9056 describes instrument calibration by the use of a first order (linear) calibration curve. Paragon employs **the type of curve fit that best fits the data generated for each analyte. Typically, a linear calibration curve may be used for fluoride, whereas** a second order (quadratic) calibration curve, **consisting of** ~~with typically~~ six points ~~for all IC analytes~~ (`zero' point response included; curve not forced through zero), **may be used for other analytes,** based on historical experience that this type of calibration curve (quadratic) provides a better fit of the **analyte** calibration data.

however, the experience of the analyst must also weigh heavily in the interpretation of chromatograms.

10.7 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study shall be performed as needed (i.e., whenever there is a significant change in operator, background, or instrument response) and at a minimum, every 6 months.

11. DEVIATIONS FROM METHOD

11.1 Section 7.3.3 of Method SW846 9056 describes instrument calibration by the ~~use~~ of a first order (linear) calibration curve. Paragon employs ~~a second~~ order (quadratic) calibration curve with typically ~~six points~~ for all IC analytes ('zero' point response included; curve ~~not~~ forced through zero) based on historical experience ~~that this~~ type of calibration curve (quadratic) provides a better fit of ~~the~~ calibration data.

11.2 Paragon notes that Method EPA 300.0, Section 7.3, prescribes an eluent concentration of 1.7mM sodium bicarbonate and 1.8mM sodium carbonate. Paragon uses an eluent concentration of 0.1M sodium bicarbonate and 0.35M sodium carbonate when using AS-14 columns, and an eluent concentration of 0.1M sodium bicarbonate and 0.8M sodium carbonate when using AS-14A columns, per the application information given with each Dionex column. This eluent profile enables run time to be decreased while maintaining adequate peak resolution throughout the analysis.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

12.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

12.1.3 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) and when handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.5 All flammable compounds must be kept away from ignition sources.

12.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name; NFPA Health, Flammability, Reactivity ratings; and date.

12.1.7 All gas cylinders shall be secured at all times. The valve stem cap must be installed in the absence of a regulator.

12.1.8 Food and drink are prohibited in all lab areas.

12.1 WASTE DISPOSAL

12.2.1 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as "empty" prior to disposal.

12.2.2 Certain clients may require that the samples and residues from their analyses be returned to them. The Waste Disposal Officer will address these sample returns.

13. REFERENCES

13.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, revision 2.1, 1993. Method 300.0, "Determination of Inorganic Anions by Ion Chromatography".

13.2 U.S. Environmental Protection Agency, SW846, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, 1996. Method 9056, "Determination of Inorganic Anions by Ion Chromatography".

DOCUMENT REVISION HISTORY

4/10/06: Added reference Program Specification directive in "Responsibilities". Added clarification and detail regarding equipment operation. Added DOCUMENT REVISION HISTORY.

8/11/07: Included discussion of particulates and filtering as INTERFERENCES 4.1. Clarified (Section 9.1, 9.5.2) that ICALs are conducted as needed (see QC Table), not daily. Also clarified that eluent working solution (not DI water) is used as the basis for calibration standards and IC rinses (Section 9.9.3), and for diluting samples/extracts when necessary (Section 9.4.1). Also that a blank comprises the 6^{th} point of the calibration curve.

3/7/08: Clarified Section 10.6.

Analytical Method: E 300.0; SW9056	**Parameter:** Determination of Anions by Ion Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Retention Time Window (RTW) Study	Performed initially and as necessary (i.e., redone when required as part of troubleshooting when daily RTWs do not agree within ±10% of expected values)	Analyte RTWs established as three times the standard deviations of the analyte retention times noted in the various concentrations of standards run during the course of the day's study	If analyte retention time not reproducible, identify and correct problem. Perform a new initial calibration. Analyte RTWs must agree within ±10% of expected values.
Linearity check; minimum of three standards and a blank; run to verify the range of capability of the instrument	At minimum every six months; whenever a significant change in operator, background, or instrument response occurs	All verification data results must agree within ±10% of expected values	Evaluate/correct instrument malfunction; reanalyze until acceptable results are generated.
Initial Calibration; minimum 6-point (includes blank, but curve not forced through zero)	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria)	**First or** Second order quadratic fit calibration curve generated electronically by instrument software. Coefficient of Determination (r^2) of the calibration curve equation must be ≥ 0.99	Evaluate/correct instrument malfunction, prepare a fresh set of calibration standards, and reanalyze initial calibration to obtain an acceptable curve.
Independent Calibration Verification (ICV); second source at or below midpoint	Run immediately following initial calibration	Analyte concentration must agree within ±10% of expected values for both Methods SW9056 and 300.0; analyte retention time must agree within ±10%	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Initial Calibration Blank (ICB)	Run immediately following the ICV	Anion content of ICB must not exceed analyte reporting limit (RL)	Check all calculations. If no computation errors are found, prepare a fresh ICB and analyze. Sample analysis cannot proceed until a successful ICB is analyzed.
Method Blank (MB)	One per each batch of ≤20 field samples of like matrix; one each time a reagent is changed	Anion content of MB must not exceed analyte reporting limit (RL) Exception: Samples with analyte concentrations >10X amount found in blank may be reported and narrated.	Prepare a fresh MB and analyze to confirm whether or not system contamination is present. If contamination in the MB is still present above the RL, perform system maintenance, analyze a CCV/CCB set, and re-analyze all samples associated with the failed MB that were not reportable.
Laboratory Control Sample (LCS)	One per batch of ≤20 field samples.	Results obtained must agree within ±10% of expected (known) analyte concentration for aqueous samples; within ±15% of known analyte concentration for solid sample extracts	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.

Analytical Method: E 300.0; SW9056	**Parameter:** Determination of Anions by Ion Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Verification (CCV) at or below midpoint	Brackets each set of 10 field sample/QC sample analyses	Analyte concentration must agree within ±5% Method SW9056 and within ±10 % Method 300.0; analyte retention time must agree within ±10%	Rerun CCV. If CCV still not compliant, evaluate/correct instrument malfunction and recalibrate. Samples analyzed after a failed CCV must be reanalyzed. If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Continuing Calibration Blank (CCB)	Analyzed immediately following each CCV.	Anion content of CCB must not exceed analyte reporting limit (RL) Exception: Samples with analyte concentrations >10X amount found in blank may be reported and narrated.	Prepare a fresh CCB and analyze. If contamination in the CCB is still present above the RL, perform system maintenance, analyze a CCV/CCB set, and re-analyze all samples associated with the failed CCB that were not reportable.
Matrix Spike (MS) and Matrix Spike (Laboratory) Duplicate	One MS/MSD set per batch of ≤20 field samples (this provides an average frequency of one per ten samples per Method SW9056 requirements).	Recoveries should meet client criteria for the spiked compounds. RPD for the MS DUP should meet advisory limit of ≤20%	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated LCS is within control limits, then sample matrix effects are the most likely cause. Note in narrative. For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	At minimum every six months; whenever a significant change in operator, background, or instrument response occurs	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and correct problem. Repeat the MDL study. Consult the Department / Project / QA Managers. The managers may determine that an adjustment to the RL is needed.

Paragon Analytics

FORM 1116

CONDUCTIVITY SCREENING WORKSHEET

Instrument ID: VWR Digital Conductivity Meter S/N A22036

Workorder ID / Sample No.		Estimated µS	Dilution(s)	Anion(s)	Date	Initials	Comments

Reviewed by / Date _____ **Form 1116r4.frm (6/29/04)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1117 REVISION 3

TITLE: **TOTAL ORGANIC CARBON IN SOIL BY RAPID DICHROMATE OXIDATION -- MSA WALKLEY-BLACK METHOD**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7-27-05
QUALITY ASSURANCE MANAGER _____ DATE 7/24/05
LABORATORY MANAGER _____ DATE 7-27-05

HISTORY: Rev0, 8/15/99; Rev1, 4/29/02; Rev2, 2/14/04 (format updated) and 3/29/05 (re-released without revision); Rev3, 7/26/05 (Program Spec. reference added). **Re-released w/o revision 8/15/07 DAS**

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- MSA Walkley-Black (1996) -- are used to determine the concentration of total organic carbon (TOC) in soil and other soil-like matrices. Rapid dichromate oxidation is the process by which TOC content is determined.

2. SUMMARY

Organic matter in soil is oxidized by treatment with a hot mixture of potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4) according to the following reaction:

$$2Cr_2O_7^{2-} + 3C + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$$

After the reaction, the excess (unreacted) dichromate ($Cr_2O_7^{2-}$) is quantified by titration with standard ferrous sulfate ($FeSO_4^{2-}$) solution. The $Cr_2O_7^{2-}$ consumed during the reaction with the soil is assumed to be equivalent to the organic carbon (C) in the soil.

The heat of dilution generated by mixing concentrated H_2SO_4 with $K_2Cr_2O_7$ solution is satisfactory for oxidizing about 75% of the organic C in most soils. In accordance with the analytical method, a correction factor of 1.3 is used to account for the incomplete combustion.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training

review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/ analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 It is assumed that C in soil organic matter has an average valence of zero and that each C atom undergoing oxidation to CO_2 releases four electrons. Therefore, the gram equivalent weight of C in this reaction is 3.0g /eq. If the average valence of C in the sample is different from zero, the average gram equivalent weight of C will be different from 3.0g /eq.

4.2 If present, ferrous iron (Fe^{2+}) will be oxidized to ferric iron (Fe^{3+}) and, therefore, consume $Cr_2O_7^{2-}$. This could potentially bias results high.

4.3 Significant amounts of Cl^- may consume $Cr_2O_7^{2-}$ by forming chromyl chloride (CrO_2Cl_2). This could potentially bias results high.

4.4 The higher oxides of manganese (largely MnO_2) can compete with $Cr_2O_7^{2-}$ for oxidizable substances. This could potentially bias results low.

4.5 The heat of dilution generated by mixing concentrated H_2SO_4 with $K_2Cr_2O_7$ solution is satisfactory for oxidizing about 75% of the organic C in most soils. In accordance with the analytical method, a correction factor of 1.3 is used to account for the incomplete combustion.

5. APPARATUS AND MATERIALS

5.1 Erlenmeyer flasks, 500mL

5.2 beaker, 150mL

5.3 graduated cylinder, Class A, 200mL capacity

5.4 magnetic stir bars, Teflon™ coated

5.5 magnetic stir plate

5.6 Eppendorf™ pipet and repeater pipet (or equivalent), capable of delivering 5.0mL

5.7 transfer pipets, plastic, disposable

5.8 analytical balance, capable of weighing to ± 0.0001g

5.9 top loading balance, capable of weighing to ± 0.01g

6. REAGENTS - Only ACS grade or better chemicals may be used.

6.1 Deionized (DI) water. Obtained from the laboratory deionized water system.

6.2 Ottawa Sand. Inert. EMD, SX0075-3 or equivalent. *Shelf Life = Indefinite.*

6.3 Sulfuric Acid (H_2SO_4), concentrated: EMD, SX1247-2 or equivalent. *Shelf Life = Per expiration date stated by manufacturer on label.*

6.4 Potassium Dichromate ($K_2Cr_2O_7$), 0.167M (1.00N): Mallinckrodt, 6770-02 or equivalent. Transfer 49.04g $K_2Cr_2O_7$ (dried at 105°C) to a 1L volumetric flask. Dissolve and bring to volume with deionized water. *Shelf Life = 1 year.*

6.5 "Ferroin" Indicator (*o*-Phenanthroline-ferrous complex), 0.025M: Obtain from a commercial vendor or dissolve 14.85g *o*-phenanthroline monohydrate and 6.95g $FeSO_4 \bullet 7H_2O$ in 1L of water. *Shelf Life = 1 year or per expiration date stated by manufacturer on label.*

6.6 Ferrous Sulfate, 0.5N: JT Baker, 2074-05 or equivalent. Dissolve 140g $FeSO_4 \bullet 7H_2O$ and 15mL concentrated H_2SO_4 in 1L water. Standardize this reagent each day before use by titrating against 1.00N $K_2Cr_2O_7$. *Made daily each day of use.*

6.7 Organic Carbon Standard, 20mg C/mL: JT Baker, 2959-00 or equivalent. Transfer 4.25g of Potassium Hydrogen Phthalate (KHP) to a 100mL volumetric flask. Dissolve and bring to volume with deionized water. Store in refrigerator. *Shelf Life = 1 year.*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples must be collected according to an approved sampling plan.

7.2 Samples should be held in the dark at 4±2°C to minimize possible microbial decomposition.

7.3 There is no established maximum holding time allowance for TOC in solids by this method. A 28-day hold time is recommended based on aqueous sample analysis methodologies.

8. PROCEDURE

8.1 FIELD AND QUALITY CONTROL (QC) SAMPLE PREPARATION

8.1.1 Appropriate sample size is determined by actual organic carbon content. When the prepared sample is titrated, ≥ 2mL of titrant should be required to reach the endpoint. If less than 2mL of titrant is needed, the sample is to be reanalyzed using one-tenth the sample size.

The sample aliquot's organic carbon content must not exceed 10 grams (see chart below). Use a maximum aliquot (10g) for samples with <0.25% organic C. If a sample aliquot consumes more than 90% of the dichromate added (i.e., requires less than 2mL titrant to reach endpoint), the sample must be reanalyzed using one tenth less soil.

Familiarization with samples through prior project experience and observation or other data may be used to determine the initial sample size for analysis.

% Organic C	Amount of Soil to Use
0.025 - 0.25%	10g
0.25 - 2.5 %	1.0g
2.5 - 25 %	0.10g

8.1.2 All test information and data are recorded on a laboratory benchsheet.

8.1.3 Label a 500mL Erlenmeyer flask. Weigh the empty flask on the top loading balance, record the weight, tare the balance while the flask is still on it. Measure a ground aliquot of soil (per chart above) into the flask. Record the weight of the sample aliquot.

Select one sample that is representative of the sample batch and prepare a second aliquot to serve as the laboratory Duplicate. One laboratory duplicate must be prepared for each batch of 20 or fewer environmental samples processed together as a unit.

8.1.4 Prepare a Method Blank (MB) with every batch of 20 samples or less, by transferring 10g of clean sand into a designated pre-weighed 500mL Erlenmeyer flask.

8.1.5 One Laboratory Control Sample (LCS) must be prepared with every batch of 20 samples or less. To prepare the LCS, transfer 10g of clean sand to a labeled pre-weighed Erlenmeyer flask. Add 0.5mL of 20mgC/mL standard. Expected concentration of the LCS is 1000mg/kg TOC.

8.2 SAMPLE DIGESTION

NOTE: Sample digestion **must** be performed in the fume hood!

8.2.1 Use a repeater pipet to add 10.0mL of 1.00N $K_2Cr_2O_7$ to each sample flask. Swirl the flask gently to disperse the soil.

8.2.2 Rapidly add 20mL of concentrated H_2SO_4, directing the stream into the soil suspension (a bottle pump dispenser may be used). Immediately swirl the flask gently until the soil and reagents are mixed, then more vigorously for approximately one minute.

CAUTION! The contents of the flask will become very hot when the acid is mixed into the dichromate solution. Use extreme care when adding the concentrated H_2SO_4. Proper eye and hand protection MUST be used!

8.2.3 Allow the hot flask + contents to stand in the fume hood approximately 30 minutes. Use a graduated cylinder to add 200mL DI water and swirl.

8.2.4 Allow the flask + contents to cool to room temperature and any suspended sediments to settle. Reweigh each flask and record in the laboratory logbook.

8.2.5 Tare a 150mL beaker containing a stir bar. Gravimetrically weigh 100g of digested sample into the beaker. Record the sample weight in the laboratory logbook.

8.3 TITRANT STANDARDIZATION

8.3.1 Three aliquots for titration must be prepared. Transfer a 5.00mL aliquot of 1.00N $K_2Cr_2O_7$ into each of three 150mL beakers. Add 100mL DI water. **IN THE FUME HOOD**, rapidly add 10mL of concentrated H_2SO_4 to each beaker. Swirl for approximately one minute. Allow beakers to cool to room temperature. Add 2-3 drops of ferroin indicator. Place the beaker + contents on the balance and tare the balance. Place the beaker onto a magnetic stir plate and agitate at a rate sufficient to thoroughly mix.

8.3.2 While still mixing on the stirplate, use a transfer pipet to carefully add $FeSO_4$ solution dropwise until the endpoint is reached (solution color changes from green to dark red). Reweigh the beaker + contents. Record the amount of $FeSO_4$ solution added.

8.3.3 Repeat the steps above for the remaining two aliquots prepared for standardization.

8.3.4 Calculate the concentration of the $FeSO_4$ solution as follows:

$$[FeSO_4] = (Con_{Cr})\,(V_{Cr}) / (V_F)$$

where:

$[FeSO_4]$ = concentration of $FeSO_4$ titrant (in N or eq/L)
Con_{Cr} = concentration of $K_2Cr_2O_7$ solution (as 1.00N or in eq/L)
VCr = volume (mL) of $K_2Cr_2O_7$ solution titrated; 5.00mL
V_{Fe} = volume (mL) of titrant required to reach endpoint

8.3.5 Average the results of the three standardizations to determine the concentration of the $FeSO_4$ solution.

8.4 SAMPLE DETERMINATION

8.4.1 To the 100g of sample digestate solution, add 2-3 drops of ferroin indicator to each beaker. Place the beaker + contents on the balance and tare the balance. Move the beaker to the stir plate. While stirring, use a transfer pipet to carefully dispense standardized $FeSO_4$ solution dropwise into the beaker until the endpoint is reached (the endpoint is the point at which the beaker solution color changes from green to dark red).

Reweigh the beaker + contents. Record the amount of $FeSO_4$ solution on the laboratory benchsheet (an amount ≥ 2mL should be required). If less than 2mL of $FeSO_4$ titrant is needed, the sample must be reprepared and reanalyzed using one-tenth the initial sample size.

NOTE: If experience shows that the endpoint of the titration cannot be easily discerned because of the suspended soil in the beaker, the sample suspension can be filtered through acid resistant filter paper (e.g., Whatman #41) under vacuum prior to analysis.

8.4.2 Calculate the organic C concentration in each sample using an Excel spreadsheet or as follows (record result in laboratory benchsheet):

$$\text{Organic C, \%} = [(V_{Cr} * Con_{Cr}) - R * (V_{Fe} * Con_{Fe})] * (0.003)\ (100) / (W_S) * 1.3$$

where:

V_{Cr} = volume (mL) of $K_2Cr_2O_7$ solution; (if this SOP is followed without deviation, V_{Cr} = 10.0mL

Con_{Cr} = concentration of $K_2Cr_2O_7$ solution, N (if this SOP is followed without deviation, Con_{Cr} = 1.0N)

R = sample Volume Ratio (total final sample wt. / wt. of aliquot titrated)

V_{Fe} = volume of $FeSO_4$ to reach endpoint

Con_{Fe} = concentration of $FeSO_4$ titrant (in N or eq/L)

0.003 = constant that converts meq to grams of C

100	=	constant that converts ratio to percent
W_S	=	dry sample weight (g) [moist wt*((100 - %moisture)/100)]
1.3	=	correction factor to account for incomplete carbon oxidation

9. QUALITY CONTROL (QC)

9.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or less field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory duplicate (DUP) and laboratory control sample (LCS). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

9.2 Method Blanks (MBs) are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. For this procedure, the MB consists of an aliquot of clean Ottawa sand. The result for the MB must be < 0.025% organic C (which was established as the lower limit of detection during the initial method demonstration).

9.3 The Laboratory Control Sample (LCS) is analyzed to measure the accuracy of the method. A known amount of analyte is prepared and analyzed. Results obtained are compared to results expected. To be acceptable, the organic carbon found in the LCS must be between 70% and 110% of that added. NOTE: These interim control limits were established as ±20% centered around an average 90% recovery rate (as determined during the initial method demonstration), and are subject to revision.

Calculate the percent recovery (%R) for the LCS as follows:

$$\text{LCS } \%R = (Con_{found} / Con_{expected}) * 100$$

where:

Con_{found}	=	Calculated concentration of TOC in LCS
$Con_{expected}$	=	Concentration of TOC expected in LCS (if this SOP is followed without deviation, $Con_{expected}$ = 1000.0mg/kg TOC)

9.4 A laboratory duplicate (DUP) is analyzed as a measure of the precision of the analytical results generated. The Relative Percent Difference (RPD) between a sample and its duplicate should not be greater than 30%. RPD is calculated as follows:

$$RPD\ (\%) = \frac{|Result_X - Result_{Dup}|}{\frac{(Result_X + Result_{Dup})}{2}} \times 100$$

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of the MSA Walkley-Black method. There are no known deviations from the method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The aqueous solution left over from the titration shall be disposed of in the Acidic Aqueous Laboratory Waste satellite collection vessel.

11.2.2 The solid residues shall be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

11.2.4 Certain clients may require that the samples and residues from their analyses are returned. The Waste Compliance Officer will address these samples.

11.2.5 The radioactive aqueous solution left over from the titration shall be disposed of in the Mixed Radioactive Aqueous Acidic Laboratory Waste (Contains Chrome) satellite collection vessel.

12. REFERENCES

American Society of Agronomy and Soil Science Society of America (SSSA), Madison, WI. SSSA Book Series No. 5, Methods of Soil Analysis (MSA), Part 3, Pages 995-996. "Walkley-Black Method". Nelson, D.W. and L.E. Sommers, 1996.

Analytical Method: MSA Walkley-Black	**Parameter:** Total Organic Carbon (TOC)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Calibration - analyte content determined by direct concentration (obtained by calculation from titration)	Titrant is standardized each day of use	Value obtained by calculation	Not Applicable.
Method Blank (MB)	One per each batch of ≤20 samples	MB must not contain 0.025% or greater organic carbon	Check all calculations. If no computation errors are found, prepare a fresh MB and analyze. Associated samples must also be reanalyzed.
Laboratory Control Sample (LCS)	One per batch of ≤ 20 samples	Concentration results obtained must agree between 70% and 110% of carbon content added as KHP	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.
Laboratory Duplicate (DUP)	One per batch of ≤ 20 samples.	RPD must be ≤30%.	Check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1119 REVISION 6

TITLE: **DETERMINATION OF TOTAL PHOSPHORUS AND ORTHO-PHOSPHATE IN WATER – METHODS EPA 365.2 AND SM4500-P B(5) and E**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 10/16/07
QUALITY ASSURANCE MANAGER _____ DATE 10/8/07
LABORATORY MANAGER _____ DATE 11-5-07

HISTORY: Rev0, 9/22/99; Rev1, 8/22/02; Rev2, 2/10/03; Rev3, 3/6/03; Rev4, 2/9/04, 3/29/05; Rev5, 7/26/05, 8/15/07; Rev6, 10/8/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- EPA Method 365.2 and Standard Methods SM4500-P B(5) and E -- are used to determine total phosphorus (P) and ortho-phosphate content in environmental water samples. These methods are applicable to the analyses of drinking, surface, and saline waters and domestic and industrial wastewaters.

2. SUMMARY

Phosphorus (P) occurs in natural waters and wastewaters mostly in the form of phosphates. These are commonly classified as ***orthophosphates, condensed phosphates,*** and ***organically bound phosphates.*** Orthophosphate reacts with ammonium molybdate and antimony potassium tartrate in an acid medium to form a heteropoly acid-phosphomolybdic acid complex that is reduced to intensely colored molybdenum blue with ascorbic acid. The color intensity is proportional to the orthophosphate concentration. Orthophosphate is the only form of phosphorus that forms a blue color in this test. The results of this test are expressed in units of "mg phosphorus per L" (mg P/L) of sample.

Total phosphorus refers to the phosphorus measured colorimetrically after a sample has been digested by the persulfate digestion method with sulfuric acid to convert polyphosphates and organic phosphorus compounds to orthophosphate. Because phosphorus may occur in combination with organic matter, a digestion method to determine total phosphorus must be able to oxidize organic matter effectively to release phosphorus as orthophosphate.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicates that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 High concentrations of dissolved iron may cause precipitation of and subsequent loss of phosphorus.

4.2 Arsenate reacts with the molybdate reagent to produce a blue color similar to that formed with orthophosphate. Arsenate concentrations as low as 0.1mg/L arsenic can interfere with the determination of orthophosphate.

4.3 Hexavalent Chromium (Cr^{+6}) and Nitrite (NO_2^-) interfere to give results biased low (approximately 3%) at concentrations of 1mg/L and biased low (approximately 10-15%) at 10mg/L.

4.4 The procedure is highly susceptible to contamination from phosphate-containing detergents and hand contact. ***All glassware, graduated cylinders, funnels, etc., used for sample preparation, standard preparation, or any phase of the analysis must be rinsed with 10% Sulfuric (H_2SO_4), Hydrochloric (HCl) or Nitric (HNO_3) acid solution three times followed by three rinses with DI water before use.***

5. APPARATUS AND MATERIALS

5.1 Sequoia Turner UV/VIS Spectrophotometer 340 or any filter photometer suitable for measurements at 650nm with a light path of 1.0cm or longer

5.2 Spectrophotometer cuvettes, optically matched, 1 inch diameter

5.3 Vortex mixer

5.4 Disposable, polypropylene beakers, 100mL

5.5 Top loading balance capable of reading to 0.01g

5.6 Analytical balance capable of weighing to 0.0001g

5.7 Eppendorf® pipettes, various sizes

5.8 Repeater pipettor capable of delivering 1.0-4.0mL

5.9 Disposable transfer pipettes

5.10 Hot plate, large or small (depending on amount of samples to be prepared)

5.11 Watch covers, Pyrex®

5.12 Beakers, Pyrex®, 250 or 150mL

NOTE: ***Use only designated acid-washed Pyrex® beakers and watch covers. These should be dedicated for phosphorus analysis only. See Section 4.4 above.***

6. REAGENTS

6.1 Deionized (DI) water

6.2 Phosphorus Stock Standard, 1000 or 10000mg phosphorus/L (**First Source**): Purchase from a commercial vendor or prepare by dissolving pre-dried potassium phosphate (KH_2PO_4) in DI water. The potassium phosphate salt should be dried in an oven at 105°C for at least one hour and then cooled to room temperature in a desiccator prior to weighing. Weigh the salt to the nearest 0.0001g using an analytical balance. Consult the Standards Database for current formulas. Example: To create 10000mg/L standard, dissolve 10.9840g KH_2PO_4 salt in 250mL DI water. *Shelf-life = One year from date of purchase or preparation.*

6.3 Intermediate Phosphorus Standard, 100mg phosphorus/L (**First Source**): Dilute the stock standard discussed above as necessary to create 100mg/L intermediate phosphorus standard. Example: A 100mg/L standard may be created by diluting 5mL of the 10000mg/L standard to a final volume of 500mL with DI water. *Shelf-life = One year from date of preparation or when parent standard expires.*

6.4 Phosphorus Stock Standard, 1000 or 10000mg phosphorus/L (**Second Source**): Purchase from a commercial vendor or prepare standard as discussed in Section 6.2 above. The salt used must be from a different source than the salt used for the first

source stock standard (i.e., from a different vendor or a different lot if from the same vendor). *Shelf-life = One year from date of purchase or parent preparation.*

6.5 Intermediate Phosphorus Standard, 100mg phosphorus/L (**Second Source**): Dilute the 2nd source stock standard as necessary to create 100mg/L intermediate standard. See Section 6.3 above. *Shelf-life = One year from date of parent preparation.*

NOTE: All phosphorus standards must be stored in polypropylene bottles at 4°C.

6.6 Sulfuric Acid (H_2SO_4), Concentrated. EMD, SX1244-5 or equivalent.

6.7 Sulfuric Acid Solution, 50%: In a 1.5L Pyrex® beaker, *slowly and cautiously* add 500mL concentrated H_2SO_4 to 500mL DI water, or any volume as long as ratio stays the same (1:1). Mix cautiously. Cool the beaker and contents in a cold water bath. *Shelf-life = One year from date of preparation.* **Store in a bottle that previously contained concentrated sulfuric acid and/or polypropylene bottles.**

6.8 Sulfuric Acid Solution, 11N: In a 1L Pyrex® beaker, *slowly and cautiously* add 220mL 50% H_2SO_4 to 140mL DI water or 310mL concentrated H_2SO_4 to 600mL DI water. Allow cooling and bring to 1000mL final volume. *Shelf-life = One year from date of preparation.*

6.9 Sulfuric Acid Solution, 5.0N: In a 500mL Pyrex® beaker, *slowly and cautiously* add 100mL 50% H_2SO_4 to 260mL DI water or 70mL concentrated H_2SO_4 to 500mL final volume with DI water. *Shelf-life = One year from date of preparation.*

6.10 Ammonium Persulfate $(NH_4)_2S_2O_8$, reagent grade. GFS Chemicals, Item No. 843 or equivalent.

6.11 Phenolphthalein Indicator: VWR, Cat. No. VW3341-2 or equivalent. Purchase from a commercial vendor or prepare by dissolving 0.5g of phenolphthalein in a solution of 50mL ethyl or isopropyl alcohol and 50mL of DI water. *Shelf-life = Per expiration date indicated on label by manufacturer.*

6.12 Sodium Hydroxide (NaOH), 10N: JT Baker, 3722-07 or equivalent. Slowly add 400g NaOH pellets to 800mL of DI water in a 1L Pyrex® beaker. Cool and dilute to volume with DI water. *Shelf-life = One year from date of preparation.*

6.13 Antimony Potassium Tartrate [$K(SbO)C_4H_4O_6 \bullet 1/2\ H_2O$] Solution: JT Baker, 0864-04 or equivalent. In a 500mL volumetric flask, dissolve 1.3715g $K(SbO)C_4H_4O_6 \bullet 1/2\ H_2O$ in approximately 400mL DI water. Bring to 500mL final volume with DI water. *Shelf-life = One year from date of preparation.* **This solution must be stored in an amber glass bottle at 4°C.**

6.14 Ammonium Molybdate [$(NH_4)_6Mo_7O_{24} \bullet 4H_2O$] Solution: Kodak, Cat. 136 5824 or equivalent. For each 15mL of solution, dissolve 0.60g $(NH_4)_6Mo_7O_{24} \bullet 4H_2O$ in 15mL of DI water. Prepare fresh for each usage. Transfer to a polypropylene bottle and store at 4°C until ready for use.

6.15 Ascorbic Acid, 0.1M: JT Baker, 0936-07 or equivalent. For each 30mL of solution, dissolve 0.53g of ascorbic acid in 30mL of DI water. *Prepare fresh for each usage.*

6.16 Combined Coloring Reagent: To prepare 100mL of reagent, mix the following in the order and volumes shown:

NOTE: Mix after adding each reagent, if turbidity forms, shake and allow to stand a few minutes until the turbidity disappears before proceeding.

1. 50mL H_2SO_4, 5N
2. 5mL Antimony Potassium Tartrate solution
3. 15mL Ammonium Molybdate solution
4. 30mL Ascorbic Acid solution

Other volumes of combined coloring reagent can be prepared as long as the various components are mixed in the same proportions as above. *Prepare fresh for each usage.*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples must be collected according to an approved sampling plan.

7.2 For Total Phosphorus, water samples are preserved by acidification with H_2SO_4 to pH < 2. The samples must be analyzed within 28 days from collection and preservation.

7.3 Samples for ortho-Phosphate are not acidified and must be kept chilled at 4±2°C. The samples must be analyzed within 48 hours of collection.

8. PROCEDURE

8.1 AMMONIUM PERSULFATE DIGESTION FOR TOTAL PHOSPHORUS

8.1.1 Prepare samples by measuring a well mixed 50mL aliquot (or smaller volume diluted to 50mL with DI water) into a 150mL acid-rinsed Pyrex® beaker.

8.1.2 Prepare a Preparation (Method) Blank by measuring 50mL DI water into a 150mL acid-rinsed Pyrex® beaker. One blank is to be prepared for each set of twenty field samples or less processed as a unit.

8.1.3 Prepare a Blank Spike (Laboratory Control Sample, LCS) by measuring 50mL DI water into a 150mL acid-rinsed Pyrex® beaker. Spike with

0.25mL of 100mg/L Intermediate Phosphorus Standard (**Second Source**). One LCS is to be prepared for each set of twenty field samples or less processed as a unit.

8.1.4 Prepare a Matrix Spike and Matrix Spike Duplicate (MS/MSD): The matrix spike duplicate serves as the laboratory duplicate. For one of the samples in the batch, measure two additional 50mL aliquots into two 150mL acid-rinsed Pyrex® beakers. Spike each of the two additional aliquots with 0.125mL of 100mg/L Intermediate Phosphorus Standard (**First Source**).

8.1.5 To all the field and QC samples prepared above, add 1mL of 11N H_2SO_4.

8.1.6 To all the field and QC samples prepared above , add 0.4g of ammonium persulfate.

8.1.7 Cover with an acid-rinsed Pyrex® watch cover. Boil gently on a hot plate until a final volume of approximately 10mL is reached (approximately one hour). **Do not allow the samples to boil dry.**

8.1.8 Allow to cool. Rinse watch glass cover with DI water directly into sample beaker in order to collect any residue on cover. Add DI water as necessary to bring sample volume to approximately 20mL.

8.1.9 pH Adjustment. Add 2-3 drops of phenolphthalein indicator. While "swirling" beaker, carefully add 10N NaOH dropwise until the sample solution just turns pink.

8.1.10 Using a top loading balance, transfer the prepared sample to a clean, tared disposable polypropylene beaker. Use a wash bottle filled with DI water to rinse the sides of the digestate beaker and collect the rinsate in the plastic prepared sample beaker. Dilute to a final volume of 50mL by adding DI water until the final solution weight = 50.1g.

NOTE: In some samples a precipitate may form at this stage, but **do not filter**. Shake samples well for any subsequent subdividing of the sample. The precipitate (which is possibly calcium phosphate) redissolves under the acidic conditions of the colorimetric analysis.

8.1.11 Proceed to Section 8.3 for Colorimetric Analysis.

8.2 PREPARATION FOR ORTHO-PHOSPHATE ANALYSIS

8.2.1 If the sample is turbid, it may be filtered through a 0.45µm porosity filter.

8.2.2 Prepare samples by measuring a 20mL aliquot (or smaller volume diluted to 20mL with DI water) into acid washed clean optically matched spectrophotometer cuvettes.

8.2.3 Prepare a Preparation (Method) Blank by measuring 20mL DI water into an acid washed clean spectrophotometer cuvette. One blank is to be prepared for each set of twenty field samples or less processed as a unit.

8.2.4 Prepare a Blank Spike (Laboratory Control Sample, LCS) by measuring 20mL DI water into an acid washed clean spectrophotometer cuvette. Spike with 0.05mL of 100mg/L Intermediate Phosphorus Standard (**Second Source**). One LCS is to be prepared for each set of twenty field samples or less processed as a unit.

8.2.5 Prepare a Matrix Spike and Matrix Spike Duplicate (MS/MSD). The matrix spike duplicate serves as the laboratory duplicate. For one of the samples in the batch, measure two additional 20mL aliquots into two acid washed clean spectrophotometer cuvettes. Spike each of the two additional aliquots with 0.05mL of 100mg/L Intermediate Phosphorus Standard (**First Source**).

8.2.6 If necessary, adjust the pH of the sample as follows: Add 1 drop of phenolphthalein indicator to 20mL of sample. If a pink color develops, add 5N H_2SO_4 solution dropwise to just discharge the color.

8.2.7 Proceed to the Colorimetric Analysis in Section 8.3.

8.3 COLORIMETRIC ANALYSIS - TOTAL PHOSPHORUS AND ORTHO-PHOSPHATE

8.3.1 Standard Curve: Prepare calibration standards in acid washed clean optically matched spectrophotometer cuvettes by diluting aliquots of 100mg/L Intermediate Phosphorus Standard (First Source) in DI water as described below:

Final Concentration of Calibration Standard (mg P/L)	Volume of 100mg P/L Intermediate Standard (mL)	Final Volume of Calibration Standard (mL)
0.00 (CCB)	0.00	20.0
0.05	0.01	20.0
0.10	0.02	20.0
0.25	0.05	20.0
0.50 (CCV)	0.10	20.0
0.75	0.15	20.0
1.00	0.20	20.0

8.3.2 Prepare an Initial Calibration Verification (ICV) check standard in an acid washed clean spectrophotometer cuvette by diluting 0.05mL of 100mg /L Intermediate Phosphorus Standard (Second Source) to 20.0mL with DI water.

8.3.3 Prepare an Initial Calibration Blank (ICB) by placing a 20mL aliquot of DI water into a clean acid washed spectrophotometer cuvette.

8.3.4 Transfer a 20mL aliquot of each digested sample or prepared sample into an optically matched acid washed spectrophotometer cuvette.

NOTE: Digestates and/or prepared samples may contain color. If color interference is an issue, take absorbance reading before coloring in order to subtract "initial" color from "final" color.

8.3.5 To each standard and sample add 4.0mL of Combined Coloring Reagent. Mix well.

NOTE: If any undissolved material is remaining in cuvette after combining color reagent, mixing, and allowing to develop, allow material to settle or filter using a 0.45µm porosity filter before analysis.

8.3.6 After the blue color has fully developed (approximately 10 minutes; not to exceed 30 minutes), measure the absorbance of the colored standards and samples with the spectrophotometer at a wavelength setting of 650nm. Absorbance measurements are performed in the following sequence:

(1) 0.00mg/L cal std.
(2) 0.05mg/L cal std.
(3) 0.10mg/L cal std.
(4) 0.25mg/L cal std.
(5) 0.50mg/L cal std.
(6) 0.75mg/L cal std.
(7) 1.00mg/L cal std.
(8) ICV (0.25mg/L Second Source)
(9) ICB (Initial Calibration Blank
(10) Preparation Blank
(11) LCS
(l2) maximum of 8 samples including MS, MSD
(13) CCV (0.50mg/L First Source)
(14) CCB (Continuing Calibration Blank
(15) maximum of 10 samples

(16) CCV (0.50mg/L First Source)
(17) CCB
(18) maximum of 10 samples
(19) CCV
(20) CCB

The analytical sequence of CCV, CCB, 10 samples, may be repeated so long as continuing calibration standard and blank quality criteria are met. The sequence must end with a CCV and CCB.

8.3.7 For each sample, the measured absorbance must not exceed the absorbance obtained for the high calibration standard (1.00mg/L). If this does occur, another aliquot of the sample solution must be diluted with DI water and the colorimetric analysis must be repeated so that the measured absorbance is within the calibration range.

8.4 CALCULATIONS

8.4.1 Record total phosphorus preparation information in Aqueous Extration logbook (e.g., standards used, reagents, QC information ect.). Enter calibration data in LIMS to perform a linear regression analysis (measured absorbance versus concentration for each calibration standard). The regression equation for the calibration standards must have a correlation coefficient (r^2) $\geq$ 0.995.

8.4.2 For each solution analyzed, calculate the phosphorus concentration from the measured absorbance using the spreadsheet.

8.4.3 Results of the ICV and CCVs must agree within ±10% of their know concentrations (0.50mg/L P for CCV's and 0.25mg/L P for ICV).

8.4.4 Calculate the phosphorus concentration in the water samples as follows:

$$\text{phosphorus mg/L} = A \times D$$

where:
A = mg/L of phosphorus determined in solution in cuvette
D = Dilution factor if dilution was necessary to produce a response within the calibration range

8.4.5 Results of the ICB and CCBs must be below the reporting limit (RL) for the method (usually 0.05mg phosphorus/L).

9. QUALITY CONTROL (QC)

9.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or less field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike and duplicate (MS/MSD). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

9.2 METHOD BLANKS

Method blanks (MB) are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. For this procedure, the method blank is run as an Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB). The blank is prepared as discussed in Section 8. See QC Table for acceptance limits.

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. A known amount of analyte is prepared and analyzed. For this method, the LCS is prepared as described in Section 8. Results obtained are compared to results expected. See QC Table for acceptance limits.

9.4 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE

Matrix spikes (MS) consist of field samples into which known concentrations of target analytes are spiked and analyzed as a means of determining the effect of matrix on target analyte detection. The matrix spike duplicate (MSD) serves as a laboratory duplicate analysis. Analyte recovery for the MS/MSD pair is calculated as shown below:

$$\%R = \frac{\text{Concentration}_{\text{Found}} - \text{Concentration}_{\text{Sample}}}{\text{Concentration}_{\text{Target}}} \times 100$$

where:

$\text{Conc}_{\text{Found}}$ = analyte concentration found in the MS or MSD sample
$\text{Conc}_{\text{Sample}}$ = analyte concentration found in the field sample
$\text{Conc}_{\text{Target}}$ = target (anticipated) analyte concentration based on amount spiked

See QC Table for advisory limits.

The laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. RPD is calculated as shown below:

$$\text{RPD (\%)} = \frac{|\text{Result}_x - \text{Result}_{\text{Dup}}|}{\frac{(\text{Result}_x + \text{Result}_{\text{Dup}})}{2}} \times 100$$

Advisory acceptance criteria for all spikes and duplicates should be met. If MS/MSD recovery or RPD criteria are not met, results of the laboratory control sample analyses must be carefully considered. If LCS results are acceptable, a sample matrix interference is suspected and a notation in the narrative comments is made.

9.5 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and near the analyte reporting limit (RL). The MDL study should be performed as needed and at a minimum, annually.

10. DEVIATIONS FROM METHOD

10.1 Section 6.2 of Method EPA 365.2 and Section 2b of SM4500-P C recommend the use of hot 1:1 HCl (followed by distilled water rinse) for the pre-treatment of glassware used for phosphorus analysis. Paragon uses an acid wash bath (H_2SO_4, HCl, or HNO_3), followed by three rinses of DI water to pre-treat glassware dedicated to phosphorus analysis.

10.2 Paragon creates a stock phosphorus solution 80X stronger than that resulting from the reagent recipe given in Section 7.8 of Method EPA 365.2 and Section 3f of SM4500-P E. The concentrations of the subsequent standard phosphorus solutions differ between the two referenced methods: 0.5mg/L Method EPA 365.2; 2.5mg/L SM4500-P E (Paragon uses a 100mg/L standard phosphorus solution). Likewise, the range of the calibration standards created from the standard phosphorus solution differs between the two referenced methods (0.00 – 0.50mg/L Section 7.9 of Method 365.2; 0.15 – 1.30mg/L SM4500-P E Section 4c). Note that the range of the calibration standards used by Paragon (0.00 – 1.00mg/L) falls within the range prescribed by the two referenced methods.

10.3 Section 7.10 of Method EPA 365.2 and Section 5a (4) of SM 4500-P B provide for the use of 1N NaOH solution to adjust the pH of the ammonium persulfate digestate. Paragon uses a stronger (10N) NaOH solution in order to minimize change to sample digestate volume.

10.4 Section 8 of Method EPA 365.2 describes the use of a pH meter to ensure pH adjustment of the ammonium persulfate digestate to 7.0±0.2 pH units. Use of a pH meter is not discussed in SM4500-P B Section 5. Paragon does not use a pH meter to determine the ammonium persulfate digestate pH.

10.5 Per Section 5c of SM4500-P B, distilled water is used to adjust the final volume of the ammonium persulfate digestate to 100mL. Paragon uses DI water to adjust to a final volume of 50mL, which is the final volume described in Section 8.1.4 of Method EPA 365.2. Section 8.1.4 of Method EPA 365.2 suggests filtering if the sample digestate is not clear, whereas Section 5c of SM4500-P B directs NOT to

filter the digestate. Paragon does not filter the prepared ammonium persulfate digestates, but may filter or allow the settling of any particulate matter after the colored digestate solution has been well mixed.

10.6 Section 9.1.1 of Method EPA 365.2 directs that blanks and calibration standards be processed exactly as the samples (samples prepared for total phosphorus analysis are subjected to ammonium persulfate digestion; samples prepared for ortho-phosphate analysis are not digested). Section 5c of SM4500-P B (Persulfate Digestion Method) directs that the calibration curve be created from standards that are carried through the persulfate digestion procedure. Paragon uses a singular calibration curve to process both total phosphorus and ortho-phosphate samples and does not subject the calibration standards to ammonium persulfate digestion.

10.7 Section 4a of SM4500-P E provides for the reading of absorbance at 880nm, whereas absorbance readings at 650 or 880nm are provided for in Section 8.3.2 of Method EPA 365.2. Paragon reads absorbance of the prepared samples at 650nm.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDS before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

11.2.2 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Waste Compliance Officer will provide specific procedures and materials for these samples.

12. REFERENCES

12.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1983. Method 365.2, "Phosphorus, All Forms (Colorimetric, Ascorbic Acid, Single Reagent)".

12.2 A.P.H.A., A.W.W.A. and W.P.C.F., Standard Methods for the Examination of Water and Wastewater, 20th edition, pp 4:142-144, 1998. Methods 4500-P B(5), "Sample Preparation - Persulfate Digestion Method" and 4500-P E "Ascorbic Acid Method".

DOCUMENT REVISION HISTORY

2/9/04: Updated format.

3/29/05: Re-released without revision.

7/26/05: Program specification language added.

8/15/07: Added DOCUMENT REVISION HISTORY Section.

10/8/07: Corrected shelf life from 3 months to one year, intermediate standards, Sections 6.3 and 6.5. Updated QC Section 9 language and QC Table.

Analytical Method: E365.2; SM4500-P B(5) & E	**Parameter:** Phosphorus by Ascorbic Acid Method		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point	Once per analytical sequence.	Correlation coefficient (r^2) for linear regression must be $\geq$0.995.	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification (ICV); second source; at or below midpoint	Daily prior to sample analyses	Must agree within $\pm$10%D of calibration curve for analyses to proceed	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV); first source; at or below midpoint	Brackets each set of 10 field sample analyses	Must agree within $\pm$10%D of calibration curve for analyses to proceed	Evaluate/correct instrument malfunction as needed and reanalyze. If CCV still non-compliant, recalibrate using a new curve. Samples analyzed after a failed CCV must be reanalyzed. If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Method Blank (MB); Initial Calibration Blank (ICB)	One per each batch of $\leq$20 field samples; one each time a reagent is changed	Phosphorus content of MB must not exceed reporting limit (RL); RL usually 0.05mg phosphorus/L, or as otherwise specified in applicable LIMS program specification	Check all calculations. If no computation errors are found, prepare a fresh MB and analyze. Associated samples must also be reanalyzed.
Continuing Calibration Blank (CCB)	One per each set of $\leq$10 field samples	Phosphorus content of CCB must not exceed RL (usually 0.05mg phosphorus/L)	Check all calculations. If no computation errors are found, prepare a fresh MB and analyze. Associated samples must also be reanalyzed.
Laboratory Control Sample (LCS)	One per batch of $\leq$20 field samples	Results obtained must agree between $\pm$10% of expected (known) ortho-phosphate concentration and between $\pm$20% of expected (known) total phosphorus concentration, or as otherwise specified in applicable LIMS program specification	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.
Matrix Spike (MS)	One per batch of $\leq$20 field samples	Results obtained should agree within $\pm$10% of expected ortho-phosphate concentration, and $\pm$20% of expected total phosphorus concentration, or as otherwise specified in applicable LIMS program specification	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.
Matrix Spike (laboratory) Duplicate	One per batch of $\leq$20 field samples	(See MS recovery criteria above)	(See MS recovery criteria above). For RPDs outside of QC limits, check

Analytical Method: E365.2; SM4500-P B(5) & E	**Parameter:** Phosphorus by Ascorbic Acid Method		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
		RPD should be ≤20%, or as otherwise specified in applicable LIMS program specification	all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	As needed; at a minimum annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with the analytical system. Repeat the MDL study. Consult with the Department/Project/QA Managers. The managers may determine that an adjustment to the RL is needed.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1120 REVISION 5

TITLE: **DETERMINATION OF TOTAL SULFIDES IN WATER -- METHODS EPA 376.1 AND SM4500-S^{2-} F**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 4/30/07

QUALITY ASSURANCE MANAGER _____ DATE 4/28/07

LABORATORY MANAGER _____ DATE 5-1-07

HISTORY: Rev0, 11/20/99; Rev1, 4/29/02; Rev2, 2/10/03, Rev3, 2/9/04 and 3/29/05; Rev4, 7/26/05; Rev5, 4/27/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- Methods EPA 376.1 and SM4500-S^2 F -- describe a procedure to determine the concentration of total sulfides in drinking, surface, and saline waters and domestic and industrial wastes. Acid soluble sulfides are not measurable by these methods (copper sulfide is the only common sulfide in this class).

Total sulfide includes dissolved H_2S and HS^-, as well as acid-soluble metallic sulfides present in suspended matter. Dissolved sulfide is that remaining after suspended solids have been removed by flocculation and settling. This procedure may also be used for the analysis of dissolved sulfides following proper sample pretreatment (see SM.4500-S^2 B).

Information regarding qualitative testing for sulfides is presented in Section 4 of the introduction to Method 4500-S^2 F. This information may be particularly useful when testing for sulfides in industrial wastes.

2. SUMMARY

Samples are preserved with zinc acetate to yield zinc sulfide. Excess standard iodine is quantitatively added to a sample aliquot. Under acidic conditions, the iodine oxidizes the sulfide in the sample to sulfur. The excess unreacted iodine is then back titrated with standard sodium thiosulfate solution in the presence of starch (used as an indicator).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of

Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/ analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

The iodometric method suffers from interferences by reducing substances that react with iodine, including thiosulfate, sulfite, and various volatile organic compounds, both solid and dissolved. Per SM4500-S^2 C, these interferences may be eliminated by first precipitating zinc sulfide, and then removing the supernatant and replacing it with deionized water.

5. APPARATUS AND MATERIALS

5.1 specimen cups, polypropylene, 250mL

5.2 transfer pipets, plastic

5.3 stir plate

5.4 magnetic stir bars

5.5 top loading balance, 0.01g sensitivity

5.6 pH meter (Accumet 50 or equivalent) or pH test strips capable of reading pH <2

5.7 Eppendorf ™ Pippette or equivalent, adjustable, capable of delivering 0.50- 1.0mL

6. REAGENTS

NOTES: Only ACS grade or better chemicals may be used.

Reagents may be stored in polypropylene containers.

6.1 Deionized (DI) water. Obtained from the laboratory deionized water system.

6.2 Sulfuric Acid (H_2SO_4) solution, 50% (18N): EMD, SX1244-5 or equivalent. Carefully add 100mL concentrated H_2SO_4 to 100mL deionized water, or different volumes as long as same ratio of 1:1. *Shelf Life = 1 year.*

6.3 Standard Iodine (I2) Solution, 0.0250N: JT Baker, 3162-01 or equivalent. Dissolve 25g of Potassium Iodide (KI) in 800mL of DI water. Add 3.2g of iodine crystals and dissolve. Dilute to 1L with DI water. *Shelf Life = 1 year.* **NOTE: *Standardize against $Na_2S_2O_3$ solution daily before use.***

6.4 Starch Indicator, 2%: VWR, Cat. No. VW3638-2 or equivalent. *Shelf-life = per expiration date indicated on label by manufacturer.*

6.5 Hydrochloric Acid (HCl), 6N: JT Baker, 9530-33 or equivalent. Carefully add a measured volume of concentrated HCl to an equal volume of DI water (1:1 dilution). *Shelf Life = 1 year.*

6.6 Standard Potassium Biiodate [$KH(IO_3)_2$] Solution, 0.025N: EM Science, PX1351-2 or equivalent. Dissolve 0.4062g of $KH(IO_3)_2$ salt in 500mL of DI water. *Shelf Life = 1 year.*

6.7 Sodium Thiosulfate ($Na_2S_2O_3$) Solution, approximately 0.025N: EM Science #SX0820-1 or equivalent. Dissolve 3.95g of anhydrous $Na_2S_2O_3$ and 0.4g of NaOH in 1L of DI water. *Shelf Life = 1 year.* **NOTE: *Standardize against $KH(IO_3)_2$ once before use.***

6.8 Sulfide (Na_2S) Spiking Solution: Dissolve 15g of Sodium Sulfide ($Na_2S \bullet 9H_2O$) in 200mL of deionized water. *Shelf Life = 1 year.* **NOTE: *Standardize daily before use.***

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references that include container and preservation requirements for compliance with the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA):

7.1 All samples must be collected according to an approved sampling plan. Samples of 500mL or larger may be collected in either plastic or glass containers and should be chilled (4±2°C).

7.2 During collection and prior to preservation and precipitation of the sulfide by zinc acetate, the samples should not be agitated. Sulfide may be volatilized by

aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.

7.3 Aqueous samples must be preserved by adding 2.0mL of 2N Zinc Acetate Solution [$Zn(C_2H_3O_2)_2 \bullet 2\ H_2O$] and 1.5 mL of 20% Sodium Hydroxide Solution (NaOH) per 500mL sample.

7.4 To meet holding time requirements, analysis must be completed within 7 days of collection.

Regulation	Holding Time	Reference
SDWA	7 days	EPA-570/9-82-002
CWA	7 days	CFR 40 Part 136.3

8. STANDARDIZATION OF REAGENTS

8.1 STANDARDIZATION OF SODIUM THIOSULFATE ONCE BEFORE USE AS FOLLOWS:

8.1.1 Transfer 10.00mL standard potassium biiodate [$KH(IO_3)_2$] solution into a 200mL beaker.

8.1.2 Dilute to about 100mL with DI water.

8.1.3 Add approximately 2g of potassium iodide (KI) pellets.

8.1.4 Add 4-5 drops of 50% sulfuric acid (H_2SO_4).

8.1.5 Add 2-3 drops of starch indicator.

8.1.6 Tare the beaker + contents on a top loading balance.

8.1.7 On the stir plate, add sodium thiosulfate solution drop wise until the beaker's contents turns from blue to colorless.

8.1.8 Record the amount of $Na_2S_2O_3$ solution used.

8.1.9 Repeat twice more and average the results of the three replicates. Calculate the concentration of the sodium thiosulfate solution as follows:

$$\text{Sodium thiosulfate conc (eq/L)} = (0.025) * (10.00) / (V)$$

where:

0.025 = normality of potassium biiodate solution titrated

10.00 = volume of potassium biiodate solution titrated

V = volume of sodium thiosulfate solution required to reach endpoint

8.2 STANDARDIZATION OF STANDARD IODINE (I_2) SOLUTION DAILY BEFORE EACH USE AS FOLLOWS:

8.2.1 Add approximately 100mL of DI water to a plastic specimen cup containing a stir bar.

8.2.2 Place on stir plate and add approximately 2.0mL of 6N HCl.

8.2.3 Place on top loading balance and tare container and contents. Add approximately 2.5mL of the iodine standard solution and record the weight to the nearest 0.01g.

8.2.4 Add 2-3 drops of starch indicator and tare container and contents on balance.

8.2.5 Place on a magnetic stir plate and add $Na_2S_2O_3$ solution drop wise until a colorless endpoint is reached.

8.2.6 Place the container and contents back on the balance and record the weight of the titrant used.

8.2.7 Repeat twice more. Calculate the concentration of the standard iodine solution as follows (this calculation can be conveniently carried out using the spreadsheet template located at i:\oprtns\wtchm\sulfide\ template\s1.xls).

$$\text{Iodine conc (eq/L)} = (CTh) * (VTh) / (VI)$$

where:

CTh = concentration (eq/L) of sodium thiosulfate solution

VTh = volume of sodium thiosulfate required to reach endpoint

VI = volume of iodine solution titrated

8.3 STANDARDIZATION OF SULFIDE SPIKING SOLUTION DAILY BEFORE EACH USE AS FOLLOWS:

8.3.1 Add approximately 100mL of DI water to a plastic specimen cup containing a stir bar.

8.3.2 Pipet 0.50mL of the prepared Sulfide Spiking Solution into the container.

8.3.3 Place container on stir plate and add approximately 2.0mL of 6N HCl.

8.3.4 Place container on top loading balance and tare the container and contents.

8.3.5 Add standard iodine solution until a brown color persists (8-15mL). Record standard iodine solution weight to the nearest 0.01g.

8.3.6 Add 2-3 drops of starch indicator and tare container and contents on balance.

8.3.7 Place on a magnetic stir plate and add $Na_2S_2O_3$ solution drop wise until a colorless endpoint (color change from dark blue to clear) is reached.

8.3.8 Weigh the container and contents; record the weight, to the nearest 0.01g, of the titrant used.

8.3.9 Repeat twice more and average the result of the three replicates.

8.3.10 Calculation the concentration of the sulfide spiking solution as follows (the spreadsheet template located at i:\oprtns\wtchm\sulfide\template\s1.xls may be used).

$$\text{mg sulfide / L} = [(A*B)-(C*D)]*16000$$

where:

A = volume (mL) of iodine solution

B = normality of iodine solution

C = volume (mL) of sodium thiosulfate solution

D = normality of sodium thiosulfate solution

16000 = constant which converts meq/mL to mg/L

9. FIELD AND QUALITY CONTROL (QC) SAMLE PREPARATION AND ANALYSIS

9.1 Prepare an Initial Calibration Verification standard (ICV), a Laboratory Control Sample (LCS), and a Continuing Calibration Verification (CCV) standard by transferring about 200mL of DI water each to three plastic cups. Pipet 0.50mL of the standardized Sulfide Spiking Solution into each container as needed.

9.2 Prepare two solutions to serve as an Initial Calibration Blank (ICB) and Method Blank (MB) by transferring approximately 200 mL of DI water to a clean plastic cup. **Note:** Prepare Continuing Calibration Blanks (CCBs) in this same manner as needed.

9.3 Prepare each field sample by mixing the sample thoroughly in the original capped container, then transferring 200mL of the well-mixed sample into a labeled plastic cup. Select a sample representative of the batch and prepare an additional aliquot to serve as the laboratory duplicate. One duplicate sample (DUP) must be prepared for every twenty or fewer environmental samples processed together as a unit.

NOTE: If dissolved sulfides is to be determined, suspended solids must first be

removed (see SM4500-S^2 B).

9.4 The sulfide determinations should be performed in the following analytical sequence:

1.	ICV
2.	ICB
3.	MB
4.	LCS
5.	DUP
6 - 22	17 field samples

If more than 17 field samples are analyzed, the sequence must continue as follows:

23.	CCV
24.	CCB
25. - 27.	3 more field samples (from same batch)

If a second batch of samples is to be analyzed, the sequence repeats beginning with a MB, LCS, DUP, 14 field samples, etc.

9.5 Place each cup on a stir plate and add a stir bar. Add approximately 2.0mL of 6N HCl and check the pH of the solution using a pH test strip. **NOTE:** The pH of the solution must be 2 or less. Add additional 6N HCl as necessary.

9.6 Place the cup on the top loading balance and tare the container and contents.

9.7 Add standard iodine solution to the sample until a brown color persists (approximately 2.5mL if non-detect).

9.8 Weigh the container and contents on the balance. Record the weight of the iodine solution added.

9.9 Add 2-3 drops of starch indicator and tare container and contents on balance.

9.10 Place on stir plate and titrate to a colorless endpoint by adding standardized sodium thiosulfate solution drop wise.

9.11 Place the container and contents back on the balance and record the weight of the titrant used.

9.12 Calculate the amount of sulfide in the field or quality control sample using the spreadsheet template located at i:\oprtns\wtchm\sulfide\template\s1.xls. The template calculates the sulfide concentration based on the following equation:

$$\text{mg sulfide / L} = \frac{[(A * B) - (C * D)] * 16000}{\text{mL sample}}$$

where:

A = volume (mL) of iodine solution

B = normality of iodine solution

C = volume (mL) of sodium thiosulfate solution

D = normality of sodium thiosulfate solution

16000 = constant that converts meq/mL to mg/L

10. QUALITY CONTROL

10.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and processed together as a unit. Batch QC samples are defined as the method blank (MB), laboratory duplicate (DUP) and laboratory control sample (LCS). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

10.2 BLANKS

Blanks are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank (MB) must be processed. The Initial Calibration Blank (ICB) is run following the ICV. A CCB must be run following each CCV analyzed if more than twenty field and QC samples are analyzed. All blanks consist of 200mL DI water. See QC Table for acceptance limits.

10.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. It consists of an aliquot of clean matrix (in this instance, 200mL DI water), into which a known amount of analyte is spiked. One LCS must be analyzed per batch of 20 or fewer field samples processed together as a unit.

Results obtained are compared to results expected. The mathematical evaluation is expressed as percent recovery, %R, calculated as follows:

$$\%R = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Target}}} \times 100$$

See QC Table for acceptance limits.

10.4 LABORATORY DUPLICATE

A second aliquot of one sample per batch of twenty (20) or fewer field samples processed together as a unit is prepared and analyzed as a laboratory duplicate

(DUP). The laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. The duplicate results are compared mathematically (shown below), with the precision expressed as Relative Percent Difference (RPD):

$$RPD\ (\%) = \frac{|\ Result_x - Result_{Dup}\ |}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

For this procedure, the RPD must not be greater than 20%.

11. DEVIATIONS FROM METHOD

Section 6.0 of Method EPA 376.1 directs that if the sample has been precipitated (i.e., if Zinc Acetate has been added), the reagents are to be added to the original sample container. Paragon processes samples by adding reagents to a well-mixed aliquot of sample.

12. SAFETY HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Read the MSDS prior to preparing standards or using any solvents or reagents for the first time.

12.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

12.1.3 Any chemicals with a Threshold Limit Value of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.4 Any non-original containers be used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

12.2 WASTE DISPOSAL

12.2.1 Solid filtrate residues and any other solid residues are disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

12.2.2 All empty solvent or reagent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12.2.3 Certain clients may require that the samples and sample residues from their samples are segregated and returned to the client's location. The

Waste Compliance Officer will provide specific procedures and materials for these samples.

13. REFERENCES

13.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1983, Method 376.1, "Sulfide, Titrimetric, Iodine".

13.2 A.P.H.A., A.W.W.A. and W.P.C.F., 1989. Standard Methods for the Examination of Water and Wastewater, 20th edition, Pages 4:167, "Method 4500-S2- F, Iodometric Method".

DOCUMENT REVISION HISTORY

2/9/04: Format updated.

3/9/05: Re-released without revision.

7/6/05: LIMS program specification language added.

4/27/07: Minor format updates. Added DOCUMENT REVISION HISTORY.

Analytical Method: EPA 376.1; SM4500-S^{2-} F	**Parameter:** Determination of Total Sulfides in Water		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Calibration: Analyte content determined by direct concentration (obtained by calculation from titration). Titrant is standardized each day of use	Daily; each day of use	Titrant must calculate to be to be approximately 0.025N	If titrant does not meet concentration criteria; prepare fresh and standardize.
Initial Calibration Verification (ICV); second source	Daily; each day of use Run following standardization and before any samples are analyzed	Results for the ICV must agree within ±20% expected value	If ICV criterion not met, check for preparatory error (remake if necessary); reanalyze. If ICV still fails, reagents must be remade and re-standardized.
Continuing Calibration ; Verification (CCV); first source	Run to bracket each set of 20 environmental samples processed	Results for the CCV must agree within ±20% expected value	If CCV criterion not met, check for preparatory error (remake if necessary); reanalyze. All field and quality control samples run since the last acceptable CCV must also be reanalyzed.
Laboratory Control Sample (LCS)	One per batch of ≤20 samples	Concentration results obtained must agree between 80% and 120% of expected value	Check calculations and preparation for documentable errors. If no errors are found, reanalyze. Associated samples must also be reanalyzed.
Blanks: Method Blank (MB), Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	The MB may be run initially as the ICB that is run following the ICV. CCBs are run following the CCVs	Sulfide content of any blank must not exceed the analyte reporting limit (typically 2mg/L S^2)	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Laboratory Duplicate (DUP)	One per batch of ≤20 samples	RPD must be ≤20%	Check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1121 REVISION 6

TITLE: DETERMINATION OF HEXAVALENT CHROMIUM IN SOLID MATRICES USING ALKALINE DIGESTION (METHOD SW3060A) AND ANALYSIS BY METHOD SW7196A

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3/7/08
QUALITY ASSURANCE MANAGER _____ DATE 3/7/08
LABORATORY MANAGER _____ DATE 3-7-08

HISTORY: Rev0, 3/27/00; Rev1, 3/2/02; Rev2, 10/15/02; Rev3, 2/9/04 (format update) and 3/18/05 (re-released without revision); Rev4, 7/26/05 (Program Spec. reference added); Rev5, 6/26/06; Rev6, 3/7/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- SW3060A and SW7196A -- describe the alkaline digestion and determination of hexavalent chromium (Cr^{+6}) in soils, sludges, sediments and similar waste materials.

2. SUMMARY

This method uses an alkaline digestion to solubilize both water-insoluble and water soluble Cr^{+6} compounds in solid and waste samples. An aliquot of sample is digested for sixty minutes at 90-95°C in a solution of sodium hydroxide and sodium carbonate. This solubilizes the Cr^{+6} and stabilizes it against reduction to Cr^{+3}.

The Cr^{+6} in the alkaline extract is determined colorimetrically by reaction with diphenylcarbazide (DPC). This reaction is highly selective for Cr^{+6}. Addition of an excess of DPC yields a red-violet complex whose absorbance is measured photometrically at 540nm.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these methods to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 The stability of Cr^{+6} in a solid sample is governed by the oxidizing/reducing tendency (redox potential) of the sample matrix. The redox potential of a particular sample matrix may be sufficiently low to favor the reduction of Cr^{+6} to Cr^{+3}. Under such circumstances, low matrix spike recovery of Cr^{+6} should not be interpreted as a failure of the analysis. Rather, failure to recover spiked Cr^{+6} in a particular sample matrix should be viewed as evidence that Cr^{+6} is not stable in that matrix and, therefore, native Cr^{+6} should not be expected.

4.2 Various organic constituents may be brought into solution when a soil sample is carried through the alkaline digestion procedure, resulting in a yellow to dark brown colored extract. The color can contribute to the absorbance measured on the spectrophotometer and thereby cause a high bias to the results if not accounted for. Furthermore, dissolved organics can interfere with the colorimetric determination of Cr^{+6} with diphenylcarbazide. It may be necessary to dilute the extract in order to alleviate this interference. Color can be accounted for by taking a sample's initial absorbance reading and subtracting it out from the sample's final absorbance reading after the addition of diphenylcarbazide.

4.3 Although not typically found in the alkaline digestates of soils, certain substances may interfere in the analytical methods for Cr^{+6} if the concentrations of these interfering substances are high and the Cr^{+6} concentration is low. Hexavalent molybdenum and mercury salts react to form color with diphenylcarbazide; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200mg/L of hexavalent molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

4.4 For waste materials or soils containing soluble Cr^{+3} concentrations greater than four times the laboratory Cr^{+6} reporting limit, Cr^{+6} results obtained using this method may be biased high due to method-induced oxidation. The addition of Magnesium (Mg^{2+}) in a phosphate buffer to the alkaline extraction solution has been shown to suppress this oxidation.

5. APPARATUS AND MATERIALS

5.1 UV/VIS Spectrophotometer, Sequoia Turner™ Model 340 or equivalent. Suitable for measurements at 540nm with a light path of 1.0cm or longer.

5.2 analytical balance, capable of weighing to 0.0001g, verified per SOP 305

5.3 laboratory balance, top loading, capable of weighing to 0.1g, verified per SOP 305

5.4 pH meter with electrode and proper calibration buffer solutions

5.5 centrifuge capable of achieving approximately 3500rpm

5.6 water bath, capable of maintaining a temperature of 90-95°C

5.7 vortex mixer

5.8 magnetic stir plate and stir bars

5.9 repeater pipet, variable Eppendorf™ or equivalent

5.10 cuvettes, optically matched, 1-inch diameter

5.11 centrifuge tubes, polypropylene with screw-cap closures, 50mL

5.12 volumetric flasks, Class A, 500mL and 1L sizes

5.13 beakers, polypropylene with snap tight lid, 220mL

5.14 graduated cylinder, 50mL capacity (delivered volume verified by laboratory)

5.15 syringe, outfitted with a 0.45µm or 0.7µm filter disk

5.16 magnetic wand

5.17 thermometer, for checking water bath temperature

6. REAGENTS

6.1 Deionized (DI) water obtained from the laboratory DI water system

6.2 Ottawa sand, clean/inert, EMD, SX0075-3 or equivalent

6.3 Lead Chromate ($PbCrO_4$), powdered, JT Baker, 0970-01 or equivalent

6.4 pH paper, basic, capable of reading pH 11–13, EM Science, Cat. #9585 or equivalent

6.5 Sulfuric Acid, (H_2SO_4), 10%: Dilute 20mL of 50 % H_2SO_4 (1:1 ratio with DI water) to a final volume of 100mL with DI water. Alternately, dilute 10mL of conc. H_2SO_4 to a final volume of 100mL with DI water. EMD, SX1247-2 or equivalent. ***Store in a polypropylene bottle.*** *Shelf Life =1 year.*

6.6 Acetone, Burdick & Jackson, Cat. 010-4 or equivalent.

6.7 Nitric Acid, (HNO_3), 2N : Dilute 100mL of concentrated HNO_3, JT Baker, 9598-34 or equivalent, to a final volume of 700mL using DI water. ***Store in a polypropylene bottle.*** *Shelf Life = 1 year*

6.8 Diphenylcarbazide (DPC) Solution: Dissolve 0.25g, EM Science, DX2200-1 or equivalent, 1,5-diphenylcarbazide in 50mL of reagent grade acetone. ***Store in a brown glass bottle in the refrigerator.*** Discard when the solution becomes discolored (approx. 3 months).

6.9 Magnesium Chloride ($MgCl_2$) Solution, 2.5M, 51% (w/v): GFS Chemicals, item no. 724 or equivalent. Dissolve 51.0g $MgCl_2 \bullet 6\ H_2O$ in DI water and diluting to 100mL. ***Store in a polypropylene bottle.*** *Shelf Life = 1 year or as indicated by vendor.*

6.10 Potassium Phosphate Buffer: Mallinckrodt, 7100-02 or equivalent. Dissolve 68.0g reagent grade KH_2PO_4 and 87.1g K_2HPO_4 in DI water and dilute to 1L**.** ***Store in a polypropylene bottle.*** *Shelf Life = 1 year.*

6.11 Sodium Hydroxide (NaOH)/Sodium Carbonate ($NaCO_3$) Digestion Reagent: Dissolve 20.0g reagent grade NaOH and 30.0g anhydrous $NaCO_3$ in 1L of DI water. ***The pH must be 11.5 or greater; if not, discard.*** *Shelf Life = 1 month.*

6.12 Cr^{+6} Stock Standard, 500mg/L (**First Source**): Purchase as a certified stock solution from a commercial vendor or prepare by dissolving 0.1414g dry Potassium Chromate ($K_2Cr_2O_7$) in DI water using a 100mL Class A volumetric flask and diluting to full volume with additional DI water. Mix thoroughly. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 1 year.*

6.13 Cr^{+6} Intermediate Standard, 10mg/L (**First Source**): Dilute 2.0mL of first source 500mg/L Cr^{+6} stock standard to 100mL with DI water. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 3 months.*

6.14 Cr^{+6} Stock Standard, 500mg/L (**Second Source**): Purchase as a certified solution from a commercial vendor or prepare by dissolving 0.1414g dry $K_2Cr_2O_7$ in DI water using a 100mL Class A volumetric flask. Bring to volume using DI water, mix thoroughly. If purchased, the certified solution must be from a different vendor than the first source stock standard. If prepared in-house, the $K_2Cr_2O_7$ salt must be from a different vendor, if possible, or at least a different lot number than

the salt used to prepare the first source stock standard. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 1 year.*

6.15 Cr^{+6} Intermediate Standard, 10mg/L (**Second Source**): Dilute 2.0mL of second source 500mg/L Cr^{+6} stock standard to 100mL with DI water. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 3 months.*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 All samples must be collected according to an approved sampling plan.

7.2 Samples should be collected in containers that do not contain stainless steel.

7.3 Samples should be stored at 4±2°C until analyzed.

7.4 The holding time for hexavalent chromium in solids is 30 days from collection. "Hexavalent chromium has been shown to be quantitatively stable in field-moist soil samples for 30 days from sample collection. In addition, Cr^{+6} has been also been shown to be stable in the alkaline digestate for up to 168 hours (i.e., 7 days) after extraction from soil." (SW3060A, Section 6.4).

8. PROCEDURE

NOTE: A batch is defined as twenty (20) field samples or less of like matrix. One of each of the laboratory quality control (QC) samples outlined below [i.e., Method Blank, Blank Spike/LCS, MS/MSD set (soluble), MS/MSD set (insoluble), and post-digestion spike], must be prepared for each batch of field samples to be analyzed.

8.1 ALKALINE DIGESTION

8.1.1 For each sample, weigh 2.5g of well-mixed moist sample into a 50mL disposable polypropylene centrifuge tube.

8.1.2 Method Blank. Weigh 2.5g clean silica sand into a 50mL disposable polypropylene centrifuge tube.

8.1.3 Laboratory Control Sample (LCS). Weigh 2.5g clean silica sand into a 50mL disposable polypropylene centrifuge tube. Spike with **0.25mL** of 500mg/L Cr^{+6} stock standard (**second source**). **Be certain to have another person witness the spiking.**

8.1.4 Soluble Matrix Spike/Matrix Spike Duplicate (MSs/MSDs). For one of the samples in the batch, spike two duplicate 2.5g aliquots with **0.25mL** of 500mg/L Cr^{+6} stock standard (**first source**). **Be certain to have another person witness the spiking.**

8.1.5 Insoluble Matrix Spike/Matrix Spike Duplicate (MSn/MSDn). For one of the samples in the batch, spike two duplicate aliquots with 10 - 20mg of powdered $PbCrO_4$. The amount of $PbCrO_4$ added must be weighed on an analytical balance and recorded in the Aqueous Extractions logbook to the nearest 0.0001g. **Be certain to have another person witness the spiking.**

8.1.6 To all of the above, add the following:

- 50mL of Sodium Hydroxide (NaOH)/Sodium Carbonate ($NaCO_3$) Digestion Reagent using a 50mL volume-verified graduated cylinder
- 0.50mL of Potassium Phosphate Buffer Solution
- 0.75mL of 51% $MgCl_2$ Solution

8.1.7 Cap each tube and mix by shaking for at least five minutes. Place each tube into the steam bath, maintained at 90-95°C (check temperature and record in laboratory logbook) and heat for one hour. During this hour, sequentially remove each sample from the steam bath, agitate and replace (approximately every 5 minutes). Continue the sequential agitation of the samples for the entire one-hour heating period.

8.1.8 After one hour of heating and agitating, remove the field and QC samples from the steam bath and let cool to room temperature. Manually agitate periodically.

8.1.9 Centrifuge for about 15 minutes at about 3500rpm.

8.1.10 Label a 220mL beaker for each field and laboratory QC sample prepared. Place a labeled 220mL polypropylene beaker on a top loading balance and tare the balance. Transfer the appropriate supernatant liquid (from the digestion tube) into the beaker. **Do not tare the balance at this time; it is critical that the balance is not disturbed.** Remove the beaker with contents from the balance and add a stir bar.

8.1.11 Place a calibrated pH probe (see manual for further instruction) into the digestate solution and, while stirring, add 2N HNO_3 drop wise until the pH = 7.5±0.5. **CAUTION: Carbon dioxide will be evolved, perform in fume hood.**

8.1.12 Using a magnetic wand on the outside of the beaker, remove the stir bar. Rinse the stir bar repeatedly with DI water during removal. Place the beaker with contents back on the previously tared balance.

Gravimetrically bring the sample solution to a 100mL final volume with DI water (100.0mL = 102.74g).

8.1.13 Attach the beaker's lid and mix well by swirling (careful, the capped beaker will build up pressure slightly).

8.2 COLORIMETRIC ANALYSIS OF STANDARDS AND SAMPLES

8.2.1 STANDARD CURVE PREPARATION

Prepared fresh on each day of analysis. Use DI water to achieve the final volume. Prepare working standards in optically matching 1" spectrophotometer cuvettes as described below:

Standard Concentration (mg/L Cr^{+6})	Volume of 10mg/L Cr^{+6} Intermediate Std (mL)	Final Volume (mL)
0	0	20.0
0.01	0.02	20.0
0.05	0.10	20.0
0.10	0.20	20.0
0.30 (CCV)**	0.60	20.0
0.50	1.00	20.0
0.10 (ICV)*	0.20 *	20.0

* Independent Calibration Verification (ICV). The ICV must be prepared from a second source that is independent of that which is used to prepare the calibration standards. ***Use the Second Source 10mg/L Intermediate Standard.*** An Initial Calibration Blank (ICB), consisting of a 20.0mL aliquot of DI water, must be analyzed immediately following the ICV.

** This standard is also analyzed repeatedly as the Continuing Calibration Verification (CCV). A Continuing Calibration Blank (CCB), consisting of a 20.0mL aliquot of DI water, must be analyzed immediately following each CCV.

8.2.2 POST-DIGESTION SPIKE RECOVERY STUDY

Alkaline soil digestates are often yellow to dark brown in color due to the presence of dissolved organic matter. Dissolved organic matter can interfere with the colorimetric determination of Cr^{+6}. The interference can often be overcome by diluting the digestates prior to analysis.
Note: All samples (including QC samples) are diluted 5X initially.

The level of further dilution necessary to overcome the interference is determined by conducting a Cr^{+6} post-digestion spike recovery study, at various levels of dilution, as follows:

- The alkaline digestate for the sample that was selected as the MS/MSD sample is usually used for the post-digestion spike.

- Transfer 16.0mL of DI water into each of two labeled 1-inch spectrophotometer cuvettes Using a pipet, remove 0.50mL of water from one of the cuvettes and replace it with 0.50mL of 10mg/L intermediate Cr^{+6} standard (first source). **Be certain to have another person witness the spiking.**

- Pipet a 4.0mL aliquot of the selected sample digestate into each cuvette. Adjust to a 20mL final volume using DI water. Mix using the vortex mixer. Note that use of a 4.0mL aliquot of digestate brought to a 20.0mL final volume constitutes a 5-fold dilution.

- To both cuvettes, add 0.5mL of 10% H_2SO_4; mix well.

- Measure the absorbance of both the unspiked and spiked post-digestion aliquots (at 540nm using the spectrophotometer. Record these "initial" readings in LIMS. **These absorbance readings are due to the native color of the sample and will be subtracted from the absorbance readings measured after adding DPC color reagent.**

- Add 0.20mL DPC color reagent to both cuvettes, mix. After allowing about 10 minutes for the reddish color to develop and stabilize, measure the absorbance of both aliquots at 540nm. Record the "final" readings in LIMS.

- An acceptable initial calibration must be generated before the Post-Digestion Recovery Study results can be evaluated (see following Sections). Evaluate the Post-Digestion Recovery Study results as discussed in Section 8.2.4 below.

- If the Post-Digestion Recovery Study results do not meet the 85-115% control criteria, the additional actions that may be taken are contingent upon the analyst's judgment, the particular set of circumstances, and client input.

  Typically the study is repeated on a further diluted aliquot of the same digestate, until satisfactory recovery is achieved. All samples are then diluted at the same level of dilution, based on the successful post-digestion spike study results. The analyte reporting limit for the diluted sample analyses is elevated accordingly.

Overall though, the objective is that any further actions taken are representative of the client's sample matrix. Consequently, for failures affecting samples in a batch that are from several client sources, several actions may be necessary. Confer with the Project Manager(s). The appropriate course of action will be developed at the time needed, particular to the circumstance.

8.2.3 STANDARD/SAMPLE DEVELOPMENT

NOTE: Be sure to properly adjust spectrophotometer. Insert the proper stray light filter into position. Adjust the wavelength to 540nm. Insert the DI water blank cuvette into the cuvette holder. While in TRANS MODE, press and hold the ZERO SET button while adjusting the ZERO knob until the display indicates 0.00. Set MODE switch to ABS and adjust 100%T/A knobs to exactly 0.000. If further information is required see Barnstead/Thermolyne Corp. Operator's Reference Manual, Model 340 Digital Spectrophotometer.

- Transfer a 4.0mL aliquot (or smaller volume if it was determined that a greater dilution is necessary) of each digestate into a 1-inch diameter spectrophotometer cuvette. Bring to a 20.0mL final volume using DI water. Use of a 4.0mL aliquot of digestate brought to a 20.0mL final volume represents a 5-fold dilution.

- Add 0.5mL of 10% H_2SO_4 to each cuvette and mix using the vortex mixer. Measure the absorbance of the samples at 540nm using the spectrophotometer. Record these "initial" readings in LIMS. This absorbance reading is due to the native color of the sample and will be subtracted from the absorbance reading measured after adding DPC color reagent.

- Add 0.20mL DPC solution to the cuvettes and vortex.

- Allow the cuvettes to stand until a stable reddish color has developed (about 10 minutes).

8.2.4 ANALYTICAL SEQUENCE

Use the spectrophotometer (set at 540nm) to read the absorbance of each of the cuvette's contents. Record each reading. The following analytical sequence must be observed:

- Absorbance measurements must begin with the calibration standards, immediately followed by the ICV/ICB.

- Analyze the Post-Digestion Study samples. The recovery quality control limits for these samples is 85-115 %. If the Post-Digestion Recovery Study results exceed these limits, address as discussed in Section 8.2.2.

- After the ICV and ICB have been analyzed, **up to ten** samples (i.e., Method Blank, BS/LCS, post-digestion spike study, field samples, etc.) can be analyzed. Prepare digestates (or dilutions thereof), develop and analyze as previously discussed. Note: Insoluble MS/MSD's should require 100X dilution.

- ***The continuing calibration verification (CCV) standard, followed by the Method Blank as the Continuing Calibration Blank (CCB), must be analyzed between each set of ten samples, and at the close of the analytical sequence.***

  NOTE: To be acceptable, no blank may yield results greater than the analyte reporting limit.

- Continue to analyze samples in sets of ten or less followed by the analysis of the CCV/CCB pair until all samples have been analyzed.

8.3 EVALUATION OF THE CALIBRATION CURVE

8.3.1 Prepare a standard curve by plotting the observed absorbance versus the standard concentration for each calibration standard. Enter the information into the LIMS system.

8.3.2 Enter the absorbance data obtained for each solution analyzed (calibration standards, QC samples and field samples). Also, enter additional data as necessary (e.g., identification, sample volumes or weights, dilutions, percent solids, etc.) This information is also entered into the LIMS system.

8.3.3 Using LIMS evaluate the linear regression analysis between absorbance and Cr^{+6} concentrations for the calibration standards. The correlation coefficient (r^2) for the regression must be ≥ 0.995.

8.3.4 Evaluate the ICV sample. The ICV result must agree within ± 10 % of the expected value.

8.3.5 Evaluate the ICB sample result (result must be less than analyte reporting limit).

8.3.6 Evaluate the CCV results. The CCV result must agree within ±10% of the expected value.

8.3.7 Evaluate the CCB results (results must be less than analyte reporting limit).

NOTE: *Acceptance criteria and corrective actions are summarized in the attached QC Summary Table.*

8.4 CALCULATION OF SAMPLE CONCENTRATION

The Cr^{+6} concentration in the samples is calculated as follows:

$$Cr^{+6}\ \text{Concentration (mg/Kg)} = \frac{(C * 100 * 20)}{(A * 2.5 * S)}$$

where:

C	=	Concentration of Cr^{+6} (mg/L) in cuvette
A	=	Aliquot (mL) of digestate pipetted into the cuvette
20	=	final volume (mL) of solution in cuvette
100	=	final volume (mL) of digestate
2.5	=	moist weight (g) of soil digested
S	=	ratio of solids in sample (% solids/100)

8.5 CALCULATION OF POST-DIGESTION SPIKE RECOVERY

8.5.1 For both aliquots, subtract the "initial" absorbance reading from the "final" absorbance reading to obtain a "corrected" absorbance reading.

8.5.2 Enter the corrected absorbance into the spreadsheet to calculate the solution Cr^{+6} concentration.

8.5.3 Calculate the post-digestion spike recovery as follows:

$$\text{Post-Digestion Spike (\% R)} = \frac{(S - N)}{0.25} * 100$$

where:

S = Cr^{+6} concentration (mg/L) in spiked aliquot

N = Cr^{+6} concentration (mg/L) in unspiked aliquot

0.25 = amount of Cr^{+6} spike added (mg/L); 0.25 if this SOP is followed without deviation

8.5.4 The Post-Digestion Spike recovery acceptance limits are 85-115%. If the recovery falls outside of this range, the digestate post-digestion spike recovery study must be repeated at greater levels of dilution until

acceptable recovery is achieved. Results of the spike recovery study are extrapolated to determine appropriate levels of dilution for the other samples in the prep batch. In other words, the other samples in the batch must be diluted such that the "initial" absorbance reading (i.e., the absorbance measured before adding DPC reagent), is not greater than the initial absorbance reading for the post-digestion spike sample at the level of dilution that was necessary for acceptable recovery.

9. QUALITY CONTROL (QC)

NOTE: *Acceptance criteria and corrective actions are detailed in the attached QC Summary Table.*

9.1 BLANKS

Method blanks (MBs) are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. For this procedure, the MB consists of clean silica sand that has been digested as described previously in this SOP. The blank must not yield positive results greater than the reporting limit (usually 2.0mg/Kg Cr^{+6}).

9.2 SPIKED SAMPLES

The nature and evaluation of Post-Digestion Spike samples are discussed in previous Sections.

9.2.1 Blank/Laboratory Control Spike (LCS) samples consist of clean matrices which are spiked with a known amount of target compound. For this SOP, silica sand is used as the clean matrix. LCS analyses are performed to evaluate the accuracy of the analytical system.

9.2.2 For this SOP, the matrix spiked samples (MSs/MSDs and MSn/MSDn) consist of aliquots of selected field sample into which known concentrations of target analytes are spiked and analyzed as a means of determining the effect of matrix on target analyte detection. The spiked sample analyses are performed to determine the effect of sample matrix interferences.

9.2.3 EVALUATION OF SPIKED SAMPLE RESULTS

Spiked samples are evaluated based on percent recovery (%R), which is a calculation of the amount of target yielded vs. the amount of target anticipated. The following equation is used to calculate spike recovery:

$$\%R = \frac{Concentration_{Found} - Concentration_{Aliquot}}{Concentration_{Anticipated}} \times 100$$

where:

$Conc_{Found}$ = amount of target yielded by the spiked analysis

$Conc_{Aliquot}$ = amount of target found in the unspiked aliquot ("zero" for clean LCS matrix aliquots; sample results for sample matrix aliquots)

$Conc_{Anticipated}$ = amount of target expected to be yielded based on amount spiked

The control limits established for the LCS analysis are 80-120 %.

Advisory limits for the MS/MSD analysis are set at 75-125 % of the anticipated value.

9.2.4 DUPLICATE PRECISION

The matrix spiked samples are prepared and analyzed in duplicate to measure analytical precision. Precision is evaluated in terms of Relative Percent Difference (RPD), and is calculated as follows:

$$RPD\ (\%) = \frac{|\ Result_x - Result_{Dup}\ |}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

An RPD of $\leq$20 is set as the advisory quality control limit.

9.3 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study should be performed as needed and at a minimum, annually.

10. DEVIATIONS FROM METHOD

10.1 According to Section 8.5 of Method SW3060A, "An acceptance range for matrix spike recoveries is 75-125 %. If the matrix spikes are not within these recovery limits, the entire batch must be rehomogenized/redigested/reanalyzed." This SOP does not require redigestion of samples when matrix spike recoveries are outside of the 75-125 % limits. Rather, recoveries outside these limits are attributed to matrix effects and the results are narrated and flagged in the data report accordingly (see also comments in Interferences Section).

10.2 Method SW3060A suggests the need for sample characterization and suggests "additional analytical parameters" such as pH, ferrous iron, sulfides, oxidation-reduction potential (ORP), total organic carbon (TOC), biological oxygen demand (BOD) and chemical oxygen demand (COD). Paragon considers these additional analyses to be beyond the scope of this analysis.

10.3 Unlike Method SW3060A, Section 8.4, this SOP does not prescribe that a sample duplicate be prepared and analyzed. In this SOP, a measure of analytical precision is provided by the RPD calculated for the soluble MS/MSD.

10.4 Section 8.6.2 of Method SW3060A prescribes that if the post-digestion spike recovery is outside of 85-115 %, either the Method of Standard Additions (MSA) is used or that additional analytical parameters should be considered in order to interpret the results. In this SOP, when a post-digestion spike is outside of 85-115% recovery, the spike is repeated on the diluted sample aliquot of the selected sample digestate. The level of dilution must be increased until satisfactory recovery is achieved. Furthermore, the other samples in the batch must be diluted according to the results from the post-digestion spike recovery study. Other corrective measures may be applied contingent upon the particular circumstance and client input.

10.5 Section 5.2 of Method SW7196A describes the creation of the chromium stock solution as dissolving 0.1414g $K_2Cr_2O_7$ in DI water and bringing the solution to a 1L final volume. Paragon creates a 10-times stronger chromium stock standard by dissolving 0.1414g $K_2Cr_2O_7$ in DI water and bringing the solution to a 100mL final volume. Furthermore, Section 5.3 of Method SW7196A describes the creation of the standard chromium solution by diluting 10.0mL of chromium stock solution to a 100mL final volume. Paragon creates the standard chromium solution by diluting 2.0mL of the chromium stock solution to a 100mL final volume. Therefore, at 10mg/L Cr^{+6}, Paragon's standard chromium solution is 2-times stronger than that provided for in the Method.

10.6 Section 7.1 of Method SW7196A prescribes that the colorimetric analysis of calibration standards and samples be performed in 100mL volumetric flasks (standards and samples are brought to 100mL using DI water). Paragon uses a 20.0mL final sample volume and conducts the color development directly in the 1-inch diameter spectrophotometer cuvettes.

10.7 In Section 7.2.1, Method SW7196A indicates that the method is suitable for the analysis of hexavalent chromium ranging in concentration from 0.5 to 5mg/L Cr^{+6}. Paragon's modifications to the Method (e.g., the use of more concentrated chromium standards), enables a typical calibration range of 0.010 to 0.50mg/L Cr^{+6} (2.0-100mg/Kg Cr^{+6}, correspondingly) to be achieved.

10.8 In Section 7.3.1, Method SW7196A indicates that the spike added concentration for the interference check standard should not be less than 30mg/L Cr^{+6}. This SOP prescribes a spike added concentration of 0.25mg/L Cr^{+6}, which is appropriate for the analytical range of Paragon's analysis.

10.9 Based on sample volumes and reagent strengths cited in the Methods, Section 4e of Method SM3500-Cr B and Section 7.1 of Method SW7196A prescribe the

addition of 2.0mL diphenylcarbazide to the 100mL final sample volume for color development. In accordance with reagent strengths, the 20.0mL final sample volume employed, and color development carried-out directly in the spectrophotometer cuvettes (all discussed above), Paragon uses 0.20mL of diphenylcarbazide to achieve color development.

10.10 Section 8.5 of Method SW7196A calls for the analysis of one matrix spike replicate OR one replicate sample for every ten samples. Paragon accomplishes this by preparing and analyzing one matrix spike/matrix spike duplicate per batch of 20 samples.

10.11 Section 7.1 of Method SW7196A discusses correcting sample absorbance by subtracting out the absorbance of the reagent water blank. Paragon does not correct absorbance readings using the reagent water blank because a 0.0 standard (consisting of reagent water) is incorporated as part of the calibration curve.

10.12 Section 7.1 of Method SW3060A suggests the use of a temperature blank to monitor the inferred temperature of the alkaline digestates while housed in the 90-95°C water bath. Paragon does not employ a temperature blank but directly monitors the water bath with a NIST-traceable verified glass thermometer.

10.13 Section 7.6 of Method SW3060A discusses filtration of the alkaline digestates. Paragon spins the digestates in a centrifuge to achieve effective control of solids interferences.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled, at a minimum, with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 All aqueous solutions may be disposed of in the Aqueous Laboratory Waste satellite collection vessel.

11.2.2 Solid residues may be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

11.2.4 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Health and Safety Officer will provide specific procedures and materials for these samples.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 3, Method 3060A, "Alkaline Digestion for Hexavalent Chromium", Revision 1, December 1996.

12.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 4, Method 7196A, "Hexavalent Chromium (Colorimetric)", Revision 1, July 1992.

DOCUMENT REVISION HISTORY

7/26/05: Added reference Program Specification directive in "Responsibilities", updated format.

6/26/06: Added thermometer to equipment list and direction to record water bath temperature. Added DOCUMENT REVISION HISTORY.

3/7/8: Provided for additional corrective measures for failed post-digestion spike analyses (Sections 8.2.2, last bullet; 8.2.3 edited post-digestion spike bullet; edited comment 10.4).

Analytical Method: SW3060A & 7196A	**Parameter:** Alkaline Digestion and Analysis of Hexavalent Chromium (Colorimetric) in Solid Matrices		**Summary of Quality Control Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point (plus blank)	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria)	Correlation coefficient (r^2) for linear regression must be $\geq$0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification (ICV); second source; at or below the midpoint	Once after each initial calibration	Response must agree within $\pm$10% of initial calibration	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV); at or below the midpoint	Run after every ten samples and to end any run sequence (must be followed by a CCB analysis)	Response must agree within $\pm$10% of initial calibration	Check that calculations and preparation are correct, evaluate/correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	ICB is run following the ICV; CCB is run after each CCV and to close a run sequence	Cr^{+6} content of the blank must be < RL; RL usually 2.0mg/Kg Cr^{+6}(which corresponds to 0.01mg/L without conversion to solid matrix units)	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Method Blank (MB)	One per batch of $\leq$20 field samples	Cr^{+6} content of the blank must be < RL; RL usually 2.0mg/Kg Cr^{+6}	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples must also be reprepared and analyzed.
Blank (laboratory control) Spike (BS, LCS)	One per batch of $\leq$20 field samples	Recoveries must be within $\pm$20% of expected values	Check for documentable errors (e.g., calculations and spike preparation). If no computation errors are found, prepare a fresh spike and analyze. If quality criteria still not met, all field and quality control samples must be reprepared and analyzed.
Matrix Spike (MSs or MS)	One per batch of $\leq$20 field samples	Recoveries should be within $\pm$25 % of expected values	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike (laboratory) Duplicate (MSDs or MSDn)	Matrix-specific; one prepared for each sample batch of $\leq$20 field samples	(See MS recovery criteria above). RPD should be $\leq$20.	(See MS recovery criteria above). For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department and QA Managers.
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	As needed; at a minimum annually.	Positive result < the analyte reporting limit (RL).	Determine the reason for failure and fix problem with the system. Repeat the MDL study. If criteria still not met, discuss with QA Manager (RL may be adjusted if required).

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1122 REVISION 6

TITLE: DETERMINATION OF HEXAVALENT CHROMIUM BY METHODS SW7196A, SM3500-Cr-B

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER Steve Workman DATE 7/21/08

QUALITY ASSURANCE MANAGER Deb Schenk DATE 7/20/08

LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: Rev0, 3/27/00; Rev1, 3/2/02; Rev2, 10/15/02; Rev3, 2/9/04 (format update) and 3/18/05 (re-released without revision); Rev4, 7/26/05; Rev5, 6/26/06; Rev6, 7/18/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW7196A, and SM3500-Cr B -- describe the determination of hexavalent chromium (Cr^{+6}) in environmental water samples. This procedure can also be applied to aqueous extracts of various solid samples and certain domestic and industrial wastes, provided that no interfering substances are present.

2. SUMMARY

Cr^{+6} in an aqueous sample or extract is determined colorimetrically by reaction with diphenylcarbazide (DPC). Addition of an excess of DPC in acid solution yields a red-violet complex whose absorbance is measured photometrically at 540nm. This reaction is highly selective for Cr^{+6}. A dilute calcium chloride solution is used to leach Cr^{+6} from soils and other solid samples to create an aqueous extract (NOTE: This is an alternate method for Cr^{+6} in soil prepared by alkaline digestion. If alkaline digestion by Method SW3060A is required, see PAR SOP 1121).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision,

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 The stability of Cr^{+6} in an aqueous solution will be governed by the oxidizing/reducing tendency (redox potential) of the sample matrix. The redox potential of a particular sample matrix (water, aqueous extract) may be sufficiently low to favor the reduction of Cr^{+6} to Cr^{+3}. Under such circumstances, low matrix spike recovery of Cr^{+6} should not be interpreted as a failure of the analysis. Rather, failure to recover spiked Cr^{+6} in a particular sample matrix should be viewed as evidence that Cr^{+6} is not stable in that matrix and, therefore, native Cr^{+6} should not be expected.

4.2 If not accounted for, turbidity and/or color in waters or aqueous extracts will cause a high bias in the analysis because suspended particles will block light in the light path of the spectrophotometer and thereby contribute an absorbance signal that is not due to Cr^{+6}. Turbid or colored samples should be filtered or centrifuged to remove or reduce cloudiness as much as possible. If turbidity and/or color is not filtered out, it can be accounted for by taking initial absorbance readings and subtracting it out from the final absorbance reading after the addition of diphenylcarbazide. Most soil extracts prepared by this SOP are free of turbidity because clay particles usually flocculate in 0.01M $CaCl_2$ solution.

4.3 Darkly colored waters and aqueous extracts may require dilution prior to color development with diphenylcarbazide. The reporting limit for the analysis must be raised accordingly.

4.4 The Cr^{+6} reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent Molybdenum (Mo) and Mercury (Hg) salts also react to form color with the reagent. However, the red-violet intensities produced by these other metal salt reactions are much lower than those for chromium at the specified pH. Concentrations of up to 200mg/L of hexavalent Mo and Hg can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

4.5 Iron may contribute a yellow color when it is present at a concentration greater than 1mg/L. However, the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.6 Use of new and/or unscratched glassware (i.e., cuvettes) will minimize chromium adsorption on glass surfaces during the oxidation process. Do not use glassware previously treated with chromic acid. Thoroughly clean glassware with nitric or hydrochloric acid to remove chromium traces.

5. APPARATUS AND MATERIALS

5.1 UV/VIS Spectrophotometer, Sequoia Turner Model™ 340 or equivalent. Suitable for measurements at 540nm with a light path of 1.0cm or longer

5.2 analytical balance, capable of weighing to 0.0001g, verified per SOP 305

5.3 TCLP tumbler, or equivalent (for mechanical agitation)

5.4 centrifuge capable of achieving approximately 3500rpm

5.5 vortex mixer

5.6 repeater pipet, variable Eppendorf™ or equivalent, operated per SOP 321

5.7 cuvettes, optically matched, 1-inch diameter

NOTE: Wash with nitric or hydrochloric acid before use.

5.8 centrifuge tubes, polypropylene with screw-cap closures, 50mL

5.9 volumetric flasks, Class A, 100mL, 500mL and 1L sizes

5.10 graduated cylinder, 50mL capacity (delivered volume verified by laboratory)

5.11 syringe, outfitted with a 0.45µm or 0.7µm filter disk

6. REAGENTS

6.1 Deionized (DI) water: Obtained from the laboratory DI water system

6.2 Ottawa sand, clean/inert, EMD, SX0075-3 or equivalent

6.3 Acetone, Burdick & Jackson, Cat. 010-4 or equivalent

6.4 Nitric Acid, (HNO_3), 2N : Dilute 100mL of concentrated HNO_3, JT Baker, 9598-34 or equivalent, to a final volume of 700mL using DI water. ***Store in a polypropylene bottle.*** *Shelf Life = 1 year.*

6.5 Sulfuric Acid, (H_2SO_4), 4N 10%: Dilute 20mL of 50 % H_2SO_4 (1:1 ratio with DI water) to a final volume of 90 - 100mL with DI water. Alternately, dilute 10mL of conc. H_2SO_4 to a final volume of 100mL with DI water. EMD, SX1247-2 or equivalent. ***Store in a polypropylene bottle.*** *Shelf Life = 1 year.*

6.6 Calcium Chloride ($CaCl_2$) Solution, 0.01M: Dissolve 1.47g $CaCl_2 \bullet 2H_2O$, JT Baker, 1332-01 or equivalent, in 1L of DI water. ***Store in a polypropylene bottle.*** *Shelf Life = 1 year.*

6.7 Diphenylcarbazide (DPC) Solution: Dissolve 0.25g of EM Science, DX2200-1 or equivalent, 1,5-diphenylcarbazide in 50mL of reagent grade acetone***. Store in a brown glass bottle and refrigerate. Discard when the solution becomes discolored (approx. 3 months).***

6.8 Cr^{+6} Stock Standard, 500 mg/L (**First Source**): Purchase as a certified stock solution from a commercial vendor or prepare by dissolving 0.1414g dry Potassium Chromate ($K_2Cr_2O_7$) in DI water using a 100mL Class A volumetric flask and diluting to full volume with additional DI water. Mix thoroughly. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 1 year.*

6.9 Cr^{+6} Intermediate Standard, 10mg/L (**First Source**): Dilute 2.0mL of first source 500mg/L Cr^{+6} stock standard to 100mL with DI water. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 3 months, or when parent expires (whichever is shorter).*

6.10 Cr^{+6} Stock Standard, 500mg/L (**Second Source**): Purchase as a certified solution from a commercial vendor or prepare by dissolving 0.1414g dry $K_2Cr_2O_7$ in DI water using a 100mL Class A volumetric flask. Bring to volume using DI water, mix thoroughly. If purchased, the certified solution must be from a different vendor than the first source stock standard. If prepared in-house, the $K_2Cr_2O_7$ salt must be from a different vendor than the salt used to prepare the first source stock standard. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 1 year.*

6.11 Cr^{+6} Intermediate Standard, 10mg/L (**Second Source**): Dilute **second source** 500mg/L Cr^{+6} stock standard to 100mL with DI water. ***Store in a polypropylene bottle and refrigerate.*** *Shelf Life = 3 months, or when parent expires (whichever is shorter).*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 All samples should be collected according to an approved sampling plan.

7.2 The maximum holding time prior to analysis is 24 hours for water samples and aqueous extracts prepared as described in this SOP. Soil samples must be extracted within 28 days of collection.

7.3 To retard the chemical activity of hexavalent chromium, all samples and extracts should be stored at 4±2°C until analyzed.

8. PROCEDURE

NOTE: A batch is defined as twenty (20) field samples or less of like matrix. One of each of the laboratory quality control (QC) samples outlined below (i.e., Method Blank, Blank Spike/LCS, MS (also serves as the aqueous interference check sample)/MSD set, must be prepared for each batch of field samples to be analyzed. **Note that the aqueous Post Spike Sample is prepared as an aqueous extract for solid matrix sample batches only.**

8.1 AQUEOUS EXTRACTION OF SOLIDS/PREPARATION OF SOLID MATRIX QUALITY CONTROL (QC) SAMPLES

8.1.1 Weigh 4.0g of moist sample into a 50mL disposable polypropylene centrifuge tube.

8.1.2 Method Blank. Weigh 4.0g clean silica sand into a 50mL disposable polypropylene centrifuge tube.

8.1.3 Blank Spike (Laboratory Control Sample, LCS). Weigh 4.0g clean silica sand into a 50mL disposable polypropylene centrifuge tube. Spike with 1.2mL of 10mg/L Cr^{+6} stock standard (second source). Be sure to have another person witness the spiking.

8.1.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD). For one of the samples in the batch, spike two duplicate 4.0g aliquots with 0.40mL of 10mg/L Cr^{+6} stock standard (first source). Be sure to have another person witness the spiking.

8.1.5 In order to determine the proper volume of extract to be processed and read by the spectrophotometer, a post spike/interference check sample (PS/ICS) analysis must be performed. Select a representative field sample and prepare an additional aliquot to be extracted for use as the PS/ICS. ***This sample is analyzed after the calibration standards and blanks, but before any field samples are analyzed, and is evaluated to determine what dilutions (if any) are required for the subsequent sample analyses.*** Where sample or extract dilution is required, DI water is used as the diluent.

8.1.6 To all of the above, add 40.0mL 0.01M $CaCl_2$ using a graduated cylinder. (**NOTE:** Remove an amount equivalent to the amount of spike added to LCS, MS and MSD from the graduated cylinder before adding $CaCl_2$ to these prepared aliquots).

8.1.7 Cap the tubes and shake the samples for 1 hour on the TCLP tumbler.

8.1.8 Centrifuge the tumbled tubes for about 15 minutes @ 3500rpm in order to settle the solids.

8.1.9 Transfer a 20.0mL aliquot of each extract (or an aliquot portion diluted to 20mL) into an acid-washed 1-inch (diameter) cuvette.

8.2 PREPARATION OF AQUEOUS FIELD AND QUALITY CONTROL (QC) SAMPLES

8.2.1 For each aqueous sample to be analyzed, pipet 20.0mL of sample (or aliquot diluted to 20mL) into an acid-washed 1-inch (diameter) cuvette.

Turbid samples should be filtered using a syringe and a 0.45µm or 0.7µm filter disk to remove or reduce suspended particles as much as possible before aliquotting. If turbidity and/or color are not filtered out, it can be accounted for by taking initial absorbance readings after the addition of the 10% H_2SO_4 and subtracting it out from the final absorbance reading after the addition of diphenylcarbazide.

8.2.2 Method Blank. Pipet 20.0mL of DI water into a 1-inch cuvette.

8.2.3 Blank Spike (Laboratory Control Sample, LCS). Pipet 20.0mL of DI water into a 1 inch cuvette. Spike with 0.20mL of 10mg/L Cr^{+6} intermediate standard (second source). Be sure to have another person witness the spiking.

8.2.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD). Select a representative water sample (i.e., similar color, odor, etc.) from the batch and transfer two duplicate 20.0mL aliquots (or aliquots diluted to 20.0mL) into two 1-inch diameter spectrophotometer cuvettes. Spike each aliquot with 0.20mL of 10mg/L stock standard (first source). **Be sure to have another person witness the spiking.**

NOTE: Since water sample aliquots are prepared and analyzed directly (i.e., no "extraction" step is involved), the aqueous MS/MSD samples also serve as the Post Spike/Interference Check Sample (PS/ICS) for the aqueous matrix.

The PS/ICS is analyzed after the calibration standards and blank, but before any field samples are analyzed, and is evaluated to determine what dilutions (if any) are required for the subsequent sample analyses.

8.3 COLORIMETRIC ANALYSIS OF STANDARDS, WATER SAMPLES AND AQUEOUS EXTRACTS

8.3.1 STANDARD CURVE PREPARATION

Prepared fresh on each day of analysis. Use DI water to achieve the final volume. Prepare working standards in matching 1-inch, acid-washed spectrophotometer cuvettes as described below:

Standard Concentration	Volume of 10 mg/L	Final Volume

(mg/L)	Intermediate Std (mL)	(mL)
0	0	20.0
0.01	0.02	20.0
0.05	0.10	20.0
0.10	0.20	20.0
0.30 (CCV)**	0.60	20.0
0.50	1.00	20.0
0.10 (ICV)*	0.20 *	20.0

* Independent Calibration Verification (ICV). The ICV must be prepared from a second source that is independent of that which is used to prepare the calibration standards. ***Use the Second Source 10mg/L Intermediate Standard.*** An Initial Calibration Blank (ICB), consisting of a 20.0mL aliquot of DI water, must be analyzed immediately following the ICV.

** This standard is analyzed repeatedly as the Continuing Calibration Verification (CCV). A Continuing Calibration Blank (CCB), consisting of a 20.0mL aliquot of DI water, must be analyzed immediately following each CCV.

8.3.2 SPECTROPHOTOMETER SETUP

The spectrophotometer must be properly adjusted before use. Insert the proper stray light filter into position. Adjust the wavelength to 540nm. Insert the DI water blank cuvette into the cuvette holder. While in TRANS MODE, press and hold the ZERO SET button while adjusting the ZERO knob until the display indicates 0.00. Set the MODE switch to ABS and adjust 100%T/A knobs to exactly 0.000. If further information is required, see Barnstead/Thermolyne Corp. Operator's Reference Manual, Model 340 Digital Spectrophotometer.

8.3.3 COLOR DEVELOPMENT

- To each cuvette, add 0.5mL of 10% H_2SO_4 and vortex (Take and record in LIMS the initial absorbance readings at this time if necessary).

  NOTE: ***If an extract is colored, or if a sample is colored or remains turbid after filtering, after the addition of the 10% H_2SO_4, place the cuvette into the spectrophotometer and measure the absorbance at 540nm. This initial absorbance reading will later be subtracted from the final absorbance reading measured after adding DPC color reagent, to yield a corrected absorbance reading.***

- Add 0.20mL DPC solution to the cuvettes and vortex.

- Allow the samples to stand until the color is fully developed (5-10 minutes).

8.3.4 ANALYTICAL SEQUENCE

The standard solutions are analyzed first, followed immediately by the ICV/ICB. Then the PS/ICS samples are analyzed so that the proper dilution needed to process the remaining field samples can be determined. Color and turbidity can interfere with absorbance readings. Dilution and other means are used to compensate for this interference.

- Absorbance measurements must begin with the calibration standards, immediately followed by the ICV/ICB. Record all measurements obtained.

- Analyze the Post Spikes/ICSs that were previously prepared in Steps 8.1.5 and 8.2.4. The quality control limits for all PS/ICS recoveries is 85-115 %. ***If the PS/ICS spike recovery falls outside of this range, the spike must be repeated on a diluted aliquot of the same sample/extract until satisfactory PS/ICS recovery is achieved. Once the necessary level of dilution (if any) is determined, the other samples in the batch must also be diluted at the same level prior to analysis. The analyte reporting limit for the diluted sample analyses is elevated accordingly.***

- After the ICV and ICB have been analyzed, **up to ten** samples (i.e., Method Blank, BS/LCS, PS/ICSs, field samples, etc.) can be analyzed. Prepare samples/extracts (or dilutions thereof), develop and analyze as previously discussed.

- ***The continuing calibration verification (CCV) standard, and the Continuing Calibration Blank (CCB), must be analyzed between each set of ten field or laboratory QC samples run, and at the close of the analytical sequence.***

- Continue to analyze samples in sets of ten or less followed by the analysis of the CCV/CCB pair until all samples have been analyzed.

8.4 EVALUATION OF THE CALIBRATION CURVE

8.4.1 Prepare a standard curve by plotting the observed absorbance versus concentration for each calibration standard. Enter the information into the LIMS system.

8.4.2 Enter the absorbance data obtained for each solution analyzed (calibration standards, QC samples and field samples). Also, enter additional data as necessary (e.g., sample volumes or weights, dilutions, percent solids, etc.). This information is also entered into the LIMS system.

8.4.3 Using LIMS, evaluate the linear regression analysis between absorbance and Cr^{+6} concentrations for the calibration standards. The correlation coefficient (r^2) for the regression must be $\geq$0.995.

8.4.4 Evaluate the ICV sample. The ICV result must agree within ±10 % of the expected value.

8.4.5 Evaluate the ICB sample result (result must be less than analyte reporting limit).

8.4.6 Evaluate the CCV results. The CCV result must agree within ±10% of the expected value.

8.4.7 Evaluate the CCB results (results must be less than analyte reporting limit).

NOTE: *Acceptance criteria and corrective actions are detailed in the attached QC Summary Table.*

8.5 CALCULATION OF SAMPLE CONCENTRATION

8.5.1 The Cr^{+6} concentration in water samples is calculated as follows:

$$Cr^{+6}\ \text{Concentration (mg/L)} = A * D$$

where:

A = abs * slope + intercept (the *slope* and *intercept* are obtained from the regression analysis)

D = Dilution factor if a dilution was necessary to produce a response within the calibration range

8.5.2 The Cr^{+6} concentration in solid samples is calculated as follows:

$$Cr^{+6}\ \text{Concentration (mg/Kg)} = \frac{A * D * V}{W}$$

where:

A = abs * slope + intercept (the *slope* and *intercept* are obtained from the regression analysis)

D = Dilution factor if a dilution was necessary to produce a response within the calibration range

V = Extract volume (V = 40mL if this SOP is followed without deviation)

W = Dry weight of sample extracted (W = 4.0g * percent solids if this SOP is followed without deviation)

9. QUALITY CONTROL (QC)

NOTE: *Acceptance criteria and corrective actions are detailed in the attached QC Summary Table.*

9.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike and duplicate (MS/MSD) and Post Spike/Interference Check Sample. All quality control samples must be carried through all stages of the sample preparation and measurement steps

9.2 BLANKS

Method blanks (MBs) are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. For this procedure, the MB consists of DI water, or clean silica sand that has been extracted as described previously in this SOP. The blank must not yield positive results greater than the reporting limit (usually 0.010mg/L, 0.10mg/Kg Cr^{+6}).

9.3 SPIKED SAMPLES

9.3.1 Blank/Laboratory Control Spike (LCS) samples consist of clean matrices that are spiked with a known amount of target compound. For this SOP, DI water is used as the clean matrix for aqueous sample batches; silica sand is used as the clean matrix for solid sample batches. LCS analyses are performed to evaluate the accuracy of the analytical system.

9.3.2 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) samples consist of additional sample aliquots which are spiked with a known amount of target compound. MS/MSD analyses are performed to determine the effect of sample matrix interferences.

9.3.3 For this SOP, a Post Spike/Interference Check Sample, consisting of an aliquot of aqueous sample or extract is prepared for each solid/aqueous matrix batch. The PS/ICS analysis is run to verify and correct for reducing conditions, and chemical, color or turbidity interferences. If the result of this spikes falls outside of the 85-115% acceptable range, the sample is diluted and reanalyzed until a dilution that produces an acceptable result is determined. All associated prepared samples are then diluted at the same level for analysis.

9.3.4 EVALUATION OF SPIKED SAMPLE RESULTS

Spiked samples are evaluated based on percent recovery (%R), which

is a calculation of the amount of target yielded vs. the amount of target anticipated. The following equation is used to calculate spike recovery:

$$\%R = \frac{Concentration_{Found} - Concentration_{Aliquot}}{Concentration_{Anticipated}} \times 100$$

where:

$Conc_{Found}$	=	amount of target yielded by the spiked analysis
$Conc_{Aliquot}$	=	amount of target found in the unspiked aliquot ("zero" for clean LCS matrix aliquots; sample results for sample matrix aliquots)
$Conc_{Anticipated}$	=	amount of target expected to be yielded based on amount spiked

The control limits established for the LCS analysis are 90-110 % (aqueous matrix) and 80-120 % (solid matrix).

Advisory limits for the MS/MSD analysis are set at 85-115 % of the anticipated value (aqueous matrix) and 75-125 % (solid matrix).

The control limits established for all Post Spike/Interference Check Sample analyses are 85-115 %. If the result of the spike falls out of the acceptable range, the sample is be diluted and reanalyzed. When acceptable recovery is achieved, all samples associated with the ICS are diluted at the same level.

9.3.5 DUPLICATE PRECISION

The matrix spike samples (both matrices) are prepared and analyzed in duplicate to measure analytical precision. Precision is evaluated in terms of Relative Percent Difference (RPD), and is calculated as follows:

$$RPD\ (\%) = \frac{|Result_x - Result_{Dup}|}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

An RPD of $\leq$20 is set as the advisory quality control limit.

9.4 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study should be performed as needed and at a minimum, annually.

10. DEVIATIONS FROM METHOD

10.1 Section 3a of Method SM3500-Cr B and Section 5.2 of Method SW7196A describes the creation of the chromium stock solution as dissolving 0.1414g

$K_2Cr_2O_7$ in DI water and bringing the solution to a 1L final volume. Paragon creates a 10-times stronger chromium stock standard by dissolving 0.1414g $K_2Cr_2O_7$ in DI water and bringing the solution to a 100mL final volume. Furthermore, Section 3b of Method SM3500-Cr B and Section 5.3 of Method SW7196A describes the creation of the standard chromium solution by diluting 10.0mL of chromium stock solution to a 100mL final volume. Paragon creates the standard chromium solution by diluting 2.0mL of the chromium stock solution to a 100mL final volume. Therefore, at 10mg/L Cr^{+6}, Paragon's standard chromium solution is 2-times stronger than that provided for in the Method.

10.2 Section 7.1 of Method SW7196A and Section 4e of Method SM3500-Cr B prescribe that the colorimetric analysis of calibration standards and samples be done in 100mL volumetric flasks (standards and samples are brought to 100mL using DI water). Paragon uses a 20.0mL final sample volume and conducts the color development directly in the 1-inch diameter spectrophotometer cuvettes.

10.3 Section 7.2.1 of SW Method 7196A indicates that the method is suitable for the analysis of hexavalent chromium ranging in concentration from 0.5 to 5mg/L Cr^{+6}. Based on use of more concentrated chromium standards and a 20.0mL final sample volume (rather than 100mL as cited in the Method), Paragon has established a typical calibration range of 0.010 to 0.50mg/L Cr^{+6} using these Methods.

10.4 Section 4e of Method SM3500-Cr B indicates the use of a 0.2N sulfuric acid solution to accomplish pH adjustment. It further cites pH adjustment to 1.0±0.3 pH units and advises use of a pH meter to check the pH. Paragon utilizes a 10% sulfuric acid solution as provided for in Section 5.4 of Method SW7196A. Method SW7196A cites pH adjustment to 2±0.5 pH units and does not specify the use of a pH meter to check the pH. Paragon follows Method SW7196A.

10.5 Based on sample volumes and reagent strengths cited in the Methods, Section 4e of Method SM3500-Cr B and Section 7.1 of Method SW7196A prescribe the addition of 2.0mL diphenylcarbazide to the 100mL final sample volume for color development. In accordance with reagent strengths, the 20.0mL final sample volume employed, and color development carried-out directly in the spectrophotometer cuvettes (all discussed above), Paragon uses 0.20mL of diphenylcarbazide to achieve color development.

10.6 Section 7.3 of Method SW7196A indicates that the spike added concentration for the post spike/interference check sample should not be less than 30mg/L Cr^{+6}. This SOP prescribes a spike added concentration of 0.20mg/L Cr^{+6}, which is in accordance with the analytical range established by Paragon's procedure as described in this SOP.

This Method reference further states that if the recovery for the PS/ICS is not within 85-115 %, the sample must be diluted and the spike repeated; and goes on

to suggest that "if the interference persists after sample dilution, an alternative method (Method SW7195, Coprecipitation, or Method SW7197, Chelation/Extraction) should be used". The Method further suggests that the presence of residual reducing agent be tested for by processing an alkaline extract. Paragon does not perform any of these additional procedures. This SOP prescribes that if the recovery of the diluted PS/ICS is outside of the 85-115 % acceptance limits, the PS/ICS analysis will be repeated at increasing dilutions until acceptable recoveries are achieved.

10.7 Section 2.3 of Method E218.4 (Atomic Absorption, Chelation-extraction) states that the diphenylcarbazide colorimetric procedure as found in "Standard Methods for the Examination of Water and Wastewater" may also be used.

10.8 Paragon does not pretreat hexavalent chromium samples to remove the cupferrates of molybdenum, vanadium, iron and copper by extraction into chloroform (followed by acid fuming digestion) as provided for in Section 1b of Method SM3500-Cr B. Nor does Paragon perform azide reduction to remove permanganate interferences.

10.9 Section 8.5 of Method SW7196A calls for the analysis of one matrix spike replicate OR one replicate sample for every ten samples. Paragon accomplishes this by preparing and analyzing one matrix spike/matrix spike duplicate per batch of 20 samples.

10.10 Section 4a of Method SM3500-Cr B and Section 7.1 of Method SW7196A discuss correcting standard and sample (respective citations) absorbances by subtracting out the absorbance of the reagent water blank. Paragon does not correct absorbance readings using the reagent water blank because a 0.0 standard (consisting of reagent water) is incorporated as part of the calibration curve.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents

and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 All aqueous solutions may be disposed of in the Aqueous Laboratory Waste satellite collection vessel.

11.2.2 Solid residues may be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

11.2.4 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Waste Compliance Officer will provide specific procedures and materials for these samples.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 4, Method 7196A, "Hexavalent Chromium (Colorimetric)", Revision 1, July 1992.

12.2 A.P.H.A., A.W.W.A. and W.E.F., 1998. Standard Methods for the Examination of Water and Wastewater, 20th edition, Revised 1998, "Method 3500-Cr B".

12.3 Barnstead/Thermolyne Corp., Operator's Reference Manual, Model 340 Digital Spectrophotometer, 34F00-01 9/12/96.

DOCUMENT REVISION HISTORY

7/26/05: Added Program Specification directive in "Responsibilities", updated format.

6/26/06: Provided for use of acid-washed glassware; added DOCUMENT REVISION HISTORY.

7/18/08: Clerical corrections. Added hold time for soils (7.2).

Analytical Method: SW7196A & SM3500-Cr B	**Parameter:** Hexavalent Chromium (Colorimetric)		**Summary of Quality Control Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point (plus blank)	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria)	Correlation coefficient (r^2) for linear regression must be $\geq$0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification (ICV); at or below midpoint	Once after each initial calibration	Response must agree within $\pm$10% of initial calibration	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV); at or below midpoint	Run after every ten samples and to end any run sequence (must be followed by a CCB analysis)	Response must agree within $\pm$10% of initial calibration	Check that calculations and preparation are correct, evaluate/correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	ICB is run following the ICV; CCB is run after each CCV and to close a run sequence	Cr^{+6} content of the blank must be <RL; RL usually 0.010mg/L, 0.10mg/Kg Cr^{+6}	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Method Blank (MB)	Matrix-specific; one prepared for each sample batch of $\leq$20 field samples	Cr^{+6} content of the blank must not exceed reporting limit (RL); RL usually 0.010mg/L, 0.10mg/Kg Cr^{+6}	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples must also be reprepared and analyzed.
Blank (laboratory control) Spike (BS, LCS)	Matrix-specific; one prepared for each sample batch of $\leq$20 field samples	Recoveries must be within $\pm$10 % of expected values (aqueous matrix); $\pm$20 % of expected values (solid matrix)	Check for documentable errors (e.g., calculations and spike preparation). If no computation errors are found, prepare a fresh spike and analyze. If quality criteria still not met, all field and quality control samples must be reprepared and analyzed.
Matrix Spike (MS)	Matrix-specific; one prepared for each sample batch of $\leq$20 field samples	Recoveries must be within $\pm$15% of expected values (aqueous matrix); $\pm$25 % of expected values (solid matrix)	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike (laboratory) Duplicate	Matrix-specific; one prepared for each sample batch of $\leq$20 field samples	(See MS recovery criteria above) RPD should be $\leq$20	(See MS recovery criteria above). For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department and QA Managers.
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	As needed; at a minimum annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with the system. Repeat the MDL study. If criteria still not met, discuss with QA Manager (RL may be adjusted if required).

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1125 REVISION 4

TITLE: DETERMINATION OF PERCHLORATE IN WATER USING ION CHROMATOGRAPHY -- METHODS EPA 314.0 AND SW9058

FORMS: 1116 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER Steve Workman DATE 4/13/06
QUALITY ASSURANCE MANAGER Rob Schell DATE 4/12/06
LABORATORY MANAGER [illegible] DATE 4-12-06

HISTORY: Rev0, 7/18/01; Rev1, 8/23/02; Rev2, 2/13/04; Rev3, 2/7/05; Rev4, 4/10/06. re-released w/o revision 7/18/08 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- US EPA 314.0 and SW9058 -- describe procedures for the analysis of perchlorate in aqueous samples and aqueous extracts of environmental solid sample matrices using ion chromatography.

2. SUMMARY

Perchlorate is separated and measured using an analytical system consisting of an autosampler, pump, ion chromatograph (IC) and personal computer (PC). The IC contains ion exchange columns, a suppressor device, and a conductivity detector.

Small volumes of sample (typically 5mL) are injected via the autosampler onto the IC to flush and fill the 1.00mL sample loop. The contents of the filled sample loop are then injected into a sodium hydroxide (NaOH) eluent stream, which is pumped through a series of two ion exchange columns (guard and analytical). The perchlorate is separated by the two exchange columns, and then carried by the eluent stream through a third (suppressor) column. The suppressor column reduces the perchlorate to its acid form ($HClO_4$) and also reduces the background conductivity of the eluent. The modified eluent stream then passes through a conductivity detector, whose signals are captured and maintained by a PC. Perchlorate is identified based on retention time and is quantitated using an external standard calibration method.

Aqueous samples and solid extracts must be screened for conductivity and must be diluted or pretreated as necessary prior to analysis.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving

this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the ability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the workorder file indicate that this review for precision, accuracy, and completeness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these methods to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Contaminants in the reagents, glassware, and/or other sample processing apparatus can produce method interferences that cause discrete artifacts or elevated baselines. These interferences can lead to false positive results or elevated detection limits as a consequence of elevated baseline noise.

4.2 Interferences can be divided into three different categories:

- ***direct chromatographic co-elution*** - where an analyte response is observed at very nearly the same retention time as the target anion;
- ***concentration dependent co-elution*** - observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion; and
- ***ionic character displacement*** - where retention times may significantly shift due to the influence of high ionic strength matrices (e.g., high mineral content or hardness), overloading the exchange sites in the column and significantly shortening the target analyte's retention time.

Direct Chromatographic Co-elution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection system, or by selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst MUST verify that these changes do not induce any negative affects on method performance by repeating and passing all associated quality control (see

Sections 8 and 17).

Some ***Concentration Dependent Co-elution or Ionic Character Displacement*** difficulties may resolve with sample dilution, however, sample dilution will proportionately elevate the analyte reporting limit. Therefore, careful consideration of project objectives should be given prior to performing dilutions. An alternative to sample dilution, may be dilution of the eluent (see Section 13).

4.3 Pretreatment cartridges (see Section 12) can be effective as a means of eliminating certain matrix interferences. With any proposed pretreatment, the analyst MUST verify that the target analyte is not affected by monitoring recovery after pretreatment via analysis of a Laboratory Fortified Matrix (LFM) (i.e., matrix spike) sample. It must also be ensured that no background contaminants are introduced by the pretreatment. This is accomplished by successful analysis of a Laboratory Reagent Blank (LRB) (i.e., method blank). With advances in analytical separator column technology that employ higher capacity anion exchange resins, the need for pretreatment cartridges has been greatly reduced.

4.4 Sample matrices with high concentrations of common anions such as chloride, sulfate and carbonate, can make the analysis problematic by destabilizing the baseline in the retention time window for perchlorate. This is evidenced by observing a protracted tailing following the initial elution of the more weakly retained anions (i.e., chloride, carbonate, and sulfate) that extends into the perchlorate retention time window. The concentrations of these common anions can be indirectly assessed by monitoring the conductivity of the matrix prior to analysis, and diluting or pretreating as necessary.

4.5 The analyst must use his/her professional experience to evaluate the potential for carry over peaks that may affect the detection of perchlorate in subsequent analyses. Chromatographic baselines, peak characteristics, etc. should be closely reviewed. Analyses yielding suspect results must be repeated. Rinse blanks may be added to the analytical sequence as necessary to control/correct carryover.

4.6 Field samples must be filtered through no larger than a 0.45µm nominal pore size membrane or frit to remove particulates and prevent damage to the analytical system. Syringe mounted, cartridge type, filters work well. Filters specifically designed for IC applications should be used.

5. APPARATUS AND MATERIALS

5.1 Dionex DX-120 ion chromatograph or equivalent, equipped with an autosampler, eluent pump and conductivity detector.

5.2 Dionex anion exchange guard (AG16) and analytical separator (AS16) columns, 4mm, or equivalent. Columns used must be rated as having low to very low

hydrophobicity. This requirement for low hydrophobicity allows the efficient, reproducible, and symmetrical band elution of polarizable anions, such as perchlorate. If the perchlorate analysis is attempted on a hydrophobic column -- such as those typically used for the analysis of common anions -- poor performance will result due to very asymmetric, tailing peaks. If the guard column is omitted from the system, the retention times will be shorter.

5.3 Anion MicroMembrane suppressor (AMMS III) column, 4mm, or equivalent. Must be capable of producing a stable baseline with no more than 5 nanosiemen (nS) noise/drift per minute of monitored response over the background conductivity.

NOTE: Proper suppressor performance is essential to analytical data reproducibility and sensitivity of the conductivity detector. If pretreated samples or sample matrices that contain appreciable concentrations of metals (e.g., Fe or Al) are frequently analyzed, cationic components may bind to the suppressor membrane and over time, affect suppressor performance. If the instrument begins to have problems with reduced peak response or asymmetrical perchlorate peaks, the suppressor membranes should be cleaned per manufacturer's instructions.

5.4 personal computer (PC) capable of running the Dionex *PeakNet* software, or equivalent

5.5 Dionex autosampler vials ("PolyVials"), or equivalent, 5mL, with filter caps

5.6 filter disks, 0.45µm, designed for IC use

5.7 insertion tool for the PolyVial filter caps

5.8 Eppendorf™ adjustable pipettor, or equivalent with tips

5.9 pasteur pipets, disposable

5.10 sample beakers, plastic, disposable, 50mL

5.11 centrifuge tubes, plastic, disposable, 50mL

5.12 volumetric flasks, various sizes, Class A

5.13 syringes, plastic, disposable, 10mL

5.14 conductivity meter, capable of measuring matrix conductance over a range of 1-10,000 µS/cm

5.15 analytical balance, capable of weighing to 0.0001g

5.16 centrifuge, table top model

5.17 magnetic stir plate, large

5.18 stir bar, Teflon-coated

5.19 water bath, capable of maintaining 25±2°C temperature

5.20 TCLP-type rotary tumbler

5.21 matrix pretreatment cartridges:

- Barium form - Dionex OnGuard-Ba cartridges, or equivalent. These cartridges are used to reduce matrix levels of sulfate.
- Silver form - Dionex OnGuard-Ag cartridges, or equivalent. These cartridges are used to reduce matrix levels of chloride.
- Hydrogen form - Dionex OnGuard-H cartridges, or equivalent. These cartridges used to reduce cations in the sample matrix. This protects the analytical column by removing silver that has leached from the Ag cartridge and may indirectly minimize the effect of carbonate by removing the cationic counter ion.

6. REAGENTS AND STANDARDS

6.1 Reagent Water: Deionized (DI) Water, 17.8MΩ or better, perchlorate-free and with particulates <0.20 microns.

6.2 Potassium Chloride (KCl) Standard Solution, 0.01N: Used to verify the performance of the conductivity meter. Made by dissolving 0.745g KCl in reagent water and diluting to a final volume of 1.00L in a Class A volumetric flask. On a properly functioning and calibrated conductivity meter, the reference conductance for this solution is 1410µS/cm at 25°C. Readings are acceptable within the range of 1380-1440µS/cm at 25°C). *Shelf Life = until deteriorates (i.e., until incapable of generating an acceptable reference reading).*

6.3 Helium (He) Compressed Gas, high purity grade or better; used to pressurize the eluent reservoir. Eluent is susceptible to carbonate contamination resulting from absorption of carbon dioxide (CO_2) from the atmosphere. Note that an ascarite trap can be placed in-line between the He tank and the eluent reservoir to further minimize possible CO_2 contamination.

6.4 Sodium Hydroxide (NaOH) Stock Solution, 50% NaOH (w/w): Used to create

the Sodium Hydroxide Eluent Solution. Purchase from a vendor. This reagent must be as free of carbonate as possible. *Shelf Life = until deteriorates (deterioration evidenced by increased perchlorate retention time and poor peak shape).*

Sodium Hydroxide (NaOH) Eluent Solution, 0.10M NaOH: Made in-house by the treatment and dilution of the commercially purchased 50% Sodium Hydroxide Stock Solution. A 4L polypropylene carboy (manufactured by Dionex) is used as a reservoir for the eluent. Prior to preparing fresh eluent, the reservoir must be emptied of all previous fluid and thoroughly rinsed with reagent water. After rinsing, a clean Teflon-coated magnetic stir bar is placed inside the carboy. The reservoir is then filled with 4L of reagent water and purged with Helium for 30-40 minutes to remove carbon dioxide (CO_2). After purging, about 15mL of 50% Sodium Hydroxide Stock Solution (allow NaOH to warm to room temperature) is quickly added to the vessel using a syringe. The reservoir is immediately capped tightly and placed on a magnetic stir plate. The eluent solution is agitated on the stir plate for 10-15 minutes to ensure complete mixing. *Shelf Life = until deteriorates (deterioration evidenced by increased perchlorate retention time and poor peak shape).* Note that this eluent is specific to the columns specified; alternative columns will likely have other eluent requirements.

NOTE: The retention time for perchlorate can change significantly when small amounts of CO_2 are absorbed by the Sodium Hydroxide Eluent Solution. Since CO_2 from the ambient atmosphere dissolves readily in solutions of NaOH, it is *critical* that every precaution be employed to minimize exposure of the solution to air.

It is recommended that two people work together as a team to prepare the eluent solution. When the container of 50% NaOH Stock Solution is uncapped, one person can direct a stream of Helium gas into the open container to minimize entry of CO_2, while the other person draws the solution up into the syringe. Then, one person can first remove and later replace the cap from the eluent reservoir, while the other person dispenses the 50% NaOH Stock Solution from the syringe into the purged reagent water in the reservoir.

According to Dionex, the 50% NaOH Stock Solution is more likely to be contaminated with carbonate at the surface of the solution and along the inside walls of the bottle. Therefore, it is helpful if the syringe used to draw and dispense the 50% NaOH Stock Solution is fitted with a long tip (i.e., like a hypodermic needle) so that the solution can be drawn out of the center of the bottle. Also, the long tip allows the 50% NaOH Stock Solution to be dispensed well below the surface of the purged water in the reservoir, thus avoiding contact with ambient air and minimizing potential CO_2 contamination.

Alternatively, use of a Dionex EG40, or equivalent, apparatus that automatically generates the hydroxide eluent is acceptable.

6.5 Sulfuric Acid (H_2SO_4) Solution, 50%: Made in-house by adding 500mL of concentrated sulfuric acid to reagent water and bringing to a final volume of 1L. *Shelf Life = no restrictions; make as needed (i.e., when solution volume is depleted).*

6.6 Sulfuric Acid (H_2SO_4) Solution, 5N: Made in-house by adding 278mL of 50% sulfuric acid solution to reagent water and bringing to a final volume of 1L. *Shelf Life = no restrictions; make as needed (i.e., when solution volume is depleted).*

6.7 Sulfuric Acid (H_2SO_4) Solution, 0.07N: Used to regenerate the AMMS III suppressor column. Made in-house by adding 29g 5N sulfuric acid solution to reagent water and bringing to a final volume of 3,600mL. *Shelf Life = no restrictions; make as needed (i.e., when solution volume is depleted).*

6.8 Perchlorate Stock Standard Solutions, 1000 mg (ClO_4^-)/L: Two stock solutions are required (i.e., "first source" and "second source"). At minimum, the lot numbers must vary. The stock solutions may be purchased as certified solutions or prepared by adding 0.1231g of ACS reagent grade perchlorate sodium salt ($NaClO_4$) to a 100mL volumetric flask and diluting to volume with reagent water. ***Note that Sodium perchlorate represents a molar weight fraction of 81.2% perchlorate anion.*** *Shelf Life = 1 year.*

NOTE: Per SOPs 300, all standards and spiking solutions must be properly documented, labeled and used within their expiration dates.

6.9 Perchlorate Intermediate Standard Solutions, 0.500mg (ClO_4^-)/L: Made each day of use by diluting 0.05mL of first source Perchlorate Stock Standard Solution to a final volume of 100mL using reagent water.

6.10 Mixed Common Anion Stock Solution, 20mg/mL each Cl^-, $SO_4^=$, $CO_3^=$: Made in-house by dissolving 4.0g sodium chloride (NaCl), 3.72g sodium sulfate ($NaSO_4$) and 4.4g sodium carbonate (Na_2CO_3) in a final volume of 100.0mL reagent water. *Shelf Life = 1 year.*

6.11 Instrument Performance Check (IPC) Solution: The IPC check solution is analyzed with each analytical batch to confirm instrument performance and the MCT. The IPC check solution is prepared to contain 25µg/L ClO_4^- and a concentration of common salts (sodium chloride, sodium sulfate and sodium carbonate) that results in a solution conductance near to (i.e., within ±10%) that specified as the MCT (see Section 8). The solution is prepared each day of use by diluting 0.25mL of the 0.500mg (ClO_4^-)/L first source Perchlorate Intermediate Standard Solution, and an appropriate aliquot (usually 0.1mL) of Mixed Common

Anion Stock Solution, to a final volume of 5.00mL using reagent water.

6.12 Intermediate Spiking Solution, 2.5mg (ClO_4^-)/L, first and second source: Pipet 0.25mL Perchlorate Stock Solution into a 100mL volumetric flask and bring to volume with reagent water. Made each day of use.

6.13 Perchlorate Calibration Standard Solutions, suite of 5 solutions, 0.004-0.100mg (ClO_4^-)/L: Made each day of use by diluting aliquots of the first source Perchlorate Intermediate Standard Solution with reagent water to create a range of standards spanning the IC's calibrated linear range (used for initial calibration). See Table below:

Perchlorate Calibration Standards

Calibration Standard Name	Amount of 1st Source 500µg/L Perchlorate Intermediate Standard Solution Used	Final Volume of Calibration Standard Prepared
100µg/L (level 6; 5X)	1.00mL	5.00mL
75µg/L (level 5; 6.66X)	0.75mL	5.00mL
50µg/L (level 4; 10X)	0.50mL	5.00mL
25µg/L (level 3; 20X)	0.25mL	5.00mL
10µg/L (level 2; 50X)	0.10mL	5.00mL
4µg/L (level 1; 100X)	0.04mL	5.00mL

6.14 Quality Control Sample (QCS), also referred to as the Initial Calibration Verification (ICV) Standard: Made from the ***second*** source 2.5mg (ClO_4^-)/L perchlorate Intermediate Spiking Solution, at a concentration near to the midpoint of the calibration curve. A 0.10mL aliquot of second source perchlorate intermediate standard solution is brought to a 5.00mL final volume using reagent water. *Shelf Life = made daily.*

6.15 Continuing Calibration Check Standard (CCCS): Made daily by bringing a 0.25mL aliquot of the first source 0.500mg (ClO_4^-)/L Perchlorate Intermediate Standard Solution to a 5.00mL final volume using reagent water.

6.16 Initial Calibration Check Standard (ICCS): Made daily, at a concentration matching the lowest point of the calibration curve. Bring a 0.04mL aliquot of the first source 0.500mg (ClO_4^-)/L Perchlorate Intermediate Standard Solution to a 5.00mL final volume using reagent water.

6.17 Laboratory Fortified Blank (LFB) or Laboratory Control Sample (LCS): Made daily by bringing a 0.05mL aliquot of the ***second*** source 2.5mg (ClO_4^-)/L perchlorate Intermediate Spiking Solution to a 5.00mL final volume using reagent water.

6.18 Laboratory Fortified Matrix (LFM) or Matrix Spike (MS) Sample: Made daily by

replacing 0.05mL of selected sample with 0.05mL of first source 2.5mg (ClO_4^-)/L Intermediate Spiking Solution (final volume 5.00mL). For solids extracts, multiply spike volumes by 8 for a 40mL final volume.

NOTE: One duplicate (i.e., field, laboratory, or spiked) must also be prepared per each batch of similarly prepared samples. It is Paragon's general policy to prepare the MS in duplicate (duplicate sample referred to as the MSD).

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 All samples should be collected according to an approved sampling plan. Samples may be collected in plastic or glass bottles. All bottles must be purchased pre-cleaned or thoroughly cleaned and rinsed with reagent water. The volume of sample collected should be sufficient to ensure a representative sample, allow for replicate and laboratory fortified matrix analyses, and to minimize waste disposal.

7.2 No chemical preservation is required.

7.3 Samples do not need to be shipped iced or stored cold in a refrigerator but every effort should be taken to protect the samples from temperature extremes. A thermally insulated sampling kit, designed to fit sampling bottles securely during shipment, may be used to protect the samples from these temperature extremes.

7.4 The maximum allowable holding time until analysis for perchlorate is 28 days from collection. Perchlorate has been shown to be stable for more than 28 days but extended holding time studies (beyond 35 days) were not conducted by EPA. Typically, when analytes are believed to be stable, a 28 day holding time is established as a sufficient time period to permit a laboratory to conduct the analysis.

8. PRELIMINARY CONSIDERATIONS

8.1 DETERMINATION OF THE MATRIX CONDUCTIVITY THRESHOLD (MCT) The conductivity of an aqueous/solid extract matrix is related to the amount of common salts present in the matrix. Salts contribute to and are measured as Total Dissolved Solids (TDS).

The anions contained in common salts can interfere with the chromatographic separation of ClO_4^- when their concentration in a sample is too high. Since conductivity is an index of salt content, samples can be screened prior to analysis for ClO_4^- by measuring the sample conductance. The Matrix Conductivity Threshold (MCT) is the maximum allowable conductance of a sample that is measurable by the ion chromatograph without requiring dilution or pretreatment. The MCT is used to evaluate the results of sample conductivity screening, it is the

value above which samples must be diluted or pretreated prior to analysis. The MCT can be established at the conductance level of the highest Mixed Common Anion Stock Solution (see Section 6) which can be successfully analyzed and quantitated, or can be determined by calculation and regression analysis based upon the data generated by analyzing a series of sequentially increasing common anion-fortified reagent water samples, each of which also contains a constant concentration of perchlorate. Because the MCT is dependent on the conditions, hardware, and state of the analytical system employed, it is not method defined and must therefore be determined by the individual analytical laboratory during the Initial Demonstration of Capability (IDC). The MCT is confirmed with each analysis batch by analyzing an Instrument Performance Check (IPC) Solution (see Section 6). Paragon's IPC check solution performance consistently confirms the MCT in the range of 3,500-4,000µmhos/cm.

8.2 METHOD DETECTION LIMIT (MDL) STUDY

The MDL is the minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. Details for conducting an MDL study are provided in the cited EPA Methods. An MDL study MUST be performed as a component of the Initial Demonstration of Capability (IDC) and whenever there is a significant change in the background, or instrument response. It is Paragon's policy to, at minimum, verify MDLs annually.

8.3 MINIMUM REPORTING LEVEL (MRL), ALSO REFERRED TO AS THE ANALYTE REPORTING LIMIT

The MRL/analyte reporting limit is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should be established at an analyte concentration either greater than three times the MDL or at a concentration which would yield a response greater than a signal to noise ratio of five. Setting the MRL too low may cause repeated quality control (QC) failure upon analysis of the ICCS. **Although the lowest calibration standard may be below the MRL, the MRL must never be established at a concentration lower than the lowest calibration standard and can only be used if quality control criteria for this standard are met.**

8.4 The Initial Demonstration of Capability (IDC) is performed after an acceptable initial calibration of the IC has been achieved. The IDC is used to characterize instrument and laboratory performance prior to performing field sample analyses by this method. Additionally, each analyst must also perform a one-time IDC prior to the analysis of client samples to assure/demonstrate method proficiency. The IDC study includes the following components:

- an initial demonstration of low system background; accomplished by the successful analysis of Laboratory Reagent Blanks (LRBs); no

contamination can be noted above ½ the MRL/analyte reporting limit.

- an initial demonstration of accuracy (IDA); accomplished by the successful analysis of a replicate series of Laboratory Fortified Blanks (LFBs; also referred to as laboratory control samples, LCSs); percent recovery must be ±15% of the true value.
- an initial demonstration of Precision (IDP); calculated %RSD of the above replicate analyses must be <10%.

Details regarding the conduct of an IDC study are provided in the cited EPA Methods.

9. SYSTEM START-UP AND SHUT-DOWN

9.1 In order to keep the NaOH eluent pressurized, the He gas tank should always be left on with the regulator set to deliver between 3-5psi.

9.2 Power on the IC by depressing the white button on the front of the instrument.

9.3 From the "**MAIN MENU**" window in *PeakNet*, click on the "**PEAKNET RUN**" icon. In the PeakNet Run window, select the "Direct Control" icon. In the Direct Control window, click to start the pump and eluent pressure. The eluent flow rate should be set at 1.00mL/min. Turn off from the Direct Control window. Alternately the pump and eluent pressure can be turned on or off by pressing Local/Remote on front panel to highlight Local and manually pressing pump, eluent pressure.

9.4 Allow the pressure to stabilize for about 30 minutes before starting an analytical sequence.

9.5 Turn off the power (white button on main instrument panel). **Do NOT turn off the He gas tank valve.**

10. SEQUENCE SET-UP

10.1 Analytical sequences are set-up using the *PeakNet* software. A new "**SCHEDULE**" is created for each day. Typically this schedule is renamed from the previous day's schedule and then edited to create the new schedule.

10.2 Each day's data are stored in a new subdirectory named for the day, using a yymmdd format (e.g., 050214, denoting February 14, 2005).

10.3 A *PeakNet* "method" is created each time a calibration is performed. The method is a subprogram that controls the events that take place throughout the analytical sequence (e.g., trigger autosampler, operate injection valve, start and end data acquisition, etc.) The method also contains the integration parameters that are used in processing the raw data, including a Table with the calibration curves and

retention time windows for each analyte. The retention time Table can be updated daily, if necessary, based on the first CCV analyzed or each time a new calibration is established.

11. INITIAL CALIBRATION

11.1 Prepare the calibration standards as prescribed in Section 6.

11.2 To setup the autosampler, prepare aliquots of standards, pre-filtered sample or extracts in 5mL Dionex vials; dilute as necessary. Place filter caps half way down on vials and vortex. Use insertion tool to push cap down fully on vials. Load vials into cassettes for the autosampler.

11.3 Analyze 1.00mL of each calibration standard. Note that the entire 5mL aliquot is drawn into the instrument, however, a 1.00mL sample loop is used for analysis.

NOTE: With the equipment designated in this SOP at the settings indicated, perchlorate should elute between 12-15 minutes.

11.4 Generate the calibration curve by tabulating peak area responses against the perchlorate concentration. Note that peak areas must be used as a measure of response since they have been found to be more consistent, in terms of quantitation, than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix that can compete for exchange sites leading to peak broadening. Using peak areas, it is the analyst's responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks, since poorly drawn baselines will significantly influence peak areas.

Paragon uses a second order quadratic fit to create the perchlorate calibration curve. Paragon typically employs six data points to establish the curve. The coefficient of determination (r^2) for the calibration curve equation must be ≥ 0.990.

11.5 Analyze a Quality Control Sample (QCS)/Initial Calibration Verification (ICV) Standard. To be acceptable, the QCS/ICV must yield results within ±10% of the true value. If this criterion is not met, identify and correct the problem, recalibrate the system and analyze an acceptable QCS/ICV.

11.6 Establish the perchlorate retention time window (RTW). The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards measured over the course of a day. Three times the standard deviation of retention time may be used as a suggested window size, but the retention time window should not extend beyond ±5% of the retention time for perchlorate. The experience of the analyst should weigh heavily in the interpretation of these chromatograms.

12. SAMPLE PREPARATION

12.1 EXTRACTION OF SOLID SAMPLES

12.1.1 Weigh 4.0g of sample into a 50mL polypropylene centrifuge tube. Add 40mL DI water.

12.1.2 Mix the suspension thoroughly and tumble using a rotary tumbler (TCLP-type) for about 60 minutes.

12.1.3 Centrifuge the resulting slurry for about 15 minutes.

12.1.4 Filter the supernatant as necessary using a 0.45µm filter disk.

12.1.5 The terminology for the supernatant will be treated the same as a water sample matrix throughout this SOP. Follow the same screening and preparation procedures described in the Sections above.

12.1.6 Analyze as described in Section 13 below.

12.2 CONDUCTIVITY SCREENING

The electrical conductivity of the aqueous/solid extract solutions are directly related to the concentration of dissolved salts in the sample.

12.2.1 CONDUCTIVITY METER CALIBRATION VERIFICATION

Periodically verify the performance of the conductivity meter as follows:

- Thoroughly rinse the conductivity electrode with reagent water. Place the electrode in the reagent water, turn on the meter and confirm the conductance of this reagent water blank at <1 µS/cm.
- Pour approximately 15mL Standard KCl Solution (see Section 6) into a small plastic disposable beaker and place the electrode into the solution.

The reference conductance for this solution is 1410µS/cm at 25°C. The conductivity meter must yield a conductance between 1380µS/cm and 1440µS/cm to be in calibration. Record reading in logbook (Form 1116).

If the conductivity meter fails calibration, recalibrate the unit per manufacturer's instruction and repeat the Steps above.

12.2.2 SAMPLE SCREENING

Prior to conducting any field sample analysis, the conductivity of that matrix must be determined. When the conductance of a field sample is

above the MCT (defined in Section 8), sample dilution or pretreatment must be performed in order to protect the instrument and to provide for sample analysis within the instrument's calibrated analytical range. Visual appearance of the sample, historical data or additional information provided by the client may provide information for determining the extent of dilution or if sample pretreatment is needed.

NOTE: Samples do not need to be refrigerated, but if samples are held chilled as standard practice for sample control, ensure that the samples have come to room temperature before performing sample preparation or analysis.

- Pipet approximately 15mL of sample into a small disposable plastic beaker. Reseal the sample bottle to protect the sample integrity.

NOTE: **Do not shake or mix the sample before acquiring the sample aliquot.**

- Place the electrode into the sample and measure the conductivity. Record in logbook (Form 1116).

- Discard the used sample aliquot. Rinse the electrode thoroughly with reagent water between each matrix conductivity measurement. Refer to the following Sections if sample dilution or pretreatment is required based on the conductivity screening results.

- Test the conductivity of an aliquot of IPC solution. Record in the dedicated conductivity laboratory logbook (Form 1116).

12.3 PREPARATION OF SAMPLES WITH MATRIX CONDUCTIVITY ABOVE THE MCT

12.3.1 MATRIX DILUTION

Reagent water can be used to dilute an aliquot of sample to bring the sample's conductivity within the MCT (defined in Section 8). Because the dilution factor will proportionately elevate the sample's analyte reporting limit, it is necessary to evaluate whether or not the elevated analyte reporting limit meets client data quality objectives (DQOs) should perchlorate not be detected upon dilution. Sample pretreatment (described in a subsequent Section below) can be used as an alternative to sample dilution. The sample pretreatment technique does not introduce any factor that requires the analyte reporting limit to be elevated proportionately.

- If the conductivity of the matrix (measured in the sample screening

step above) exceeds the MCT, estimate the dilution required by dividing the measured matrix conductance by the MCT; round up as necessary. Example: For a sample with a matrix conductivity of 12,000 and with an MCT of 3,500, the necessary dilution would be 4X.

- Dilute two sample aliquots accordingly to create a 15mL sample analysis volume. Record the dilution factor required in the dedicated conductivity laboratory logbook (Form 1116).

NOTE: The recorded dilution information is hand-entered into the *PeakNet* sample analysis sequence set-up so that the sample's dilution factor can be incorporated in the automated calculation of perchlorate following analysis.

- Measure the conductance of one of the diluted sample aliquots to confirm that the matrix conductance is now below the MCT. Discard this aliquot and filter and analyze the other prepared aliquot.

Remember that if perchlorate is not detected above the elevated analyte reporting limit and the elevated analyte reporting limit does not meet the client's DQOs, sample pretreatment techniques should be employed.

12.3.2 PRETREATMENT

Pretreatment is accomplished using a series of three types of cartridges arranged in a specific order. The barium cartridge is used to reduce matrix levels of sulfate. The silver cartridge is used to reduce matrix levels of chloride. The hydrogen cartridge is used to remove silver that may have leached from the silver cartridge, and may also have an indirect effect by removing carbonate. ***Note that these pretreatments will not effectively reduce matrix concentrations of other anions such as nitrate or phosphate.***

NOTE: Extreme caution should be exercised in using pretreatment cartridges. Artifacts that can foul the guard and analytical columns are known to leach from certain cartridges, causing loss of column capacity (indicated by shortened retention times and irreproducible results).

Sample matrix pretreatment may be used as standard practice to assist in the quantitation of low levels of perchlorate or to prolong IC column life.

The procedure for use of the pretreatment cartridges is described below:

- Individually and thoroughly rinse each pretreatment cartridge with reagent water in order to ensure that all residual background contaminants are removed from the cartridge. Perform this rinse per manufacturer's instructions.

  Where pretreatment cartridges are used, the LRB/laboratory method blank, LFB/laboratory control sample, and LFM/matrix spike sample and duplicate must also be passed through the pretreatment cartridges. The LRB/laboratory method blank should be prepared and analyzed ***before*** processing any client samples to determine if any artifacts are introduced by the cartridges. If artifacts are noted at a concentration greater than ½ the MRL/analyte reporting limit, triple or quadruple the volume of reagent water rinse suggested by the manufacturer and repeat until an acceptable blank is generated. ***If additional rinsing is required, it must be consistently applied to all the cartridges prior to conducting any matrix pretreatment.***

- Attach the three prepared cartridges in the following order: Barium (Ba), Silver (Ag) and Hydrogen (H). *It is recommended that all three cartridges be employed unless the analyst has specific knowledge that a matrix primarily has high levels of a specific common anion.*

- Filter 3mL of field or QC sample through the series of rinsed, stacked cartridges to condition/rinse the cartridges. Use a plastic syringe to push the fluid through at a flow rate of 1.0mL/min or less (approximately one drop every 3 to 4 seconds). ***This flow rate is critical to the pretreatment and must be carefully followed.***

- Discard the conditioning/rinse fraction and begin collecting the aliquot of field or QC sample.

- When sufficient sample volume has been collected (e.g., 15mL), measure the conductance of the pretreated aliquot being certain that the conductivity meter's probe has been thoroughly rinsed with reagent water and excess water has been shaken from the tip.

If the matrix conductivity is below the MCT, discard the measured

aliquot and collect more pretreated field or QC sample for analysis.

If the matrix conductivity is still above the MCT, the flow rate through the pretreatment cartridge is likely too fast and the pretreatment should be repeated with new cartridges.

In some instances, double pretreatment cartridges (Ba, Ba, Ag, Ag, H, H) may need to be applied.

- Note total volume of reagent water rinse employed (Step 1) and the number and types of pretreatment cartridges used on the laboratory benchsheet.
- Appropriately filter and place an aliquot of pretreated field or QC sample (matrix conductivity below MCT) into an autosampler vial.
- Analyze as described in Section 13.

12.4 PREPARATION FOR MATRICES WHICH DO NOT EXCEED THE MCT

12.4.1 Pour an aliquot of field sample into a small plastic beaker. Reseal the sample bottle to protect the sample's integrity.

12.4.2 Using a Luer-lock, plastic 10mL syringe, withdraw approximately 10mL of sample from the beaker and attach a clean 0.45µm particulate filter directly to the syringe.

12.4.3 Filter the sample into an autosampler vial.

NOTE: If the autosampler vials or vial caps are designed to automatically filter the sample matrix as the sample is loaded on the IC system, this filtration procedure can be omitted and the sample can be directly transferred to the autosampler vial.

12.4.4 Prepare and load the necessary QC samples into the autosampler.

12.4.5 Analyze as described in Section 13 below.

13. SAMPLE ANALYSIS

A sample analysis sequence may be initiated once a successful calibration and verification (see Section 11) has been achieved.

13.1 Analyze an ICCS (see Section 6). The ICCS is a standard analyzed at a concentration equal to the lowest standard of the calibration suite. To be acceptable, percent recovery (%R) for this standard must be ±25%. If this

criterion is not met, re-prepare and analyze the ICCS. If the ICCS still fails, the system must be recalibrated.

13.2 The IPC Solution sample must be analyzed first in the sequence. ***All quality control criteria for this analysis (see Section 17) must be met before sample analyses can proceed.***

13.3 Analyze the laboratory fortified blank (LFB), also referred to as the laboratory control sample (LCS). The %R acceptance limits are ±15% (aqueous) and current laboratory-derived limits (soils).

13.4 Analyze the laboratory reagent water blank (LRB), also referred to as the laboratory method blank (MB). The concentration of target analyte in the blank must be < the analyte RL. Note that if reporting data for regulatory purposes, the target analyte cannot be present at levels greater than ½ the RL (Method 314.0) or must be free of contamination <MDL (Method SW9058). If a blank is not acceptable, the source of the contamination must be determined and resolved prior to conducting any sample analysis.

13.5 Up to 10 field samples plus the laboratory fortified matrix (LFM)/matrix spike sample and duplicate (see Section 17) can be analyzed. Note that the QC samples are not included as part of the 10 sample analysis allotment.

NOTE: One Laboratory Fortified Blank (LFB)/Laboratory Control Sample (LCS), one duplicate, one Laboratory Fortified Matrix (LFM)/Matrix Spike (MS) Sample and one Laboratory Reagent Blank (LRB)/Laboratory Method Blank (MB) are prepared with each batch of similarly prepared samples. These QC samples may or may not be pretreated contingent upon whether or not the associated samples were pretreated. Because of LIMS (Paragon's in-house Laboratory Information Management System) restrictions, in instances where an analysis batch contains *both* not pretreated and pretreated samples, the pretreated QC samples are analyzed as representing the most rigorously treated samples and therefore representative of the entire mixed sample batch.

13.6 Analyze a CCCS (also referred to as a continuing calibration verification, CCV, standard). To be acceptable, the CCCS must yield results within +15% (i.e., between 85-115%) of the known value. If the CCCS fails the acceptance criteria, the source of the problem must be identified and resolved before continuing analyses. All samples analyzed since the last acceptable CCCS must be reanalyzed.

Up to 10 field samples and QC samples can be analyzed between CCCS analyses.

13.7 Compile the peak response information for the analyzed samples. If the response of a sample analyte exceeds the calibration range, the sample must be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible, then three new calibration concentrations must be employed to create a separate high concentration calibration curve, one standard near the estimated sample concentration and the other two bracketing an interval equivalent to approximately ±25% around the estimated sample concentration. ***Important! The response generated by these three new high concentration calibration standards must not exceed the upper linear range for the conductivity detector.***

13.8 Should more complete resolution be needed between perchlorate and a co-eluting shoulder peak, the eluent may be diluted. This will spread out the peaks, causing later elution of perchlorate. Analysts are advised to carefully evaluate use of eluent dilution since other coelutions may be encountered which were not initially evident when these eluent changes are incorporated. ***Additionally, the analyst must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Sections 8 and 17, and by re-establishing a valid initial calibration curve (Section 11). Additionally, note that eluent dilution adversely effects the MDLs for each analyte.***

14. DATA ACQUISITION AND PROCESSING

14.1 Data acquisition begins by clicking on the "**START**" icon in the "**PEAKNET RUN**" window. Usually a new injection is made every 20 minutes or less. Each chromatogram is stored in a separate file. Filenames are automatically given to each chromatogram based on information that is entered when the sequence is created (i.e., a filename prefix, and a value for the counter). The filename prefix is the date of acquisition, and the counter is set to increment by one for each injection (e.g., 02140005 designates the 5th injection made on February 14th).

14.2 Data processing (peak identification, integration, quantitation) is performed after the chromatograms have been acquired. Identify perchlorate in the sample chromatogram by comparing the retention time of the suspect peak to the established RTW. If the perchlorate retention time has slightly shifted (generally towards shorter times) since the initial calibration, but is still within acceptance criteria and are reproducible during the analysis batch, the analyst should use the retention time in the daily calibration check standards to confirm the presence or absence of perchlorate anion.

14.3 ***It is important to review the integration to ensure that baselines are drawn correctly.*** In cases where it is necessary to modify a baseline, the raw data must include printouts of the chromatogram before and after the baseline correction (refer to SOP 939 for further directives).

14.4 Compute sample concentration using the initial calibration curve generated in

Section 11. Only values that fall between the lowest and highest calibration standards are reported. Samples yielding results that exceed the highest standard should be diluted and reanalyzed. When this is not possible, the alternate calibration procedure described in Section 13 must be followed.

14.5 Report results in µg/L units.

15. RUN LOG

A record of each day's analyses is entered into the instrument run logbook. This can be accomplished by taping a printout from the *PeakNet* program into a hardbound laboratory notebook. The following information is recorded:

- Date of analysis
- Analyst's initials
- Solution ID (including any dilutions)
- Filename
- Schedule ID

16. MAINTENANCE AND TROUBLESHOOTING

A maintenance logbook is used to record all information concerning instrument maintenance. The logbook documents all repairs and symptoms of problems.

16.1 The fritted disks (sometimes called "bed supports") at the ends of the guard and analytical columns and inside the in-line filter case should be changed periodically. The system backpressure will gradually increase over time as the fritted disks become clogged with small particles.

16.2 Small peaks may be observed in the blanks in the perchlorate RTW after analyzing samples high in dissolved salts. This carryover can be addressed by either:

- Setting up the autosampler to pass an aliquot of reagent water through the sample loop between injections.

  To accomplish this, place a vial of reagent water between each vial containing sample or standard in the autosampler. The autosampler recognizes the added vial as a "rinse vial" because the filter cap is pushed down to the first position using the special insertion tool.

- Cleaning the sample loop and the tubing that carries the sample solution from the autosampler to the IC with 0.1N HCl using a syringe with a Luer-lock connector. ***All traces of HCl must be removed from the system by rinsing the line thoroughly with reagent water before analyzing samples.***

17. QUALITY CONTROL (QC)

17.1 ANALYSIS BATCH

An analysis batch is defined as a sequence of no more than 20 field samples or extracts thereof and the following required QC samples:

- Instrument Performance Check Standard (IPC)
- Laboratory Reagent Blank (LRB), also known as the laboratory method blank (MB). If pretreatment cartridges were used to process samples in the batch, a pretreatment LRB/MB must also be analyzed.
- Initial Calibration Check Standard (ICCS)
- Laboratory Fortified Blank (LFB), also known as the laboratory control sample (LCS). If pretreatment cartridges were used to process samples in the batch, a pretreatment LFB/LCS must also be analyzed.
- Continuing Calibration Check Standard (CCCS), when the batch contains more than 10 field samples, also known as the continuing calibration verification (CCV) standard. The CCCS run at the end of an analytical sequence after all samples have been analyzed is known as the End Calibration Check Standard (ECCS).
- Laboratory Fortified Matrix (LFM), also known as the matrix spike (MS) sample. If pretreatment cartridges were used to process samples in the batch, a pretreatment LFM/MS sample must also be analyzed.
- Either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM. Usually a duplicate of the LFM is analyzed and is referred to as the matrix spike duplicate (MSD) sample.

Additional batches may be added sequentially on to the end of the sample analysis sequence as long as all QC samples that define an individual batch (i.e., IPC, LRB, ICCS, LFB, LFM and duplicate) are individually reanalyzed with each successive serial batch and the QC criteria for these analyses are continually met.

NOTE: One LFB/LCS, one LFM/MS and duplicate, and one LRB/MB are prepared with each batch of similarly prepared samples. These QC samples may or may not be pretreated contingent upon whether or not the associated samples were pretreated. Because of LIMS restrictions (LIMS only permits unique sample references), in instances where an analysis batch contains *both* not pretreated and pretreated samples, the pretreated QC samples are analyzed as representing the most rigorously treated samples and therefore representative of the entire mixed sample batch.

17.2 INSTRUMENT PERFORMANCE CHECK (IPC) SOLUTION

The IPC solution (see Section 6) contains a specific concentration of perchlorate and other test substances (namely chloride, sulfate and carbonate) used to evaluate the performance of the analytical system with respect to a defined set of criteria. An IPC is analyzed with each sample analysis batch to verify the MCT (MCT defined in Section 8).

To be acceptable, the IPC solution must meet ***all*** of the following criteria:

- the conductance must be within ±10% of the initial value.
- the resultant peak area/height ratio must not exceed 25%D when compared to the area/height ration of the LCS.
- the recovered perchlorate must be ±20% of the true value.
- the perchlorate retention time cannot shift more than 5%.

If any of the above conditions are not met, reanalyze the IPC. If quality criteria are still not met, the MCT (see Section 8) must be repeated and revised to a more appropriate lower matrix conductivity threshold or the source of the problem must be determined and corrected and the IPC reanalyzed. A new IDC must also be performed.

17.3 BLANKS

Blanks are run to demonstrate that interferences from the laboratory environment, analytical system, reagents and glassware are under control. A Laboratory Reagent Blank (LRB), also referred to as a laboratory method blank (MB), is an aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, reagents and equipment. The concentration of target analyte in the blank must be < the analyte RL. Note that if reporting data for regulatory purposes, the target analyte cannot be present at levels greater than ½ the RL (Method 314.0) or must be free of contamination <MDL (Method SW9058). If a blank is not acceptable, the source of the contamination must be determined and resolved prior to conducting any sample analysis. Any samples analyzed prior to the noncompliant blank must be reanalyzed.

17.4 INITIAL CALIBRATION CHECK SAMPLE (ICCS)

The ICCS is a standard analyzed at a concentration equal to the lowest standard of the calibration suite. It is analyzed prior to any field samples to verify the previously established calibration curve and to verify the ability to quantitate perchlorate at the MRL. To be acceptable, percent recovery (%R) for this standard must be ±25%. If this criterion is not met, re-prepare and analyze the ICCS. If the ICCS still fails, the system must be recalibrated.

17.5 LABORATORY FORTIFIED BLANK (LFB)/LABORATORY CONTROL SAMPLE (LCS)

The LFB/LCS is an aliquot of reagent water to which a known quantity of perchlorate is added. The LFB/LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

The LFB/LCS is analyzed immediately following the ICCS. By analyzing the LFB/LCS initially, a control check is performed on the concentrated solution used to prepare the LFM/MS. If any deviations in the perchlorate concentration are present, it will be reflected in the LFB/LCS and not exclusively attributed to a matrix upon analysis of the LFM/MS.

Percent Recovery (%R) for the LFB/LCS is calculated as shown below:

$$\%R = \frac{Concentration_{Found}}{Concentration_{Expected}} \times 100$$

where:

$Conc_{Found}$ = actual analyte concentration found in the LFB/LCS
$Conc_{Expected}$ = anticipated/known concentration of the LFB/LCS (based on the amount spiked)

The recovery for perchlorate must fall in the range of 85-115% (aqueous), within laboratory-derived limits (soils). An acceptable LFB/LCS must be achieved before field samples can be analyzed. If the LFB/LCS recovery does not meet the recovery criterion, the source of the problem must be identified and resolved before analyses can proceed.

17.6 CONTINUING CALIBRATION CHECK SAMPLE (CCCS)/CONTINUING CALIBRATION VERIFICATION (CCV) STANDARD

The CCCS/CCV is a first source mid-level calibration standard analyzed bracketing each set of 10 field sample analyses to verify the continuing validity of the previous calibration. To be acceptable, the CCCS/CCV must yield results within $\pm$15% of the known value. If the CCCS/CCV fails the acceptance criteria, the source of the problem must be identified and resolved before continuing analyses. All samples analyzed since the last acceptable CCCS/CCV must be reanalyzed.

17.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFM)/MATRIX SPIKE (MS)

The LFM/MS is an aliquot of an environmental field sample to which a known quantity of perchlorate is added. The LFM/MS is analyzed exactly like a sample,

and its purpose (when compared to the LFB/LCS results) is to determine whether the sample matrix contributes bias to the analytical result. LFM/MS samples that exceed the calibration range must be diluted for analysis.

The background concentration of perchlorate present in the native sample matrix must be initially determined by analysis of a separate sample aliquot, and the measured value of the spiked LFM/MS is corrected for this background concentration as follows:

$$\%R = \frac{Concentration_{Spike} - Concentration_{Native}}{Concentration_{Expected}} \times 100$$

where:

$Conc_{Spike}$ = analyte concentration found in the LFM/MS
$Conc_{Native}$ = analyte concentration found in the unspiked native sample
$Conc_{Expected}$ = anticipated/known concentration of the LFM/MS (based on the amount spiked)

If the perchlorate percent recovery falls outside the acceptance range of ±20%, check freshness of the spiking standard, spike preparation, and calculations. Narrate if sample matrix interference is suspected.

To be valid, the concentration of the spike added must be equal to or greater than the concentration present in the native sample. In the event that the fortified level is less than the observed level of the native matrix, the recovery should not be calculated.

17.8 DUPLICATES

Field Duplicates (FDs) are two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Field duplicate samples may or may not be provided by the client. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

Laboratory Duplicates (LDs) are two sample aliquots (LD_1 and LD_2), taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD_1 and LD_2 indicate precision associated specifically with the laboratory procedures by removing variation contributed from sample collection, preservation and storage procedures.

In short, duplicates are analyzed as a measure of the precision of the analytical results generated. The laboratory must analyze some type of duplicate for a minimum of 5% of the collected field samples, or at least one with every analysis

batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and ensure the quality of the data. Without prior knowledge or strong suspicion that an unknown sample has measurable perchlorate concentration, the best alternative is to analyze a duplicate LFM/MS. It is Paragon's policy to analyze the LFM/MS in duplicate; this sample is referred to as the Matrix Spike Duplicate (MSD).

The precision between the duplicate analyses is expressed as Relative Percent Difference (RPD), calculated as follows:

$$RPD\ (\%) = \frac{|Result_1 - Result_2|}{\frac{1}{2}(Result_1 - Result_2)} \times 100$$

where:

$Result_1$ = analyte concentration found in the initial analysis
$Result_2$ = analyte concentration found in the duplicate analysis

For this procedure, the RPD between duplicates should not exceed 15%. If the RPD criteria are not met, check freshness of the spiking standard, spike preparation, and calculations. Narrate if sample matrix interference is suspected.

17.9 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study consists of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the Minimum Reporting Limit (MRL) for the analyte. The MDL study is performed in conjunction with the IDC (see Section 8) and should be performed as needed and at a minimum, annually.

18. DEVIATIONS FROM METHOD

18.1 Section 9.4.1.2 of Method EPA 314.0 suggests that concentrations of the LFM/MS "should be varied to reflect the range of concentrations expected in field samples". Paragon prepares a spiking solution of unvaried concentration, as expected concentrations of client field samples are not known.

18.2 Section 10.3.2 of Method EPA 314.0 states, "If more than 10 field samples are included in an analysis batch, the analyst must alternate between the middle and high continuing calibration check standard levels." Paragon consistently analyzes a CCCS/CCV that falls between the mid and high calibration standard levels.

18.3 Method EPA 314.0 makes one mention of a "well mixed sample" (Section 11.1.5). Based on the belief that the dissolved anions exist in equilibrium in a sample solution, Paragon does not mix or shake the field sample prior to preparation and

analysis. Particulate interferences are allowed to settle before a sample aliquot is obtained. Furthermore, the sample aliquot is centrifuged or filtered to further minimize the effects of particulates.

18.4 The note following Section 7.5 and Section 8.2 of Method SW9058 recommends that both samples and standards be stored at 4±2 °C. Method EPA 314.0 specifically states that refrigeration is not required. Paragon refrigerates field samples as standard practice. Text in this SOP discusses the need for samples and standards to be at room temperature prior to use.

18.5 One Laboratory Fortified Blank (LFB)/Laboratory Control Sample (LCS), one Laboratory Fortified Matrix (LFM)/Matrix Spike (MS) Sample and duplicate, and one Laboratory Reagent Blank (LRB)/Laboratory Method Blank (MB) are prepared with each batch of similarly prepared samples. These QC samples may or may not be pretreated contingent upon whether or not the associated samples were pretreated. Because of LIMS restrictions (LIMS only permits unique sample references), in instances where an analysis batch contains both not pretreated and pretreated samples, the pretreated QC samples are analyzed as representing the most rigorously treated samples and therefore representative of the entire mixed sample batch.

19. SAFETY, HAZARDS AND WASTE DISPOSAL

19.1 SAFETY AND HAZARDS

19.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

19.1.2 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

19.1.3 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

19.1.4 Sodium Hydroxide (NaOH), used in the preparation of the eluent is considered caustic.

19.1.5 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

19.1.6 All flammable compounds must be kept away from ignition sources.

19.1.7 Wear gloves, safety glasses, and a lab coat when working with any

chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

19.1.8 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

19.1.9 Food and drink are prohibited in all lab areas.

19.2 WASTE DISPOSAL

19.2.1 Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

19.2.2 The eluent waste shall be disposed of in the Aqueous Laboratory Waste satellite collection vessel, otherwise known as the CLE Waste Stream.

19.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

19.2.4 Certain clients may require that the samples and residues from their analyses be returned. The Waste Compliance Officer will address these samples.

20. REFERENCES

20.1 USEPA Method 314.0, "Determination of Perchlorate in Drinking Water Using Ion Chromatography", Revision 1.0. National Exposure Research Laboratory (NERL); Office of Research and Development (ORD); United States Environmental Protection Agency (USEPA), Cincinnati, OH. Hautman, Daniel P. and David J. Munch, USEPA Office of Ground Water and Drinking Water, Andrew D. Eaton and Ali W. Haghani, Montgomery Watson Laboratories. November 1999.

20.2 USEPA SW-846, Method 9058, "Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection", Revision 0, November 2000.

DOCUMENT REVISION HISTORY

4/10/06: Added reference Program Specification directive in "Responsibilities". Added clarification and detail regarding equipment operation. Added DOCUMENT REVISION HISTORY.

Analytical Method: EPA 314.0; SW9058	**Parameter:** Determination of Perchlorate by Ion Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
MCT Determination; verified in each analysis batch via the analysis of the IPC solution. The MCT is used to determine if sample dilution or pretreatment is needed.	One-time study done in conjunction with method development and as needed (based on significant analytical system changes) to determine the maximum ionic strength of a solution capable of being analyzed by the IC system.	The MCT cannot exceed the instrument's linear calibration range and should be about 20% under the maximum capability of the IC system.	If MCT must be modified as evidenced by unacceptable IPC solution results, lower the MCT by 10% (or some other value deemed appropriate) and recalibrate the system accordingly. New MDLs and a revised MRL must also be generated. The data generated by the performance of these procedures can serve as the analyst's IDC for the new operating conditions. Sample analyses cannot proceed until a suitable MCT is established.
Initial Demonstration of Capability (IDC)	A one-time study during method development, and also performed by each analyst prior to processing client samples, to demonstrate acceptable proficiency.	All quality criteria defined by the cited EPA Methods (as presented in SOP Sections 8 and 17) must be met.	Sample analyses cannot proceed until an acceptable IDC is performed.
Initial Calibration; minimum 5-point	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria). Because the initial calibration spans the linear range of the instrument, analysis of the initial calibration satisfies the linear calibration range verification requirements discussed in Section 9.2.2 of Method SW9058.	Second order quadratic fit calibration curve generated electronically by instrument software. Coefficient of Determination (r^2) of the calibration curve equation must be ≥ 0.990.	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve. Sample analyses cannot proceed until an acceptable initial calibration is achieved.
Quality Control Sample (QCS)/ Independent Calibration Verification (ICV) Standard	Run once after each initial calibration at a concentration at or above the midpoint of the calibration curve.	Response must agree within ±10% of known value.	Prepare another QCS/ICV and analyze. If QCS/ICV still fails, system must be recalibrated (see quality requirements above).
Retention Time Window (RTW)	Derived from data obtained over the course of a day.	May be 3X standard deviation of RTs observed, not to exceed ±5% of the retention time value.	If perchlorate retention time is not reproducible, problem must be identified and corrected and a new IDC and initial calibration must be performed.
IPC Solution	Run once with each analysis batch at the beginning of the analytical sequence.	Conductivity of the solution must be within ±10% of the initial value. Resultant peak area/height ratio must agree within 25% when compared to analysis batch LCS. Perchlorate %R must be within ±20% of true value.	If any of the QC criteria are not met, reanalyze the IPC solution. If IPC criteria still not met, the MCT must be revised and confirmed via the analysis of a new IPC solution. A new IDC and initial calibration must also be performed.

Analytical Method: EPA 314.0; SW9058	**Parameter:** Determination of Perchlorate by Ion Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
		Retention time for perchlorate must not shift by more than 5%.	
Laboratory Reagent Blank (LRB)/ Method Blank (MB)	Run early in the sample analysis batch sequence. Reagent water blank that is processed in the same manner as the associated samples.	Must not contain perchlorate at a concentration greater than the RL. If reporting data for regulatory purposes the target analyte cannot be present at levels greater than ½ the RL (Method 314.0) or must be free of contamination <MDL (Method SW9058)	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable LRB/MB must also be reanalyzed.
Initial Calibration Check Sample (ICCS)	A standard at a concentration equal to the lowest standard of the calibration suite, analyzed once per analysis batch near the beginning of the analytical sequence.	%R must be ±25% of the known value.	If quality criterion not met, re-prepare and analyze the ICCS. If the ICCS still fails, the system must be recalibrated.
Laboratory Fortified Blank (LFB)/ Laboratory Control Sample (LCS)	Run early in the sample analysis batch sequence. Aliquot of reagent water blank is spiked with a known amount of analyte and QC sample is processed in the same manner as the associated field samples.	%R must be ±15% (aqueous), within laboratory-derived limits (soils)	If quality criterion not met, re-prepare and analyze the LFB/LCS. If the LFB/LCS still fails, the problem must be identified and corrected before sample analyses can proceed.
Continuing Calibration Check Sample (CCCS)/ Continuing Calibration Verification (CCV) Standard	Near to mid-level standard run to bracket the analysis of 10 field samples.	Response must agree within ±15% of known concentration.	Check that calculations and preparation are correct, evaluate/correct instrument malfunction; reanalyze. If CCCS/CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCCS/CCV must be reanalyzed.
Laboratory Fortified Matrix (LFM)/ Matrix Spike (MS) and LFM/MS (laboratory) Duplicate	One MS/MSD set per batch of ≤20 field samples (this provides an average frequency of one per ten samples per Method SW9058 requirements).	%R ±20% of the expected values Method 314.0 (Method SW9058 allows for ±25%). RPD should be ≤15.	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative. For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.
Method Detection Limit (MDL) Study	Run initially as part of the IDC then as needed, at a minimum annually.	Positive result < the MRL.	Determine the reason for failure and fix problem with the system. Repeat the MDL study.

Analytical Method: EPA 314.0; SW9058	**Parameter:** Determination of Perchlorate by Ion Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
	Run at the reporting limit (MRL).		If criteria still not met, discuss with QA Manager (MRL may be adjusted if required).

Paragon Analytics

FORM 1116

CONDUCTIVITY SCREENING WORKSHEET

Instrument ID: VWR Digital Conductivity Meter S/N A22036

Workorder ID / Sample No.		Estimated µS	Dilution(s)	Anion(s)	Date	Initials	Comments

Reviewed by / Date ______________________________

Form 1116r4.frm (6/29/04)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1126 REVISION 16

TITLE: **DETERMINATION OF pH BY ELECTROMETRIC MEASUREMENT METHODS EPA 150.1, SW9040B, SW9045C, AND SM4500-H^+ B**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 4/30/07

QUALITY ASSURANCE MANAGER _____ DATE 4/28/07

LABORATORY MANAGER _____ DATE 5-7-07

HISTORY: **SOP 620:** Rev0, 2/11/92; Rev1, 7/23/92; Rev2, 3/4/93; Rev3, 1/28/94; Rev4, 1/25/95; Rev5, 7/19/95; Rev6, 3/15/96; Rev7, 1/30/97; Rev8, 5/23/97; Rev9, 3/2/99; Rev10, 4/4/01. **SOP 1126:** Rev11, 1/23/02; Rev12, 12/16/02; Rev13, 2/10/03; Rev14, 4/16/04; Rev15, 11/2/05; Rev16, 4/27/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- EPA Method 150.1, SW9040B (aqueous), SW9045C (soils, sludges and wastes), and SM4500-H^+ B -- describes the electrometric measurement of pH in environmental matrices. Some water content is required to conduct the pH measurement. Method SW9040B is used to measure the pH of single or multiphase matrices whose aqueous phase constitutes at least 20% of the total volume of the sample matrix. Method SW9045C is used to measure the pH of solid, sludge, or non-aqueous liquid matrices, whose water content, if present at all, constitutes less than 20% of the total volume of the sample matrix. The corrosivity of concentrated acids and bases, or concentrated acids and bases mixed with inert substance, cannot be measured using this SOP.

2. SUMMARY

The basic principle of electrometric pH measurement is to determine of the activity of the hydrogen ion [H+] by potentiometric measurement using standard buffers and a reference electrode. Paragon uses a pH meter equipped with a combination pH electrode to measure pH. The pH is measured directly in water samples (while stirring). The pH of soils and wastes is measured by mixing with deionized water (1:1 ratio) and measuring the pH of the aqueous suspension. The pH-unit measuring device is calibrated with a series of standard buffer solutions of known pH at a temperature of 25±2°C.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 In general, the glass electrode is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate salinity (<0.1 molar salinity).

4.2 The sodium ion is the most likely interference for the pH electrode. The electrode used in this SOP is constructed from a special low sodium error glass. Error due to sodium is negligible when measuring pH values less than 12.

4.3 pH measurements are affected by temperature in two ways (1) mechanical effects that are caused by changes in the properties of the electrode, and (2) chemical effects caused by equilibrium changes. Temperature difference between calibration buffers and samples could cause errors. If the sample temperature differs by more than ±2°C from the buffers, it is necessary to make corrections for temperature. In order to overcome these temperature differences, all standards (buffers) and samples are placed in a water bath maintained at 25±2°C until equilibrated (approximately 1 hour).

4.4 Errors will occur if the electrode becomes coated. If the electrode becomes coated with an oily material, rinse the electrode with mild detergent or methanol. If inorganic deposits are coating the electrode, soak the electrode in 0.1M HCl for one-half hour, followed by soaking in the electrode storage solution for at least one hour. Refer to the electrode's instruction manual for additional information on cleaning the electrode.

4.5 The electrode junction should be flushed by holding the probe and pressing down on the top after use in especially dirty or viscous samples or when the electrode

response becomes sluggish. After flushing the junction, the probe should be filled with internal filling solution.

5. APPARATUS AND MATERIALS

5.1 pH meter, Fisher Accumet 50 or equivalent capable of reading two decimal places

5.2 Combination pH electrode, Orion ROSS-SURE FLOW or equivalent with internal filling solution

5.3 Centrifuge tubes, 50mL, plastic, disposable

5.4 Magnetic stir plate and Teflon^{TM}-coated stir bars

5.5 Laboratory balance, capable of weighing ±0.01g

5.6 Water bath maintained at 25±2°C

6. REAGENTS

NOTE: Only reagent grade chemicals and deionized (DI) water shall be used in all pH tests.

6.1 Standard buffer solutions: Certified; purchased from vendors. These commercially available solutions must be validated by comparison with NIST standards. These buffer solutions may be purchased at various pH units (e.g., 4, 5, 7, 9, and 10). For the procedures described in this SOP, solutions at 2.00, 4.01, 7.00, 10.01, 12.45 pH units are used. A second source (at a pH of 7.00) buffer is also required. *Shelf Life* = per manufacturer's expiration date as long as condition is good.

6.2 Electrode internal filling solution: Use only Orion ROSS Reference Electrode Filling Solution 3M KCl Cat. No. 810007 with the ROSS SURE-FLOW pH electrode. *Shelf Life* = one year after date of opening.

6.3 Electrode storage solution: Add 0.25g of potassium chloride (KCl) to 50mL of pH 7 buffer solution. *Shelf Life* = replenish as needed to maintain sufficient volume.

6.4 Hydrochloric Acid (HCl), 0.1M: Dilute 0.83mL concentrated HCl to 100mL using deionized water. *Shelf Life* = one year.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 All samples should be collected according to an approved sampling plan.

7.2 The measurement of pH is intended to be a field parameter, as the buffering capacity of a sample may change the pH of the sample. EPA Methods 150.1 and SW-846 9040B and 9045C state that "samples should be analyzed as soon as possible." Paragon strives to analyze all pH samples as soon as possible after

receipt; prior notification and/or special arrangements for Saturday sample receipt and analysis are encouraged between the client and the laboratory. However, the intention of this 4 day window is to accommodate the scenario of Friday sample collection, followed by login and release of the sample to the laboratory for analysis the following Monday, with the laboratory performing the analysis within 1 day of internal receipt.

7.3 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere. Therefore, the sample containers should be filled completely and kept sealed prior to analysis.

7.4 Samples must be refrigerated at 4±2°C until analysis.

8. PROCEDURE

8.1 pH METER STANDARDIZATION, GENERAL OPERATION AND ELECTRODE CARE

Over time, a pH electrode's slope and its zero potential will change. ***Therefore, the pH electrode must be standardized each day before use.*** Standardization requires the use of at least three certified buffer solutions. Paragon uses 4.01, 7.00 and 10.01 buffer solutions to standardize the pH meter. For corrosivity characterization, and if the sample pH is <4 or >10 pH units, the calibration of the pH meter should include a buffer of pH 2.00 for acidic wastes and pH 12.45 for caustic wastes. The procedure for standardizing the pH meter follows.

8.1.1 If not already prepared, turn on the water bath and set to maintain a temperature of 25±2°C.

8.1.2 To clear the existing values from the pH meter's previous standardization, press "channel" on the main screen until the display indicates the current pH channel (channel B). Then press "pH" to select pH mode. Next press "standardize". A menu of standardization options will appear. Press "2" to clear the existing standards. The pH meter will return to the main screen (all pH standardization points have been cleared from the memory).

8.1.3 Check the pH electrode's internal filling solution level. The level of the filling solution must cover the coil and be at least one inch above the sample level. Uncover the filling hole and add more internal filling solution if needed. The filling hole must remain uncovered during analysis.

8.1.4 Place fresh aliquots (approximately 20mL) of the pH 4.01, 7.00 and 10.01 buffers in 50mL centrifuge tubes and cap the tubes. Record the IDs of the buffers on the bench sheet. Place all buffers into the water bath and allow to equilibrate for at least 1 hour.

NOTE: If corrosivity is the requested method or the sample pH is <4 or >10 pH units, the meter must be re-calibrated using the 2.00, 7.00 and 12.45 pH buffer solutions.

NOTE: The pH buffer aliquots dispensed into the centrifuge tubes are useable only for that day's calibration. These buffer aliquots must be disposed of daily.

8.1.5 pH meter standardization can begin once the pH buffers have come to temperature in the water bath. Press "channel" on the pH meter's screen until the display indicates the current pH channel (channel B). Then press "pH" to select pH measurement. Make sure the filling hole of the pH electrode is uncovered.

8.1.6 Remove the centrifuge tube containing the first source pH 7.00 buffer from the water bath and record the temperature of the water bath on the bench sheet. Uncap the centrifuge tube, add a stir bar, and stir gently on the stir plate.

NOTE: All aqueous samples and buffer standards must be stirred while taking pH measurements. Place an insulation pad on top of the stir plate to prevent error from the transfer of heat to the solution being measured.

8.1.7 Place the pH electrode in the pH 7.00 buffer solution. Allow the pH meter's display to stabilize (i.e., no change in pH reading for at least ten seconds).

8.1.8 Press "standardize" (a menu of standardization options is displayed). Press "1" to select "Update or Add a Standard". Enter the value of the pH buffer being used for standardization, then press "enter". The screen will display on-screen instructions, press "enter". The pH meter will return to the main screen with the added buffer point shown. Record the buffer point on the bench sheet. If the buffer tube is to be re-read later in the run as a continuing calibration verification (CCV), it must be placed back into the water bath immediately to maintain the proper temperature.

NOTE: The pH electrode must be rinsed thoroughly between measured solutions using deionized water.

8.1.9 With the pH meter in measurement mode, repeat Steps 8.1.6 through 8.1.8 for the pH 4.01 and pH 10.01 buffers to complete the three-point standardization. **If corrosivity is the requested method or the**

sample pH is <4 or >10 pH units, the meter must be re-calibrated using the 2.00, 7.00 and 12.45 pH buffer solutions.

8.1.10 Additional pH electrode considerations:

- Rinse the pH electrode with DI water between each measured solution. Avoid rubbing or vigorous wiping of the glass electrode to reduce the chance of error due to polarization.
- After analyzing dirty or viscous samples, or when electrode response becomes sluggish, it may be necessary to empty the electrode completely and hold the junction open under running deionized water. Empty any water from the electrode and refill with fresh ROSS filling solution. Flush the electrode by pushing down on the top briefly, check the internal filling solution level again and add more if necessary.
- Alternately, the general cleaning procedure can be performed. Soak the electrode in 0.1M HCl for thirty minutes, followed by soaking in the pH storage solution for at least one hour.
- Store the pH electrode by immersing in the storage solution. The filling hole is covered during storage and the meter is placed in standby mode.

8.2 FIELD AND QC SAMPLE PREPARATION AND ANALYSIS

NOTE: All samples and buffer solutions, including the Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV), must be placed in the water bath for at least 1 hour prior to pH measurement.

8.2.1 Prepare the ICV by transferring an aliquot (approximately 20mL) of second-source pH 7.00 buffer to a 50mL centrifuge tube. Place the centrifuge tube in the water bath and allow to equilibrate for at least one hour.

8.2.2 The previously prepared first-source pH 7.00 buffer aliquot can be used as the CCV. Keep the centrifuge tube in the water bath to maintain the proper temperature.

8.2.3 Label a series of 50mL centrifuge tubes with the identities of the samples to be analyzed (or mark otherwise).

8.2.4 For each aqueous sample, transfer a 20mL aliquot into a designated centrifuge tube, cap and place the tubes in the water bath. Prepare one out of every ten field samples in duplicate.

8.2.5 For each solid matrix sample to be analyzed, place a 20g aliquot of sample into a 50mL centrifuge tube and add 20mL of DI water. Record the sample weight and DI water volume on the bench sheet. Cap the tubes and shake the mixtures manually for five minutes. Additional DI water may be added if the sample readily absorbs water and no free aqueous phase is present. Place the prepared tubes in the water bath. Prepare one out of every ten field samples in duplicate.

NOTE: Analysis can proceed once the prepared solutions have been allowed to equilibrate in the water bath for at least one hour. This time period also allows the solids to settle for the solid matrix samples being analyzed.

8.2.6 When analysis is ready to proceed, press the "pH" and "meas/monitor" keys to place the pH meter in continuous pH mode. **Make sure the filling hole of the pH electrode is uncovered.**

8.2.7 **The ICV must be analyzed following standardization of the pH meter before any samples can be analyzed.** Remove the ICV from the water bath and record the temperature of the water bath on the bench sheet. Uncap the tube and add a stir bar. Stir gently on the stir plate. Use an insulation pad to prevent the transfer of heat to the measured solution. Immerse the pH electrode into the ICV.

8.2.8 Wait until a stable reading is achieved (i.e., no change in reading for at least ten seconds). Record the ICV's pH value on the bench sheet.

The ICV is run to verify the pH meter's initial standardization. The ICV result must agree within ±0.05 pH units of the known value (i.e., pH 7.00) before sample analyses can proceed. If the ICV fails, check the integrity of the second source buffer. Replace the ICV and reanalyze. If the ICV still fails, the pH meter must be restandardized.

8.2.9 Following an acceptable ICV analysis, up to 10 samples (including a Duplicate) can be analyzed, followed by a CCV. The CCV must be analyzed to bracket the first ten sample analyses between the ICV and CCV. Following the CCV, up to 10 more samples can be analyzed, followed by the CCV again. The sequence of up to 10 sample analyses followed by the CCV can be continued until all of the samples have been analyzed. Put the CCV back into the water bath after each reading to maintain it at the proper temperature.

If any of the CCV results fails to agree within ±0.1 pH units from the expected value, the pH meter must be restandardized and all samples run after the last acceptable CCV analysis must be reanalyzed.

8.2.10 For aqueous samples, uncap the tube and add a stir bar. Stir gently on the stir plate. Use an insulation pad to prevent the transfer of heat to the measured solution. Immerse the pH electrode into the sample solution. Wait until a stable reading is achieved then record the sample's pH on the bench sheet. Report the results as "pH in water at 25°C."

8.2.11 Do not add a stir bar to the centrifuge tubes containing the prepared solid matrix samples. For solid sample analysis, immerse the pH electrode just deep enough into the aqueous phase to make electrical contact; do not push the electrode into the settled solids. Wait until a stable reading is achieved, then record the sample's pH on the bench sheet. Report solid results as "solid pH in water at 25°C."

8.2.12 A laboratory duplicate is run for every ten environmental samples analyzed. The pH results for aqueous sample duplicates should agree within ±0.2 pH units of each other. The pH results for solid sample duplicates should agree within ±0.5 pH units of each other. If these criteria are exceeded, consideration will be given to the CCV standard performance. If no problems occurred with the CCV analyses, the laboratory will remark in the case narrative that the duplicate precision criteria have been exceeded, and will report the analysis results as is.

9. QUALITY CONTROL

Calibration checks and duplicate analyses are discussed in PROCEDURE above.

10. DEVIATIONS FROM METHOD

10.1 Paragon does not employ a temperature sensor to provide temperature compensation control at the pH meter. Instead, temperature compensation is facilitated by the use of a water bath maintained at 25±2°C. This approach allows for a consistent temperature between calibration buffers and samples without the need for additional calculations due to temperature differences.

10.2 Method SW9040B, Section 7.4 and Method EPA 150.1, Section 8.4 states that successive aliquots be measured (usually 3) until the difference is less than 0.1 pH units. Paragon does not employ this practice, but runs a duplicate sample per 10 environmental samples.

10.3 Method SW9040B, Section 7.1.2 states that for corrosivity characterization, the sample must be measured at 25±1°C if the pH is above 12.0. Paragon maintains the water bath at 25±2°C.

10.4 Method SW9040B, Section 7.1.2 states that for corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and

a pH 12 buffer for caustic wastes. Paragon uses a pH 12.45 buffer for caustic wastes.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs before preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Used buffer solutions may be disposed of in the sanitary sewer system.

11.2.2 Corrosive only wastes such as glacial acetic acid and sulfuric acid waste are disposed of by discharging into the waste water tanks (down the lab sink drains). Materials which are corrosive only (i.e., no hazardous components or characteristics other than corrosivity) may be neutralized using on-site water treatment procedures.

11.2.3 The aqueous samples or supernatant of solid samples shall be disposed of in the Aqueous Laboratory Waste.

11.2.4 The soil/solid samples and sediments of solid samples shall be disposed of in the Contaminated Soils and Solids.

11.2.5 All empty solvent bottles must be disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1971. Method 150.1, “pH (Electrometric)”.

12.2 U.S. Environmental Protection Agency, SW846, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, Revision 2, January 1995. Method 9040B, "pH Electrometric Measurement".

12.3 U.S. Environmental Protection Agency, SW846, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, Revision 3, January 1995. Method 9045C, "Soil and Waste pH".

12.4 A.P.H.A., A.W.W.A. and W.P.C.F., 1989. Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998. Method 4500-H^+ B, "(pH) Electrometric Method", pp 4-87 to 4-91.

12.5 Orion ROSS SURE-FLOW pH electrode instruction manual (227355-001 Rev.C).

12.6 Fisher Model 50 Accumet pH meter operating instructions (Rev. C 2/92).

DOCUMENT REVISION HISTORY

11/2/05: LIMS program specification language added.

4/27/07: Updated format, removed redundancies contained in text. Added DOCUMENT REVISION HISTORY.

Analytical Method: EPA 150.1, SW9040B, SW9045C, SM4500-H^+ B	**Parameter:** pH		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
pH Meter Standardization	Must be performed each day pH meter is used.	N/A	The pH meter must be successfully standardized before sample analyses can proceed.
Initial Calibration Verification (ICV)	Run following the initial standardization, before any samples are analyzed.	ICV results must agree within ±0.05 pH units of the known value.	If ICV fails, check the integrity of the second-source buffer solution. Replace and reanalyze. If ICV still fails, problem must be identified and corrected and pH meter restandardized before analyses can proceed.
Continuing Calibration Verification (CCV)	Run following the analyses of every ten sample set and to close-out the run sequence.	CCV results must agree within ±0.1 pH units of the expected value.	If CCV fails, pH meter must be restandardized and all samples run since the last acceptable CCV must be reanalyzed.
Laboratory Duplicate (DUP)	One per batch of ≤10 field samples.	Aqueous duplicate values should agree within ±0.2 pH units of each other; solid matrix duplicate values should agree within ±0.5 pH units of each other.	If criteria are not met and CCV analyses are within QC limits, narrate client data package report.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1127 REVISION 7

TITLE: DETERMINATION OF NITROGEN AS NITRATE PLUS NITRITE (NO_3^--N + NO_2^--N), NITRITE (NO_2^--N), AND NITRATE (NO_3^--N) IN ENVIRONMENTAL WATER AND SOIL SAMPLES USING A COLORIMETRIC, AUTOMATED, CADMIUM REDUCTION PROCEDURE -- METHODS EPA 353.2, SM 4500-NO_3^- I, AND QUIKCHEM 10-107-04-1-C

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER Steve Wahlman DATE 7/21/08

QUALITY ASSURANCE MANAGER Deb Schaefer DATE 7/20/08

LABORATORY MANAGER K. Hurd DATE 7/21/08

HISTORY: Rev0, 3/2/02; Rev1, 8/23/02; Rev2, 12/13/02; Rev3, 3/6/03; Rev4, 12/15/04; Rev5, 7/26/05; Rev6, 4/10/06; Rev7, 7/20/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) references EPA Method 353.2, Standard Method (SM) 4500-NO3- I, and Quikchem Method 10-107-04-1-C for the determination of nitrate + nitrite (NO_3^--N + NO_2^--N) and nitrite only (NO_2^--N) in environmental water and soil samples. Nitrate (NO_3^--N) is determined by calculating the difference of [(NO_3^--N + NO_2^--N) - NO_2^--N] results. A Lachat Auto Flow Injection Analyzer, using a copperized cadmium reduction column procedure, is used to analyze the prepared samples. Values are reported as nitrogen, in the forms of nitrate + nitrite (NO_3^--N + NO_2^--N), nitrite (NO2--N), and nitrate (NO_3^-).

2. SUMMARY

Solid samples are first extracted with deionized water (at approximately a 1:10 ratio) by shaking using a rotary tumbler. The total nitrate + nitrite (NO_3^--N + NO_2^--N) content of the aqueous leachates or samples is determined quantitatively by first reducing nitrate (NO_3^--N) to nitrite (NO_2^--N) by passing the sample through a copperized cadmium column. The resultant nitrite (NO_2^--N), which consists of the original nitrite plus the reduced nitrate, is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylendiamine dihydrochloride to form a highly colored azo dye. This azo dye is then measured colorimetrically at 520nm. Aqueous samples are quantitated using a calibration curve created from standards made in deionized water. Native nitrite (NO_2^--N) *only* content is determined by conducting the analysis in a manner that bypasses the cadmium reduction column. The NO_2^--N is diazotized and coupled to yield an azo dye that is measured colorimetrically and quantitated using calibration curves. Finally, native nitrate (NO_3^--N) content is determined by subtracting the native nitrite ***only*** results from the combined nitrate + nitrite results.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the ability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of a proficiency evaluation test.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, and completeness and is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these methods to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Nitrate is very common in the laboratory environment because nitric acid is used extensively throughout the laboratory. Nitrate contamination of samples and blanks can be very troublesome. It is extremely important to use clean laboratory technique at all times. Use clean, disposable containers whenever possible and minimize the use of glassware.

4.2 This colorimetric procedure requires an optically clear sample. Further, turbid samples or samples with suspended solids can cause a build up of suspended matter in the reduction column and restrict flow. Because nitrate and nitrite are found in a soluble form, if necessary, the sample should be pre-filtered through a 0.45µm pore diameter membrane filter. Sample color may also be corrected for by dilution to overcome the color interference, or by running the samples through the manifold with the cadmium column in the off-line position and without the addition of color reagent (the absorbance reading can then be calculated by subtracting the final from the initial absorbance reading, to obtain a corrected absorbance reading).

4.3 Concentrations of iron (Fe), copper (Cu) or other metals above several µg/mL lower reduction efficiency. EDTA is added to the buffer solution to eliminate this interference.

4.4 Residual chlorine can interfere by oxidizing the cadmium (Cd) column, thereby reducing efficiency. Removal of residual chlorine can be achieved by adding sodium thiosulfate ($Na_2S_2O_3$) solution.

4.5 Samples that contain large concentrations of oil and grease will coat the Cd granules surface. This interference can be removed by pre-extracting the sample with an organic solvent.

4.6 Sample color that absorbs at about 520nm interferes with the colorimetric determination. This may be corrected by diluting the sample or by running the sample through the manifold with the cadmium column in the off-line position and without the addition of color reagent for color formation, and calculating the corrected absorbance reading.

4.7 Samples that are over acidified with sulfuric acid preservative will cause a negative response within the peak area during analysis. Standard procedures recommend acidifying samples for nitrate + nitrite (NO_3^--N + NO_2^-- N) to a pH of less than 2 for preservation. All samples will have the pH adjusted to between 2 - 9 prior to analysis.

4.8 If the absorbance reading is too high on the laboratory blank, try flushing the column with DI water. If the buffer appears to be contaminated, prepare a fresh batch of solution using clean laboratory techniques. If high blanks continue to be a problem, remove the Cu-Cd granules from the column, treat with 6N HCl and 2% $CuSO_4$ and repack the column (see Section 12 of this SOP).

4.9 If the nitrite (NO_2^-- N) check sample's percent recovery becomes too high (>120%), treat reduction column granules as described in Section 12 of this SOP or repack the column in order to improve the column's efficiency.

5. APPARATUS AND MATERIALS

5.1 Flow injection analysis equipment designed to deliver and mix/react sample and reagents in the required order and ratios. Lachat QuikChem 8000, or equivalent, equipped with the following:

5.1.1 Autosampler, with sample tubes (12x75)

5.1.2 Peristaltic multichannel pump

5.1.3 Reaction unit or analytical manifold with Cadmium

5.1.4 Absorbance detector with 520nm filter

5.1.5 Data system (Windows 3.1 and Omnion software Version 1.4, or equivalents)

5.2 Volumetric dispensers, Eppendorf™ or equivalent, capable of dispensing 0.01-5.0mL

5.3 TCLP-type mechanical tumbler, capable of 1 hour soil extraction by agitation

5.4 Corning pH meter, Model 320 or equivalent, and appropriate buffer solutions for calibration. Capable of a two-point calibration.

5.5 Centrifuge, capable of sustaining approximately 3500rpm

5.6 Centrifuge tubes with caps, disposable, 50mL

5.7 Volumetric flasks, various sizes, Class A

5.8 Magnetic stir bars, Teflon coated

5.9 Magnetic stir plate, capable of variable speed control

5.10 Analytical balance, capable of weighing ± 0.0001g, verified per SOP 305

5.11 Syringe, with 0.45µm filter disk

6. REAGENTS

NOTES: Only ACS grade or better chemicals and reagents may be used. Reagents and solutions may be stored in either plastic or glass containers.

To prevent bubble formation, degas all solutions, except the standards or otherwise noted reagents, with helium. Use He at 140KPa (20lb/in^2) through a helium degassing tube. Bubble the He through the solution for one minute.

6.1 Ammonium Chloride/EDTA Buffer: Make in-house by dissolving 85g of ammonium chloride (NH_4Cl) and 1.0g Disodium Ethylenediamine Tetraacetate EDTA ($C_{10}H_{14}N_2O_8 \bullet 2H_2O$) salt in 800mL degassed DI water. Adjust to pH 8.5 with 10N Sodium Hydroxide (NaOH). Dilute to 1000mL with degassed DI water. *Shelf life = 1 year.*

6.2 Sodium Hydroxide Solution, 10N: Dissolve 160.0g Sodium Hydroxide (NaOH) to a final volume of 400mL using DI water. Not degassed. *Shelf life = 1 year.*

6.3 Color reagent: To 250mL degassed DI water, add 50mL concentrated Phosphoric Acid (H_3PO_4) and 20.0g Sulfanilamide. After dissolving the sulfanilamide completely, add 1.0g N-(1-naphthyl)-ethylenediamine dihydrochloride. Mix to dissolve, then dilute to 500mL with degassed deionized water. *Store refrigerated in an amber container. Shelf life = 6 months.*

6.4 Copper Sulfate ($CuSO_4$) Solution, 2%: Dissolve 4g Copper Sulfate ($CuSO_4 \bullet 5H_2O$) in 100mL DI water. Use a magnetic stirring bar and stir plate to speed dissolution. Not degassed. *Shelf life = Make fresh daily.*

6.5 Copper Sulfate ($CuSO_4$) Solution, 0.2%: Dilute 2% copper sulfate solution (above) ten-fold. *Shelf life = Make fresh daily.*

6.6 Hydrochloric Acid (HCl), 6N: Cautiously add 1 part concentrated HCl to 1 part DI water. Not degassed. *Shelf life = 1 year.*

6.7 Cu-Cd granules: Wash 10-20g new or used 0.3-1.5mm diameter (40 - 60-mesh) Cadmium (Cd) granules with 6N HCl and rinse with DI water. Swirl the Cd granules in portions of 100mL of 2% $CuSO_4$ until a dark colloidal precipitate begins to develop. Gently flush with DI water to remove all precipitated Cu. *Self life = Indefinite, good as long as darkened color persists; regenerate as needed as described in Section 12 of this SOP.*

6.8 Ottawa sand, EMD, SX0075-3 or equivalent. *Keep container sealed tightly. No special storage or shelf life considerations.*

6.9 Ammonium Hydroxide (NH4OH), conc., 15N: Purchased from vendor. Not degassed. *Shelf life = 1 year.*

7. NITRATE CALIBRATION STANDARDS (USED IN NITRATE + NITRITE TEST)

7.1 Nitrate (NO_3^--N) Stock Solution, 10000mg/L: Purchased from a commercial vendor or created from KNO_3 reagent grade salt. Dissolve 36.085g of KNO_3 salt in 500mL deionized water. *Store in refrigerator. Shelf life = 1 year from purchase or creation.*

7.2 Nitrate (NO_3^--N) Stock Solution, 1000mg/L, second-source: Purchased from a commercial vendor or created from KNO_3 reagent grade salt. Dissolve 3.6085g of KNO_3 salt in 500mL deionized water. KNO_3 salt must be from a different vendor or lot number than that used for the first source standard. *Store in refrigerator. Shelf life = 1 year from purchase or creation.*

7.3 Nitrate (NO_3^--N) Intermediate Standards, 100mg/L (first and second source): First-source solution is made by diluting 5.0mL of the 10000mg/L "First Source" NO_3^--N Stock Solution with deionized water, to a final volume of 500mL. This "First Source" Intermediate Standard is used to prepare the daily calibration standards and the continuing calibration verification (CCV) standards. *Store in refrigerator. Shelf Life = 1 year from purchase or creation (note: cannot exceed expiration of parent standard).*

Second-source solution is made by diluting 25.0mL of the "Second Source" 1000mg/L NO_3^--N Stock Solution with deionized water, to a final volume of 250mL. The "Second Source" Intermediate Standard is used to prepare the

Laboratory Control sample (LCS) and initial calibration verification (ICV) standard. *Store in refrigerator. Shelf Life = 1 year from purchase or creation.*

7.4 NO_3^--N Calibration Standards (per Table below): Made in-house on *each day of calibration* by dilution of the Intermediate Standard (100mg/L, first source).

Note that DI water is used as the diluent to prepare calibration standards for aqueous sample analyses. The final volume of all calibration standards is 5.0mL.

CONCENTRATION OF INITIAL SOLUTION (mg/L)	VOLUME OF INITIAL STANDARD USED (mL)	CONCENTRATION OF FINAL SOLUTION (mg/L)
100	0.10	2.0
100	0.05	1.0
100	0.025	0.50
2.0	0.50	0.20
1.0	0.50	0.10
0.5	0.50	0.05
0.1	0.50	0.01
0	0.00	0.0

7.5 Initial Calibration Verification Standard, (ICV), 0.50mg/L: Dilute 0.025mL of the 100mg/L"second source" NO_3^--N Intermediate Standard into 5.0mL, using deionized water.

7.6 Continuing Calibration Verification Standard, (CCV), 1.0mg/L: The "first source" intermediate standard is used to prepare the continuing calibration verification (CCV) standard. Dilute 0.050mL of the 100mg/L "first source" NO_3^--N intermediate standard into 5.0mL deionized water.

7.7 NO_2^--N Cadmium Column Check Standard, 1.0mg/L: Dilute 0.1mL of the 50mg/L NO_2^--N Intermediate Standard (from section 8.0) into 5.0mL deionized water.

NOTE: The Calibration Standards with concentrations of 10mg/L or less are made daily upon use.

8. NITRITE CALIBRATION STANDARDS (USED IN NATIVE NITRITE *ONLY* TEST)

8.1 Nitrite (NO_2^--N) Stock Solutions, 1000mg/L: Created from $NaNO_2$ reagent grade salts, first and second sources. Used to create the first and second source NO_2^--N 200mg/L Intermediate Standards. Dissolve 0.4925g of $NaNO_2$ salt into 100mL deionized water. *Store in refrigerator. Shelf life = 1 month.*

8.2 Nitrite (NO_2^--N) Intermediate Standards, 200mg/L (first source): First-source solution is made by diluting 20.0mL of the 1000mg/L NO_2^--N Stock Solution with deionized water, to a final volume of 100mL. This "First Source"

Intermediate Standard is used to prepare the daily calibration standards and the continuing calibration verification (CCV) standards. *Shelf Life = 1 month (note: cannot exceed expiration of parent standard).*

Note that the Laboratory Control sample (LCS) and Initial Calibration Verification (ICV) standard are made from the "second source" 1000mg/L stock solution or 200mg/L solution, described below.

8.3 Nitrite (NO_2^--N) Intermediate Standards, 200mg/L (second source): Second source solution is made by diluting 20.0mL of the 1000mg/L NO_2^--N Stock Solution with deionized water, to a final volume of 100mL. This "second Source" Intermediate Standard is used to prepare the initial calibration verification (ICV) standard and the Laboratory Control Sample (LCS) standard, which are identical. *Shelf Life = 1 month (note: cannot exceed expiration of parent standard).*

Note that the Laboratory Control sample (LCS) and Initial Calibration Verification (ICV) standard are made from the "second source" 1000mg/L stock solution or 200mg/L solution.

8.4 NO_2^--N Calibration Standards (per Table below): Made in-house *each day of calibration* by dilution of the first source 100mg/L NO_2^--N Intermediate Standard.

Note that DI water is used as the diluent to prepare calibration standards.

CONCENTRATION OF INITIAL SOLUTION (mg/L)	VOLUME OF INITIAL STANDARD USED (mL)	CONCENTRATION OF FINAL SOLUTION (mg/L)	FINAL VOLUME OF SOLUTION (mL)
200	0.050	0.50	20
200	0.020	0.20	20
200	0.010	0.10	20
0.50	0.50	0.05	5
0.20	0.50	0.02	5
0.10	0.50	0.01	5
0	0.0	0.0	5

8.5 Initial Calibration Verification Standard, (ICV), 0.1mg/L: Dilute 0.01mL of the 1000mg/L"second source" NO_2^--N Stock Standard into 100mL, using deionized water or 0.01mL of 200mg/L second source standard into 20mL of DI water.

8.6 Continuing Calibration Verification Standard, (CCV), 0.2mg/L: The "first source" intermediate standard is used to prepare the continuing calibration verification (CCV) standard. Dilute 0.02mL of the 200mg/L "first source" NO_2^--N intermediate standard into 20.0mL deionized water.

NOTE: The Calibration Standards with concentrations of 10mg/L or less are made daily upon use.

9. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

9.1 All samples must be collected according to an approved sampling plan.

9.2 Sampling and storage of samples in glass bottles or in plastic bottles are permissible. Samples should be kept cool at 4±2°C.

9.3 For analysis of NO_2^--N only, aqueous samples must be analyzed within 48 hours after collection. There is no promulgated preservation or holding time for soils.

9.4 For NO_2^--N + NO_3^--N analysis using the Cd Column, aqueous samples must be acidified to a pH≤2 with Sulfuric Acid (H_2SO_4), with analysis occurring within 28 days after collection.

10. AQUEOUS EXTRACTION OF SOLID SAMPLES AND ASSOCIATED QUALITY CONTROL (QC) SAMPLE PREPARATION

10.1 Weigh a representative 4.0g aliquot of moist sample into a labeled 50mL disposable polypropylene centrifuge tube.

10.2 Method Blank: Weigh 4.0g clean Ottawa sand into a 50mL disposable polypropylene centrifuge tube.

10.3 As applicable, prepare both NO_2^--N + NO_3^--N and NO_2^--N Blank Spike, Laboratory Control Samples (LCSs) as follows:

10.3.1 Weigh 4.0g clean silica sand into a 50mL disposable polypropylene centrifuge tube. Spike with 0.40mL of 100mg/L "second source" NO_3^--N Intermediate Standard (expected concentration = 1.0mg/L NO_3^--N).

10.3.2 Weigh 4.0g clean silica sand into a 50mL disposable polypropylene centrifuge tube. Spike with 0.010mL of 1000mg/L second source NO_2^--N intermediate standard or .050mL of 200mg/L second source standard (expected concentration = 0.25mg/L NO_2^--N).

10.4 As applicable, prepare both NO_2^--N + NO_3^--N and NO_2^--N Matrix Spike (MS), Matrix Spike Duplicate (MSD) samples as follows:

10.4.1 Select a representative sample of the batch. Spike two duplicate 4.0g representative aliquots with 0.16mL of 100mg/L "first source" NO_3^--N Intermediate Standard (expected concentration = 0.4mg/L NO_3^--N).

10.4.2 Select a representative sample of the batch. Spike two duplicate 4.0g representative aliquots with 0.02mL of 200mg/L "first source" NO_2^--N intermediate standard (expected concentration = 0.10mg/L NO_2^--N).

10.5 To all of the above add 40.0mL of deionized (DI) water.

10.6 Shake samples for 1 hour on the TCLP tumbler.

10.7 Centrifuge for approximately 15min @ 3500rpm.

11. AQUEOUS FIELD SAMPLE, AQUEOUS EXTRACT AND ASSOCIATED QUALITY CONTROL (QC) SAMPLE PREPARATION

11.1 pH ADJUSTMENT OF AQUEOUS SAMPLES
If the samples were preserved with sulfuric acid, as is the case with nitrate + nitrite samples, adjust the pH to greater than 2 but no more than 9 as follows (see comment Section 4.7):

11.1.1 Place approximately 20mL of aqueous sample into a disposable centrifuge tube containing a stir bar.

11.1.2 Place a previously calibrated pH probe into the sample aliquot and adjust the pH using 10N NaOH until the pH is between 2 - 9. If the pH exceeds 9, add the original preserved sample drop wise to bring the pH back down into range.

NOTE: If samples are drinking water samples analyzed for compliance monitoring, then use concentrated ammonium hydroxide (NH_4OH) as the pH-adjusting reagent.

NOTE: After the pH of the sample is adjusted above pH 2, a 48-hour hold time begins. Samples are normally analyzed immediately after pH adjustment. Note also that for nitrite (only) analysis, samples are unpreserved.

11.2 Aliquot 5mL of each aqueous sample or previously prepared solid sample extract (including associated QC samples) into a designated auto sampler tube. If the aqueous sample or extract contains suspended solids, filter through a 0.45µm pore-diameter membrane filter.

11.3 Prepare the aqueous Method Blank (MB) by aliquotting 5mL of DI water into an auto sampler tube.

11.4 As applicable, prepare both the NO_2^--N + NO_3^--N and NO_2^--N aqueous Blank Spike, Laboratory Control Samples (LCS) as follows:

11.4.1 Aliquot 0.025mL of 100mg/L "second source" NO_3^--N Intermediate Standard into 5mL DI water (expected concentration = 0.5mg/L NO_3^--N).

11.4.2 Aliquot 0.010mL of 1000mg/L second source NO_2^--N into 100mL DI water or 0.010mL of 200mg/L second source solution into 20mL of DI water and mix. Transfer 5mL into a designated auto sampler tube (expected concentration = 0.10mg/L NO_2^--N).

11.5 As applicable, prepare both the NO_2^--N + NO_3^--N and NO_2^--N aqueous Matrix Spike (MS), Matrix Spike Duplicate (MSD) as follows:

11.5.1 Select a representative sample for the batch. Spike two duplicate 5mL aliquots with 0.020mL of 100mg/L "first source" NO_3^--N Intermediate Standard (expected concentration = 0.40mg/L NO_3^--N).

11.5.2 Select a representative sample for the batch. Spike two duplicate 5mL aliquots with 0.01mL of 200mg/L NO_2^--N. Mix well. Transfer 5mL into a designated auto sampler tube (expected concentration = 0.10mg/L NO_2^--N).

12. PREPARATION, USE AND MAINTENANCE OF CADMIUM REDUCTION COLUMN

12.1 CADMIUM PREPARATION

Place 10-20g of coarse cadmium granules (0.3 - 1.5mm diameter) in a 150mL beaker. Wash with two 25mL portions of 6N hydrochloric acid. Rinse several times with DI water.

CAUTION: Collect and store all waste cadmium. Cadmium is toxic and carcinogenic. Wear gloves and follow the precautions described on the Material Safety Data Sheet (MSDS).

12.2 COPPERIZATION

Repeatedly mix the Cd granules in portions of 100mL 2% Copper Sulfate Solution ($CuSO_4$). Swirl for about 5 minutes, then decant the liquid (discard in appropriate waste stream) and repeat with a fresh portion of 2% copper sulfate solution. Continue this process until the blue aqueous copper color persists. Decant and wash the copperized Cd granules at least five times with DI water to remove colloidal copper. The cadmium should be black or dark gray. The copperized cadmium granules may be stored in a stoppered bottle in ammonium chloride buffer.

12.3 PACKING THE CADMIUM COLUMN

The empty cadmium column is available as Lachat Part #50230. Wear gloves and do all cadmium transfers over a special tray or beaker dedicated to this purpose. Clamp the empty column upright so that your hands are free. Unscrew one of the colored fittings from an end of the column, and pull out and save the foam plug (if necessary, glass wool fiber and be used in lieu of the foam plug). When replacing the cap, it may be necessary to apply Teflon thread tape in order to prevent leakage. The column and threads are glass, so be careful not to break or chip them.

Scoop up prepared copperized cadmium granules with a spatula and pour them into the top of the column so that they sink down to the bottom of the column. Continue pouring the copperized cadmium in while gently tapping the column with a screwdriver handle or similar device to dislodge any air bubbles and also to prevent gaps in the cadmium filling. When the cadmium granules reach about 5 mm from

the open end of the column, push in the foam plug and screw on the top fitting. Rinse the outside of the column with DI water.

If air remains in the column or is introduced accidentally, a leur-lock syringe can be used to flush the column with ammonium chloride solution and push the air out.

Carefully cap both column ends for storage.

12.4 CADMIUM COLUMN INSERTION PROCEDURE

12.4.1 Before inserting the column, pump all reagents into the manifold making sure that there are no leaks.

12.4.2 Turn the pump to the lowest setting.

12.4.3 On the column, connect one of the union connectors to the outlet tubing of the buffer mixing coil.

12.4.4 Connect the open tubing on the column to the tee fitting where the color reagent is added. **BE CAREFUL TO NOT LET AIR ENTER THE COLUMN!!**

12.4.5 Turn column valve to open position. Return the pump to normal speed.

NOTE: The direction of reagent flow through the column is not relevant.

12.5 MONITORING COLUMN EFFICIENCY

12.5.1 Visually inspect the column. Check for air bubbles in the column or lines, gaps in the column packing, or any change in the cadmium surface characteristics (cadmium granules should be dark gray). If column treatment is necessary, see Note below.

12.5.2 Condition the column by running a 5mg/L NO_3^--N standard through it three times followed by reagent washing for approximately 1min.

12.5.3 Check the flow efficiency by disconnecting the cadmium column from the manifold and reconnecting to a green pump tube. Pump buffer through the packed column and collect the effluent in a graduated cylinder. The flow rate with the column thusly connected should be greater than 4.0mL/min.

NOTE: The presence of air in the column will decrease efficiency. Usually the problem can be corrected and the granules re-activated by using a leur-lock syringe to flush the column with solution (50mL ammonium chloride solution to push out the air, or 50mL of 0.2% copper sulfate solution followed by 50mL of ammonium chloride solution to re-activate the cadmium

granules). However, if the problem cannot be corrected, the column should be repacked per Section 12.3 of this SOP.

12.5.4 If the nitrite (NO_2^-N) check sample's percent recovery becomes too high (i.e., >120%), empty the column and retreat the cadmium granules as described in the Note above. Repacking and reinstalling the column should improve the column's efficiency.

13. GENERAL LACHAT OPERATION AND MAINTENANCE PROCEDURES

13.1 LACHAT INSTRUMENT SET UP

13.1.1 Turn power switches on for auto sampler, pump and the sample-processing module. Turn on the computer.

NOTE: The auto sampler will automatically perform an operation check by lifting the probe out of the rinse reservoir and advancing the sample cartridges by one position. The sample-processing module will open and shut each of the two valves, the LED of the heater control will display the current temperature of the block, and the lamp will come on.

13.1.2 Install the proper manifold for the analysis to be conducted (e.g., nitrate + nitrite analysis).

13.1.3 Place the appropriate interference filter into the upper slot of the detector.

13.1.4 Connect the "sample loop" to ports one and four of the injection valve.

13.1.5 Connect the "carrier" line to port two of the injection valve.

13.1.6 Place the manifold on to the sample processing module and connect the "to manifold" line to port three of the injection valve.

13.1.7 Connect the heating unit tubing to the manifold (if necessary).

NOTE: No heat is necessary for NO_2^--N + NO_3^-N and NO_2^--N analysis.

13.1.8 Insert each pump tube into a pump tube cartridge and place on the pump. Adjust the tension levers to maximum tension. ***Be sure that the pump tubes are seated correctly in the cartridges. This will prevent pinching of the tubes, which may restrict flow.***

NOTE: When preparing for any analysis that requires a column, make sure the column is in the ***off-line*** position at this time.

13.1.9 If you are running a heated procedure, set the heat controller temperature to the required setting by pressing the "on" button. To

adjust the temperature, press the "up" and "down" buttons. Press the "on" button again to lock in the setting.

NOTE: ***Be sure to turn the heat controller off at the end of the run!***

13.1.10 Prepare the appropriate working standards and place them in the sampler in order of decreasing concentrations. Complete filling of the sampler tray using the prepared samples to be analyzed.

13.1.11 After flushing the lines with deionized water, place the reagent lines into the proper reagent solutions and begin pumping reagent through the system.

NOTE: ***Some chemistries require a certain sequence in which reagents are introduced. Check the Lachat's operator's manual.***

13.1.12 If running a chemistry that requires a column, place the column ***on-line*** at this time by first turning the pump speed to the lowest setting, then placing the column switch to the "on-line" position. Turn the pump speed back to the required setting of 35rpm slowly, avoiding the introduction of any air bubbles.

13.1.13 Allow the reagents to be pumped through the entire system for at least 3-5 minutes.

13.1.14 Set up the computer as described in Section 13.2. Once the computer is set up, the system is ready to be started to begin calibration and data collection. Refer to the specific analyte procedure Sections of this SOP.

13.1.15 System shut down procedures are addressed in SOP Section 18.0.

13.2 COMPUTER SET UP PROCEDURE

13.2.1 From the Program Manager in Windows, double click on the "Lachat Instruments" icon. Then double click on the "Omnion FIA" icon. Click "OK" in the Omnion data system window.

NOTE: The sample probe will return to the wash reservoir and the injection valves will open and close.

13.2.2 Type your user name and password then click "OK". Click on the "Flow Injection Analysis" icon. If a username and password has not been assigned, have the System Manager assign one, or refer to the installation section of the *QuickChem 8000 Continuum Series*

Automated Ion Analyzer Omnion FIA Software Installation and Tutorial manual.

13.2.3 Load the method for the analyte(s) you want to run. From the menu bar, click on "File", then "Open Method". The path for Channel 1 is c:\Omnion\methods\method_temp\noxtemp.met. A new "Method" is created for each analysis each day of use. Each day's data are stored in an analyte subdirectory named for the year, using a mmdd format (e.g., c:\Omnion\methods\nox\2004\0412nox.met). This method pathway refers to NO_3^--N + NO_2^--N run on 04/12/2004.

NOTE: For native nitrite (only) analysis, substitute NO2 for NOX in all pathways. Example: c:\Omnion\methods\no2\2004\ 0412no2.met).

13.2.4 Load the master trays for the analyte(s) you want to run. From the "File" option on the menu bar, click on "Open Tray". Select the appropriate tray. The path for the default tray is c:\Omnion\trays\traytemp\noxtemp.tra. Each day's analysis data are stored in a subdirectory named for the year using a mmdd format (e.g., c:\Omnion\trays\2004\0412nox.tra). Fill in the sample identifications and dilution factors and save the tray by clicking "File", then "Save Tray As".

13.2.5 Check the calibration curve information by clicking on the "Review" icon, or pull down the "Method" menu and click on "Review Analyte Calibration Curve". If calibration curve data appears, clear the previous data by pulling down the "Method" menu and clicking on "Calibration Clear".

NOTE: You must clear the previous calibration curve before analyzing calibration standards.

13.3 MANIFOLD CLEANING PROCEDURE

If the baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure:

13.3.1 Place all reagent lines in deionized water and pump 2-5 minutes to clear the lines of all residual reagents.

13.3.2 Place the reagent lines and carrier in 1M hydrochloric acid (i.e., 82.6mL concentrated HCl brought to a final volume of liter using DI water). Allow the pump to run for several minutes to flush and clean the lines.

13.3.3 Place all the flushed lines in deionized water and pump until the HCl is thoroughly washed out.

13.4 Reattach all the reagent lines and resume pumping the reagents.

Note that the manifold cleaning procedure should be done with the column off-line or not attached.

14. PROCEDURE FOR DETERMINING NITRATE PLUS NITRITE

NOTE: When particulate matter is present, the sample must be filtered prior to the analyses. The sample may be centrifuged in place of filtration.

14.1 Prepare the calibration standards as described in Sections 7.0.

It should be noted that only the NO_3^--N standards and an NO_2^--N column check standard are used in the determination of nitrate + nitrite (see sequence below). This is done so that the standards are processed in the same manner as the samples (i.e., NO_3^--N content is reduced to NO_2^--N via the cadmium reduction column).

14.2 Prepare the samples as described in Sections 10.0 (aqueous leachates) or 11.0 (aqueous samples).

14.3 Fill the autosampler tubes with the appropriate standards and samples (including QC); load the auto sampler as described in Step 13.1.10 and per the run sequence depicted below:

Stage the autosampler per the following run sequence:

(1) 2.00mg/L NO_3^--N calibration standard
(2) 1.00mg/L NO_3^--N calibration standard
(3) 0.50mg/L NO_3^--N calibration standard
(4) 0.20mg/L NO_3^--N calibration standard
(5) 0.10mg/L NO_3^--N calibration standard
(6) 0.05mg/L NO_3^--N calibration standard
(7) 0.01mg/L NO_3^--N calibration standard
(8) 0.00mg/L NO_3^--N calibration standard
(9) 1.00mg/L NO_2^--N column check
(10) ICV (second source). Results must agree within ±10% of known value.
(11) ICB (Initial Calibration Blank, aqueous matrix Method Blank). *See also note below.* Any analyte concentration found must be less than the analyte reporting limit.
(12) Preparation (Method) Blank. Any analyte concentration found must be less than the analyte reporting limit.
(13) Laboratory Control Sample (LCS)

(14-21) maximum of 8 Field Samples (including MS/MSD)
(22) CCV (prepared like the 1.0mg/L calibration standard). Results must agree within ±10% of known value.
(23) CCB (DI water). Any analyte concentration found must be less than the analyte reporting limit.
(24-33) maximum of 10 Field Samples
(34) CCV
(35) CCB
(36) repeat Steps 24 through 35

NOTES: *It is often helpful to refer to your tray as a guide to ensure proper placement of standards and samples in the auto sampler.*

No more than ten samples (including QC) may be analyzed between the ICV/ICB and first CCV/CCB.

No more than ten samples (including QC) may be analyzed between CCV/CCB sets.

A CCV/CCB set must be analyzed to close-out the run sequence.

14.4 Complete the proper instrument set up as described in Steps 13.1.11 through 13.1.14.

14.5 Make sure the method and tray pathways are correctly set up and that the previous calibration information has been cleared as described in Section 13.2.

14.6 Start the run by clicking on the "Run Tray" icon. Click "Catalogue". Save the run data catalogue in the proper path using a mmdd format (i.e., c:\Omnion\data\nox\2004\0412nox.fdt). Click "Run" to begin the analysis process.

NOTE: The analysis may be paused or stopped in the middle of the run by clicking on the "Stop" icon. You can add samples or sample dilutions to your run by clicking on the "Tray" window and typing them in at the end of your saved tray. Save the updated information by first clicking "File", then "Save Tray". Restart the run by clicking "Resume". If you edit your tray by deleting standards or samples, you must "Save Tray As" by using the original file name with a "b" ("c", "d", etc.) added; example: 0412noxb.tra. Restart the analysis by renaming the data file in the same manner; example: 0412noxb.fdt.

15. PROCEDURE FOR DETERMINING NITRITE (ONLY) CONTENT

Prepare samples as described previous in Sections 10.0 or 11.0. To analyze for nitrite (only) content, use the same determination steps described in Section 14.0 above, with the following exceptions:

- Only the nitrite calibration standards (Section 8.0), and only the NO_2^--N QC samples (i.e., LCS and MS/MSD; Sections 10.0 and 11.0) need to be loaded into the autosampler (Step 13.1.10). *See run sequence below.*

- Aqueous field samples and the aqueous extracts of solid field samples analyzed for nitrite (only) do not require pH adjustment.

- The analyzer's cadmium column switch is placed in the "off-line" position for this analysis. The cadmium column is not used in nitrite determination.

- The pathway and naming convention used for the method is c:\Omnion\ methods\no2\2004\0412no2.met (substitute proper date, mmdd, for 0412).

  The pathway and naming convention used for the tray is c:\Omnion\trays\ 2004\0412no2.tra (substitute proper date, mmdd, for 0412).

  The pathway and naming convention used for the run data file is c:\Omnion\ data\no2\2004\0412no2.fdt (substitute proper date, mmdd, for 0412).

- <u>Stage the autosampler per the following run sequence:</u>

  (1) 0.50mg/L NO_2^--N calibration standard
  (2) 0.20mg/L NO_2^--N calibration standard
  (3) 0.10mg/L NO_2^--N calibration standard
  (4) 0.05mg/L NO_2^--N calibration standard
  (5) 0.02mg/L NO_2^--N calibration standard
  (6) 0.01mg/L NO_2^--N calibration standard
  (7) 0.00mg/L NO_2^--N calibration standard
  (8) ICV (second source). Results must agree within ±10% of known value.
  (9) ICB (Initial Calibration Blank, aqueous matrix Method Blank). *See also note below.* Any analyte concentration found must be less than the analyte reporting limit.
  (10) Preparation (Method) Blank. Any analyte concentration found must be less than the analyte reporting limit.
  (11) Laboratory Control Sample (LCS)
  (12-19) maximum of 8 Field Samples (including MS/MSD)
  (20) CCV (prepared like the 0.25mg/L calibration standard). Results must agree within ±10% of known value.
  (21) CCB (aqueous matrix method blank, DI water or KCl solution). Any analyte concentration found must be less than the analyte reporting limit.
  (22-31) maximum of 10 Field Samples
  (32) CCV
  (33) CCB
  (34) repeat Steps 22 through 33

NOTES: *It is often helpful to refer to your tray as a guide to ensure proper placement of standards and samples in the auto sampler.*

No more than ten samples (including QC) may be analyzed between the ICV/ICB and first CCV/CCB.

No more than ten samples (including QC) may be analyzed between CCV/CCB sets.

A CCV/CCB set must be analyzed to close-out the run sequence.

16. PROCEDURE FOR DETERMINING NITRATE (ONLY) CONTENT

Nitrate (only) is determined by subtracting the nitrite (only) sample results from the combined Nitrate + Nitrite sample results. An Excel spreadsheet is used to conduct all nitrate sample calculations. Refer to SOP Section 19.0.

17. REPORTING RESULTS

After the analysis is complete, print a copy of the following analyzer reports (access proper menu, "Open", "Print") and copy data to a data disk (access proper menu, "Import" and save to drive A:\, to be transferred to the LIMS:

- Tray Table(s) with any written comments and handwritten date and initials of analyst.
- Run Time Report(s); must be hand dated and initialed by the analyst.
- Import data (as txt. File) to be transferred i:\oprtns\wtchm\limsdata.

Results are calculated as described in SOP Section 19.

18. SYSTEM SHUT DOWN PROCEDURE

NOTE: ***Some methods require certain reagents to be removed last. Check the Lachat's operator's manual.***

18.1 If applicable, turn the pump setting down then switch the column to the "off-line" position.

18.2 Turn the heat down.

18.3 Remove the reagent lines from each reagent and place into deionized water. Turn the pump setting up so that the DI water is pumped through. Continue to run the system and allow the transmission lines to rinse for 5-10 minutes. ***This is a critical step in preventive maintenance of the manifolds.*** Then, allow the lines to suck air briefly to remove any liquid.

18.4 Release the cartridge tension on the transmission line to the sipper bath and remove the line from the deionized water. Turn the heat controller off (if required).

18.5 Make sure the appropriate files are saved, then exit and log off from the current Omnion session. Exit Windows and shut down the computer.

18.6 Remove the reagent transmission lines from the deionized water and allow all liquid to be pumped out of the manifold by pumping air through the lines.

18.7 Turn off the pump, auto sampler and manifold unit by switching off the power strip.

18.8 Release the pump tube cartridges tension completely to avoid the tubing from becoming crushed.

18.9 To remove the manifold, follow the Lachat set up procedure (Section 13.1) ***in reverse order***, starting with Step 13.1.8.

19. CALCULATIONS

19.1 Excel spreadsheets are used to verify spike information and calculate nitrate results by difference. The pathways for each Excel spreadsheet template are as follows:

Nitrate + nitrite, Nitrite, (aqueous and soil samples), spike verification information: i:\oprtns\wtchm\nox\template\noxautowver.xls.

Nitrate, calculation by difference:
i:\oprtns\wtchm\no3\template\no3temp.xls.

Call up each Excel spreadsheet template you need to use and rename it in the year's subdirectory using the identity of the mmdd (without the year reference) in the batch as a naming convention.

Example: i:\oprtns\wtchm\nox\2002\1211nox.xls.

19.2 The standard curve is plotted by the Lachat and is imported, along with all run data, to LIMS. Linear regression analysis of the standard curve yields a coefficient of determination (r^2) value. For the standard curve to be accepted, the r^2 value must be $\geq$ 0.995.

19.3 Applicable sample adjustments (i.e., dilutions, % solids) are made in LIMS and final sample analyte concentrations are quantitated. LIMS also calculates QC sample % recoveries and RPD values.

The representative sample calculation for NO_3^--N + NO_2^--N in soil samples is as follows:

$$\text{Concentration (mg/L)} = \frac{A \bullet D \bullet V}{W_{dry}}$$

where:

A = mg/L NO_3^--N + NO_2^--N (calculated from the sample peak area using the standard curve equation)

D = Dilution factor (if applicable)

V = Extract volume (mL); (40mL if this SOP is followed without deviation)

W_{dry} = Dry weight (g) of soil extracted (see equation below)

$$W_{dry} = \frac{W_{moist} \bullet \% \text{ solids}}{100}$$

where:

W_{moist} = moist weight of soil extracted

20. QUALITY CONTROL

20.1 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and are processed together as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike and duplicate (MS/MSD). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

20.2 METHOD BLANKS

Method blanks (MB) are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. For this procedure, the MB consists of 5mL DI water or 4.0g clean sand. Any analyte concentration found in the blank must be less than the analyte reporting limit.

20.3 LABORATORY CONTROL SAMPLE

The Laboratory Control Sample (LCS) is analyzed to measure the accuracy of the method. A known amount of analyte is spiked into an aliquot of representative clean matrix and analyzed. For this method, 5mL DI water (representative of aqueous samples) and 4.0g clean sand (representative of solid samples) were used as the clean matrices.

LCS results obtained are compared to results expected using the equation presented below:

$$\text{Percent Recovery (\%R)} = \frac{\text{Concentration}_{Found}}{\text{Concentration}_{Expected}} \times 100$$

where:

$Conc_{Found}$ = analyte concentration found in the LCS

$Conc_{Expected}$ = anticipated analyte concentration based on known amount spiked

To be acceptable, LCS recovery must be between 90% and 110% (aqueous matrix) and 85% and 115% (soil matrix) of the expected concentration.

20.4 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE

Matrix spikes (MS) consist of representative field samples into which known concentrations of target analyte(s) are spiked. MSs are analyzed as a means of determining the effect of matrix on target analyte detection.

The matrix spike is prepared in duplicate (MSD) to serve as a laboratory duplicate, which is analyzed to measure the precision of the analysis.

Analyte recovery for the MS/MSD is calculated as shown below:

$$\%R = \frac{Concentration_{Found} - Concentration_{Sample}}{Concentration_{Target}} \times 100$$

where:

$Conc_{Found}$ = analyte concentration found in the MS or MSD
$Conc_{Sample}$ = analyte concentration found in the native field sample
$Conc_{Target}$ = analyte concentration anticipated based on known amount spiked

The advisory quality control limits for MS/MSD recovery are set at 75-125%.

Precision is evaluated as the Relative Percent Difference (RPD) between the sample and its duplicate. RPD is calculated as shown below:

$$RPD\ (\%) = \frac{|Result_x - Result_{Dup}|}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

The RPD should be $\leq$20 to be accepted.

20.5 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study should be performed as needed and at a minimum, every 6 months.

20.6 LINEAR CALIBRATION RANGE STUDY

A linear calibration range (LCR) study must be performed at minimum, every six months, or whenever there is a significant change in operator, background or instrument response. The study must consist of a blank and a minimum of three standards. The range of the linearity study is broader than that defined as the linear calibration range, since the purpose of the linearity study is to verify the

instrument's overall capabilities. All verification data must agree within ±10% of expected values.

21. DEVIATIONS FROM METHOD

21.1 Section 6.5 of Method 353.2 provides for treated distilled water for the preparation of samples, standards and reagents. Paragon uses deionized (DI) water generated by the in-house laboratory deionization system. It has been demonstrated, through the analysis of MDL studies and PT samples that Paragon's DI water is free of NO_3^--N and NO_2^--N and meets ASTM Type I and II standards. Therefore, no additional treatment is applied.

21.2 SM 4500-NO_3^- I reagent citations, Section 6 of Method 353.2, and QuickChem Method 10-107-04-1-C all provide for the preservation of NO_3^--N and NO_2^--N stock standards with chloroform. Paragon closely monitors the performance of and assigned shelf lives of the 1000 mg/L nitrate (NO_3^--N) and nitrite (NO_2^--N) stock standards and does not preserve these standards with chloroform.

21.3 Section 6.9 of Method 353.2 discusses the creation and use of a wash solution. Because the type of automated flow injection analyzer used by Paragon provides a constant flow of reagents through the system, the use of a separate wash solution is not required.

21.4 The amount of EDTA used in the creation of the ammonium chloride/EDTA buffer solution presented in Section 6.10 of Method 353.2 (0.1g) differs from that presented in the reagent citations of SM4500-$NO3^-$ I (1.0g). Paragon uses an approximate median amount of 1.0g, because this amount is cited in the manufacturer's method, QuickChem Method 10-107-04-1-C.

The recipe for the ammonium chloride/EDTA buffer solution presented in Section 6.10 of Method 353.2 mentions the addition of 1/2mL "Brij-35" (available from Technicon Corporation) to the ammonium chloride/EDTA buffer solution. The addition of this material is not provided for in SM4500-$NO3^-$ I or in the manufacturer's method. Paragon does not add this material the ammonium chloride/EDTA buffer solution.

21.5 Section 6.0 of Method 353.2 provides for the use of KNO_2 in the creation of the nitrite standards. Paragon uses $NaNO_2$ to make the nitrite standards as provided for in Section 3g of SM4500-NO3- I.

21.6 Paragon uses a 200mg/L intermediate nitrite solution rather than the 100mg/L intermediate nitrite solution described in Method 353.2 (Section 6.0).

21.7 Section 10 of this SOP describes a solid preparation procedure. Paragon notes that Method EPA 353.2 is applicable to the measurement of nitrate/nitrite in surface and saline waters, and domestic and industrial wastes (Section 1.1).

21.8 Section 7.1 of Method 353.2, and QuickChem Method 10-107-04-1-C all provide for the adjustment of sample pH with Ammonium Hydroxide and Hydrochloric Acid. Paragon uses 10N Sodium Hydroxide and the actual preserved sample to adjust the pH. If samples are drinking water samples analyzed for compliance monitoring, then concentrated ammonium hydroxide (NH_4OH) will be used as the pH-adjusting reagent.

22. SAFETY, HAZARDS AND WASTE DISPOSAL

22.1 SAFETY HAZARDS

22.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

22.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

22.1.3 Wear gloves, safety glasses, and lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

22.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids)

22.1.5 All flammable compounds must be kept away from ignition sources.

22.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

22.1.7 Food and drink are prohibited in all lab areas.

22.2 WASTE DISPOSAL

22.2.1 Solid filtrate residues and any other solid residues shall be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

22.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

22.2.3 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Health and Safety Officer will provide specific procedures and materials for these samples.

23. REFERENCES

23.1 A.P.H.A., A.W.W.A. and W.P.C.F., 1989. Standard Methods for the Examination of Water and Wastewater, 20th edition, Revised 1998, Method 4500-NO_3 I.

23.2 Keeny, D.R. and D.W. Nelson, 1982. Methods of Soil Analysis, Part 2, Agronomy 9:649, American Society of Agronomists, Madison, WI. "Nitrogen - Inorganic Forms".

23.3 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, Revision 2.1, 1993, Method 353.2, "*Determination of Nitrate and Nitrate plus Nitrite by Colorimetric, Automated, Cadmium Reduction Procedure*".

23.4 Lachat Automated Ion Analyzer Methods Manual, Method Number 10-107-04-1C, Determination of Nitrate/Nitrite, Nitrite in Surface Water, Wastewater.

DOCUMENT REVISION HISTORY

7/6/06: Added reference Program Specification directive in "Responsibilities".

4/10/06: Updated Excel spreadsheet references to LIMS. Added DOCUMENT REVISION HISTORY.

7/20/08: Minor clerical corrections and procedural clarifications. Use of 0.2% copper sulfate solution added to REAGENTS and PROCEDURE. Use of leur-lock syringe to flush column rather than putting column under vacuum changed Section 12.

Analytical Method: EPA 353.2, SM 4500-NO_3 I	**Parameter:** Nitrate, Nitrate plus Nitrite, and Nitrite in water and soil		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point	As needed (i.e., at on-set of analyses or repeated when continuing calibration does not meet criteria)	Coefficient of determination (r^2) for linear regression must be $\geq$0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification (ICV); second source; at or below midpoint	Once after each initial calibration	Response must agree within $\pm$10% of initial calibration	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Blanks: Method Blank (MB), Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	The MB may be run initially as part of the calibration curve, the ICB is run following the calibration curve. CCBs are run following the CCV (after every ten samples), and to close an analytical run sequence	NO_2^--N / NO_3^--N content of the blank must be < RL	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Laboratory Control Sample (LCS)	One LCS must be run per 20 environmental samples of similar matrix	Results must agree within $\pm$10% of expected values for aqueous sample analyses; within ±15% for solid matrix extract analyses	Check all calculations. If no computation errors are found, prepare a fresh LCS and analyze. If criteria are still not met, system must be recalibrated and all samples run since the last acceptable LCS must be reanalyzed.
Continuing Calibration Verification (CCV); at or below midpoint; first source	Run after every ten samples and to end any run sequence (must be followed by a CCB analysis)	Response must agree within $\pm$10% of initial calibration	Check that calculations and preparation are correct, evaluate/ correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Matrix Spike (MS)	One per batch of $\leq$20 field samples of similar matrix	Recoveries should meet advisory limits of ±25% of the expected values; client-specified criteria may apply	Compare with LCS results and check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike (laboratory) Duplicate	One per batch of $\leq$ 20 field samples of similar matrix	(See MS recovery criteria above). RPD advisory limit is $\leq$20; client-specified criteria may apply	(See MS recovery criteria above). For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.

Analytical Method: EPA 353.2, SM 4500-NO_3 I	**Parameter:** Nitrate, Nitrate plus Nitrite, and Nitrite in water and soil		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	As needed; at minimum every 6 months.	Positive result < the analyte reporting limit (RL).	Determine the reason for failure and fix problem with the system. Repeat the MDL study. If criteria still not met, discuss with QA Manager (RL may be adjusted if required).
LCR Study	As needed, at minimum every 6 months.	All verification data must agree within ±10% of expected values.	Determine the reason for failure and fix problem with the system. Repeat the LCR study. If criteria still not met, discuss with QA Manager.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1128 REVISION 9

TITLE: DETERMINATION OF SPECIFIC CONDUCTANCE – METHODS EPA 120.1, SW9050A AND SM2510B

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/6/07

QUALITY ASSURANCE MANAGER _____ DATE 11/6/07

LABORATORY MANAGER _____ DATE 11-6-07

HISTORY: **SOP 643:** Rev0, 2/12/92; Rev1, 6/30/92; Rev2, 2/16/95; PCN# 357; Rev3, 3/15/96; Rev4, 10/7/99. **SOP 1128:** Rev5, 4/29/02; Rev6, 2/10/03; Rev7, 4/16/04, re-released w/o revision 3/29/05; Rev8, 7/23/05, re-released w/o revision 8/15/07; Rev9, 11/6/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the measurement of specific conductance of drinking, ground, surface, and saline waters and domestic and industrial aqueous wastes. This SOP is based on Methods EPA 120.1, SW9050A and SM2510B. This SOP also includes adapted procedures for determining specific conductance of solid matrix samples (via conductivity determination of aqueous leachates).

2. SUMMARY

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electrical current. Conductivity is measured using a Wheatstone bridge apparatus (a component of the conductivity meter). The ability of the solution to carry an electrical current is dependent on the presence of ions, their total concentrations, mobility, valence, relative concentrations, and on the temperature at the time of measurement. Solutions containing compounds that dissociate well are good conductors.

The specific conductance of a sample is measured in µmhos/cm using a conductivity meter equipped with a dip type conductivity cell. The measurements are made at 25±2°C. Results are reported at 25°C.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to the SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate and interpret acceptable

results utilizing these methods. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency evaluation test.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the bench sheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Temperature will affect specific conductance results due to the change in mobility of charged ions with changes in temperature. For most accurate results, the temperature of the calibrating standard and samples should be the same and as close to 25°C as possible. In order to provide an acceptable controlled measurement temperature, the calibration standards and samples are placed in a water bath maintained at 25±2°C for at least 1 hour and until just before analysis. Record the temperatures of the standards and samples on the bench sheet based on the actual water bath temperature.

4.2 A clean conductivity cell is critical to ensure accurate measurement of specific conductance. The specific conductance cell can become coated with oil and other materials. It is essential that the cell be thoroughly rinsed and, if necessary, cleaned between samples. A chromic-sulfuric acid cleaning mixture is used for cleaning; see manufacturer's instructions.

4.3 The electrodes of the conductivity cell are coated with platinum black. If the coating appears to be wearing or flaking off the electrodes, the cell should be cleaned and the electrodes re-platinized. Section 2c of Method SM2510B details the re-platinizing procedure.

5. APPARATUS and MATERIALS

5.1 Fisher Model Accumet 50 combination pH/conductivity meter or equivalent

5.2 Conductivity cell, YSI dip type, Model 3440, constructed from Pyrex™ glass with platinum electrodes or equivalent

5.3 Water bath maintained at 25±2°C

5.4 Centrifuge tubes, polypropylene, 50mL and 250mL, with caps

5.5 Wash bottle (filled with DI water to rinse cell between sample analyses)

5.6 Pipet, plastic, disposable

5.7 TCLP tumbler for soil preparation

6. REAGENTS

6.1 Deionized (DI) water with a conductivity less than 1µmho/cm.

6.2 Standard Potassium Chloride (KCl), 0.01M: First source. Dissolve 0.7456g anhydrous KCl in deionized water and bring to 1000mL final volume. This solution has a specific conductance of 1,413µmho/cm (1.413mmho/cm) at 25°C. *Shelf Life = 1 year.*

6.3 Standard Potassium Chloride, 0.005M: Second source. Dissolve 0.3728g anhydrous KCl in deionized water and bring to 1000mL final volume. This solution has a specific conductance of 718µmho/cm. *Shelf Life = 1 year.*

7. SAMPLE COLLECTION, HANDLING, PRESERVATION, AND HOLDING TIME

7.1 All samples should be collected according to an approved sampling plan.

7.2 Sample containers must be prewashed and thoroughly rinsed (certified clean containers may be used). Both plastic and glass containers are suitable.

7.3 The determination of conductivity is ideally a field measurement. Referenced laboratory methods state that conductivity should be analyzed within 24 hours, and if analysis within this time frame is not possible, samples should be filtered through a 0.45-micron filter and stored at 4±2°C. Paragon strives to analyze all conductivity samples as soon as possible, but allows for up to 4 days after receipt. Prior notification and/or special arrangements for Saturday sample receipt and analysis are encouraged between the client and the laboratory. However, the intention of the 4-day window is to accommodate the scenario of Friday sample collection, followed by login and release of the sample to the laboratory for analysis the following Monday, with the laboratory performing the analysis within 1 day of internal receipt. See also Section 10.1.

8. PROCEDURE

8.1 INSTRUMENT CALIBRATION

8.1.1 Connect the conductivity probe and turn the conductivity meter on. On the keypad of the conductivity meter, press “conductivity” to set the meter to conductivity mode.

8.1.2 Pour a portion of 0.01M Standard KCl solution into a centrifuge tube to use for cell preparation purposes. Use a plastic disposable transfer pipet to rinse the conductivity cell with the aliquotted 0.01M Standard

KCl solution. Use several small volumes, totaling about 5mL. Collect the wash solution in a waste beaker.

8.1.3 Immerse the conductivity cell in 45mL of 0.01M KCl standard, in order to fully submerge the probe's inlet holes when 50mL centrifuge tubes are used. Dip the electrode a few times to properly wet the cell and remove air bubbles. Allow the electrode to soak in 0.01M KCl solution until the displayed reading stabilizes.

8.1.4 The measurement of conductivity is temperature sensitive. In order to maintain consistent solution temperatures (and to obviate the need to apply temperature correction factors), Paragon uses a water bath maintained at 25±2°C.

Invoke the electronic spreadsheet (I:\Oprtns\ WTCHM\Specific Cond\template\spctemp.xls), and 'Save As' the current date. Record the temperature of the water bath to the nearest 0.5°C on the spreadsheet.

8.1.5 Remove the conductivity cell from the soak solution and rinse with DI water. Obtain an aliquot of 0.01M KCl solution that has been equilibrated in the water bath. Rinse the conductivity cell with several small volumes of solution; immerse the conductivity cell in the remaining solution. Press, "standardize" on the meter's keypad.

8.1.6 Set cell constant equal to "1 cm^{-1}" and press, "enter".

8.1.7 Note the conductivity value. This is the "displayed conductivity value". **The displayed conductivity value should be 1.41±0.14mmho/cm.**

NOTE: The instrument displays conductivity readings in milli-Siemens/cm (mS/cm) for conductivities greater than 1mS/cm. Siemens/cm units are the same as mho/cm units. For conductivities less than 1mS/cm, the display will show results in micro-Siemens/cm (µS/cm). 1mho/cm is equal to 1000mmho/cm units. 1mmho/cm is equal to 1000µmho/cm. *Be careful to use the correct units for the numerical value recorded.*

8.1.8 Use the following equation to calculate the actual cell constant:

$$\text{Cell Constant} = \frac{1.41\ \text{mmho/cm}}{\text{"displayed conductivity value" (mmho/cm)}}.$$

The cell constant value should be close to "1".

8.1.9 After calculating the cell constant, press, "standardize" on the keypad of the meter and enter the calculated result.

8.1.10 The instrument is now calibrated.

8.2 AQUEOUS EXTRACTION OF SOLID SAMPLES

8.2.1 Weigh a representative 10.0g aliquot of moist sample into a labeled 250mL disposable polypropylene centrifuge tube.

8.2.2 Select one sample representative of the batch and prepare a second 10.0g aliquot of moist sample to serve as the laboratory duplicate.

8.2.3 To all of the above add 100mL DI water.

8.2.4 Cap centrifuge tubes and shake for 1 hour on the TCLP tumbler.

8.2.5 Centrifuge for about 15min @ 3500rpm.

8.3 SAMPLE PREPARATION FOR ANALYSIS

8.3.1 Pour approximately 45mL of aqueous sample or extract into a labeled, dedicated, clean 50mL polypropylene centrifuge tube. Select one aqueous field sample per every ten field samples and prepare a duplicate aliquot for analysis.

8.3.2 Prepare the Initial Calibration Verification (ICV) standard from a ***second source standard*** by pouring an approximate 45mL aliquot of 0.005M Standard Potassium Chloride solution into a labeled polypropylene centrifuge tube.

8.3.3 Prepare the Continuing Calibration Verification (CCV) standard from a ***first source standard*** by pouring an approximate 45mL aliquot of 0.01M Standard Potassium Chloride solution into a labeled polypropylene centrifuge tube.

8.3.4 Place the centrifuge tubes in the water bath (at 25±2°C) and allow the solution temperatures to equilibrate (approximately 1 hour).

8.4 SAMPLE ANALYSIS

8.4.1 Record the temperature of the water bath to the nearest 0.5°C on the spreadsheet. Remove the conductivity cell from its soak solution and rinse thoroughly with deionized water.

8.4.2 Obtain the ICV from the water bath. Use a disposable pipet to rinse the conductivity cell with several small volumes of solution. Immerse the

conductivity cell in the remainder of this solution. Dip the electrode a few times to properly wet the cell and remove bubbles. The solution should completely cover the electrode.

8.4.3 Allow the reading to become stable. Record the stabilized conductivity reading (µmhos/cm) on the laboratory bench sheet template to 3 significant figures.

NOTES: Do not remove samples from the water bath until **just before** analysis in order to maintain proper temperature.

The ICV must be successfully analyzed before sample analyses can begin. The result must be 718±72µmho/cm. If the result is not within these limits, a problem exists and must be corrected before analyzing samples.

8.4.4 Clean the conductivity probe with deionized water between samples and repeat the techniques above until all samples have been analyzed. A CCV must be analyzed after every 10 samples and to close out the analysis sequence. The CCV result must be **1.41±0.14mmho/cm**. If the CCV result is outside these limits, a problem exists. When the problem has been corrected, restandardize the instrument and reanalyze all affected samples (i.e., samples that are not bracketed by passing calibration verifications). **Return the CCV to the water bath following each reading to maintain its temperature at 25±2°C.**

9. QUALITY CONTROL

A duplicate sample is analyzed per every 10 field samples as a measurement of analytical precision. Precision is expressed as the Relative Percent Difference (RPD) between a sample and its duplicate (see calculation below):

$$\text{RPD (\%)} = \frac{|\text{Result}_x - \text{Result}_{Dup}|}{\frac{(\text{Result}_x + \text{Result}_{Dup})}{2}} \times 100$$

The RPD should be $\leq$15% to be accepted.

10. DEVIATIONS FROM METHOD

10.1 Section 4.2 of Method EPA 120.1 states that analysis should be performed within 24 hours of collection. If not, samples should be filtered and stored at 4±2°C. Section 6.3 of Method SW9050A states that aqueous samples should be stored at 4±2°C and analyzed within 28 days. It is Paragon's policy to perform the analysis immediately upon receipt if the sample is received within 24 hours after sampling. If this is not possible, the laboratory will perform the analysis as soon as possible after receipt (sample stored at 4±2°C), but within four days of receipt.

Because Paragon analyzes the sample as soon as possible, samples are not filtered prior to storage.

10.2 Methods SW9050A and SM2510B reference use of a thermometer graduated to 0.1°C and directs that conductivity measurements be made and recorded to 0.1°C. Method EPA 120.1 stipulates the use of a thermometer graduated to 0.5°C and directs that 2% of the reading be added for each degree below 25°C and that 2% of the reading be subtracted for each degree above 25°C. Paragon equilibrates all standards and samples in a water bath maintained at 25±2°C. Because of the uniformity with which standards and samples are treated within prescribed temperature control limits, Paragon does not apply temperature correction factors to the analysis results. Based on the directives contained in Method EPA 120.1, maximum error is ±1% of the conductivity reading obtained.

10.3 Section 5.2 of Method SW9050A states that suitable conductivity water should be generated by passing distilled water through a mixed-bed deionizer and discarding the first 1,000mL. Conductivity should be less than 1µS/cm. It should be noted that deionized (DI) water available from the Paragon's deionized water system taps generates DI water of quality that meets or exceeds this criterion. Details regarding Paragon's DI water system and its monitoring can be found in SOP 319.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, Reactivity ratings and date opened.

11.2 WASTE DISPOSAL

11.2.1 The aqueous samples shall be disposed of in the Aqueous Laboratory Waste.

11.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 Fisher Model 50 Accumet pH meter operating instructions (Rev. C 2/92).

12.2 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, Revision 2.1, 1993. Method 120.1, "Specific Conductance, μmhos at 25°C".

12.3 A.P.H.A., A.W.W.A. and W.P.C.F., 1989. Standard Methods for the Examination of Water and Wastewater, 20th edition, Revised 1998. Method 2510B.

12.4 U.S. Environmental Protection Agency, SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 6. Method 9050A, "Specific Conductance, Revision 1, December 1996.

DOCUMENT REVISION HISTORY

3/29/05: Updated format.

7/23/05: Program specification language added.

8/15/07: Added DOCUMENT REVISION HISTORY Section.

11/6/07: Expanded Section 7.3 discussion and referenced Section 10.1 as well.

Analytical Method: E 120.1; SW 9050A; SM 2510B	**Parameter:** Specific Conductance		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Calibration: Conductivity meter standardized per manufacturer's instruction	Daily; each day of use.	0.01 M Standard KCl used for standardization; displayed conductivity value must read 1.41 0.14mmho/cm.	If targeted conductivity value not displayed; check meter settings and connections and condition of the conductivity cell. Check temperature of standardization solution and reanalyze. If problem not corrected, prepare fresh KCl standard (oven conditioning of KCl salt may be required prior to preparation) and repeat standardization.
Initial Calibration Verification (ICV); second source	Daily; each day of use. Run following standardization and before any samples are analyzed.	Results for the ICV must agree within ±10 % of the 718µmho/cm expected (true) value (646 - 790µmho/cm).	If ICV criterion not met, check for preparatory error (remake if necessary) and conductivity cell function; reanalyze. If ICV criterion still not met, restandardize meter.
Continuing Calibration Verification (CCV); first source	Run to bracket each set of 10 environmental samples processed and to closeout the analytical sequence.	Results for the CCV must agree within ±10 % of the 1.41mmho/cm expected (true) value (1.27-1.55mmho/cm).	If CCV criterion not met, check for preparatory error (remake if necessary) and conductivity cell function; reanalyze. All samples run since the last acceptable CCV must also be reanalyzed.
Laboratory Duplicate (DUP)	One per set of ≤10 field samples.	RPD must be ≤15%.	Check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1129 REVISION 6

TITLE: **DETERMINATION OF AMMONIA USING AN AUTOMATED PHENOLATE PROCEDURE -- METHODS EPA 350.1, SM4500 NH_3-N H AND QUIKCHEM METHOD 10-107-06-1-C**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/6/07

QUALITY ASSURANCE MANAGER _____ DATE 11/6/07

LABORATORY MANAGER _____ DATE 11-6-07

HISTORY: Rev0, 4/29/02; Rev1, 12/13/02; Rev2, 2/10/03; Rev3, 3/6/03; Rev4, 3/29/05; Rev5, 7/26/05; Rev6, 11/6/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) references EPA Method 350.1, Standard Method (SM) 4500 NH_3-N H, and Quikchem Method 10-107-06-1-C for the determination of ammonia as nitrogen (NH_3-N) in drinking, ground and surface waters, domestic and industrial wastes, and solid samples.

2. SUMMARY

This procedure is based on the Berthelot reaction and uses a Lachat Quikchem auto flow injection analyzer procedure. Ammonium (NH^{4+}) present in the sample or extract reacts with alkaline phenol and then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (sodium nitroferricyanide) is added to enhance color development. The absorbance of the reaction product is measured at 630nm, and is directly proportional to the original ammonium concentration. Test values are reported as NH_3-N.

To analyze solid matrix samples, first an aqueous sample extract is created by extracting an aliquot of solid sample with 2M potassium chloride (KCl) solution (1:10 ratio), and shaking on a TCLP-type rotary tumbler. The exchangeable NH^{4+} cations contained in the sample aliquot are displaced from the soil by the high concentration of K^+ cations available in the extraction solution. The ammonium displaced to the extract is then determined with the auto analyzer.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of

Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Calcium and magnesium ions may precipitate if present in sufficient concentrations. EDTA solution is added to the prepared sample in-line in order to prevent this problem.

4.2 Excessive color, turbidity and certain organic species may interfere. Turbidity is removed by manual filtration through a 0.45µm pore diameter membrane filter. Sample color may be corrected for by running the samples through the manifold without color formation. A corrected absorbance reading is then obtained by subtracting the initial absorbance (without color formation) from the final absorbance reading to obtain a corrected absorbance reading. Paragon does not routinely correct for color.

4.3 Standard procedures recommend acidifying samples to be analyzed for ammonia as nitrogen to pH < 2 for preservation. Samples that are over-acidified with sulfuric acid preservative will cause a negative response within the peak area during analysis. To overcome this, EDTA buffer is added to all prepared samples as part of the analysis process.

5. APPARATUS AND MATERIALS

5.1 Flow injection analysis equipment designed to deliver and mix/react sample and reagents in the required order and ratios. Lachat Quikchem 8000, or equivalent, equipped with the following:

- Autosampler
- Disposable autosampler tubes
- Multi-channel peristaltic pump
- heating unit
- Instrument manifold
- Spectrophotometric detector with 630nm filter in place
- Data system (Windows 3.1 and Ominion software version 1.4), or equivalents

5.2 volumetric dispensers, Eppendorf™ or equivalent, capable of dispensing 0.01-5.0mL

5.3 TCLP-type mechanical tumbler, capable of 1 hour soil extraction by agitation

5.4 centrifuge, capable of sustaining 3500rpm

5.5 centrifuge tubes with caps, disposable, 50mL

5.6 volumetric flasks, various sizes, Class A

5.7 magnetic stir bars, Teflon coated

5.8 magnetic stir plate, capable of variable speed control

5.9 analytical balance, capable of weighing to 0.0001g

5.10 Corning pH meter, Model 320 or equivalent, and appropriate buffer solutions for calibration. Capable of a two-point calibration.

5.11 syringe, with 0.45µm filter disk

6. REAGENTS

NOTES: To prevent bubble formation, degas all solutions, *except those noted*, with helium (He). Use He at 140kPa (20lb/in^2) applied through a helium degassing tube (Lachat Part 50100, or equivalent). Bubble He vigorously through the solution for one minute.

Only ACS grade or better chemicals and reagents may be used. Unless otherwise noted, reagents may be stored in polypropylene containers.

6.1 Deionized (DI) water. Obtained from the laboratory DI water system.

6.2 Ottawa sand. EMD, SX0075-3 or equivalent. *Shelf life = indefinite.*

6.3 Sodium Phenolate Solution: In a 500mL volumetric flask, dissolve 44mL of 88 % liquefied phenol or 41g of crystalline phenol (C_6H_5OH) in approximately 300mL of DI water. While stirring, *slowly* add 16g sodium hydroxide (NaOH). Cool. When cool, dilute to 500mL with DI water. Cap tightly and gently invert several times to mix. *Do not degas this reagent. Shelf Life = 1 year.*

CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin.

6.4 Sodium Hypochlorite (NaOCl) Solution: In a 200mL volumetric flask, dilute 100g Regular Clorox bleach (5.25% sodium hypochlorite, can be purchased a local store) to the mark with degassed DI water. Cap and invert several times to mix. *Shelf Life = 1 year.*

6.5 EDTA Buffer, 5%: JT Baker, L693-07 or equivalent. In a 1L volumetric flask, dissolve 50.0g of disodium ethylenediamine tetraacetate ($C_{10}H_{14}Na_2O_8 \bullet 2H_2O$) and 11.0g of sodium hydroxide (NaOH) in about 900mL of degassed DI water. Dilute to 1L with degassed DI water. Cap and gently invert several times to mix. *Shelf Life = 1 year.*

6.6 Sodium Nitroprusside (Sodium Nitroferricyanide) Solution, 0.35%: Mallinckrodt, 7828-02 or equivalent. In a 1L volumetric flask containing a small amount of degassed DI water, dissolve 3.50g sodium nitroprusside (sodium nitroferricyanide; $[Na_3Fe(CN)_5NO \bullet 2H_2O]$) and dilute to 1L with degassed DI water. *Store in amber glass and refrigerate. Shelf Life = 1 year.*

6.7 Potassium Chloride (KCl) Solution, 2M: JT Baker, 3052-01 or equivalent. Dissolve 235g potassium chloride (KCl) in 1500mL DI water. *Do not degas this solution. Shelf Life = 1 year.*

6.8 Sodium Hydroxide Solution, 10N: JT Baker, 3722-07 or equivalent. Dissolve 160.0g Sodium Hydroxide (NaOH) to a final volume of 400mL using DI water. Not degassed. *Shelf life = 1 year.*

7. STANDARDS -- DO NOT degas standards.

7.1 Ammonia as N Stock Solutions, 1000mg/L NH_3 as N, 1st and 2nd sources: GFS Chemicals, Item No. 645 or equivalent. Purchased from different commercial vendors or created in-house by dissolving 3.821g ammonium chloride (NH_4Cl) salt (the two measures of ammonium chloride salt must be obtained from two different lot numbers) in DI water and diluting to 1L with DI water. *Store in a polypropylene bottle; refrigerate. Shelf Life = 1 year.*

7.2 Ammonia as N Intermediate Standard Solutions, 50mg/L NH_3 as N, 1st and 2nd sources: Made from diluting 5.0mL 1st and 2nd source ammonia as N stock solutions to 100mL using DI water and 100mL volumetric flasks. Cap and invert several times to mix. The working calibration standards and the continuing calibration verification standard (CCV) are made from the 1st source ammonia as N intermediate standard solution; the initial calibration verification standard (ICV) and the laboratory control sample (LCS) are made from the 2nd source ammonia as N intermediate standard solution. *Store in polypropylene bottles; refrigerate. Shelf Life = 3 months.*

7.3 Ammonia as N Calibration Standards (per Table below): Made in-house on each day of calibration by dilution of the 50mg/L intermediate ammonia as N standard, 1st source, with DI water. The final volume for all calibration standards is 5.0mL.

Pipet 5.0mL DI water into a clean auto sampler tube to prepare each calibration standard. Before pipetting the appropriate aliquot of intermediate standard into the tube, first remove an equivalent volume of water from the auto sampler tube, using the pipet, so that the final volume contained in the autosampler tube is 5.0mL.

VOLUME OF 50mg/L Ammonia as N INTERMEDIATE STANDARD SOLUTION, 1st SOURCE (mL)	CONCENTRATION OF FINAL CALIBRATION SOLUTION (mg/L NH_3 as N)
0.00	0.00
0.01	0.10
0.02	0.20
0.05	0.50
0.10	1.00
0.20	2.00
0.50	5.00

7.4 Initial Calibration Verification (ICV) Standard, 1.00mg/L: Use 0.10mL of 50mg/L Ammonia as N Intermediate Standard Solution, *2nd source*, to create 5.0mL of ICV standard in DI water.

7.5 Continuing Calibration Verification (CCV) Standard, 2.00mg/L: Use 0.20mL of 50mg/L Ammonia as N Intermediate Standard Solution, *1st source*, to create 5.0mL of CCV standard in DI water.

8. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

8.1 Samples must be collected according to an approved sampling plan.

8.2 Water samples must be acidified with Sulfuric Acid (H_2SO_4) to pH <2 at the time of collection. The acidified samples should be kept chilled (4±2°C) until analysis. Properly preserved water samples must be analyzed within 28 days of collection.

8.3 There are no chemical preservation considerations or holding time requirements for solid sample matrices. Soil samples should be chilled (4±2°C) until analysis.

9. AQUEOUS EXTRACTION OF SOLID SAMPLES AND ASSOCIATED QUALITY CONTROL (QC) SAMPLE PREPARATION

9.1 Weigh a representative 4.0g aliquot of moist sample into a labeled 50mL disposable polypropylene centrifuge tube.

9.2 Prepare a Method Blank (MB) by weighing 4.0g clean Ottawa sand into a labeled 50mL disposable polypropylene centrifuge tube. One method blank must be prepared for each batch of twenty (or fewer) solid matrix environmental samples processed together as a unit. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. An MB should also be prepared and analyzed each time there is a change in reagents.

9.3 Prepare a Laboratory Control Sample (LCS) by weighing 4.0g clean silica sand into a labeled 50mL disposable polypropylene centrifuge tube. Add 0.08mL of 1000mg/L Ammonia as N Stock Standard Solution (or 1.6mL of 50mg/L Ammonia as N solution), *2nd source*. One LCS should be prepared for each batch of twenty (or fewer) solid matrix environmental samples processed together as a unit. The Laboratory Control Sample (LCS) is analyzed to measure the accuracy of the method. The concentration of the LCS is expected to be 2.00mg/L.

9.4 Prepare a Matrix Spike (MS), Matrix Spike Duplicate (MSD) set as follows: Select a representative sample of the batch. To two 4.0g representative moist aliquots of selected sample, add 0.04mL of 1000mg/L Ammonia as N Stock Standard Solution (or 0.8mL of 50mg/L Ammonia as N solution), *1st source.* Matrix spiked samples are analyzed as a means of determining the effect of matrix on target analyte detection. The matrix spiked sample is prepared in duplicate to serve as a laboratory duplicate, which is analyzed to measure the precision of the analysis. One MS/MSD set should be prepared for each batch of twenty (or fewer) solid matrix environmental samples processed together as a unit. The concentration of the MS and MSD is expected to be 1.00mg/L.

9.5 To all of the above add 40.0mL 2M KCl solution.

9.6 Cap the prepared sample aliquots and shake for 1 hour on the TCLP tumbler.

9.7 Centrifuge the aqueous extracts for about 15 minutes at 3500rpm.

10. AQUEOUS FIELD SAMPLE, ASSOCIATED AQUEOUS QUALITY CONTROL (QC) SAMPLE, AND AQUEOUS EXTRACT PREPARATION FOR ANALYSIS

10.1 The reference methods discuss pH adjustment to between 5 and 9 for acid-preserved samples. This is only necessary in cases where the addition of EDTA buffer is not capable of producing adequate pH adjustment. Should pH adjustment be required, follow the Steps below:

10.1.1 Place approximately 20mL of aqueous sample into a disposable centrifuge tube containing a stir bar.

10.1.2 Place a previously calibrated pH probe into the sample aliquot and adjust the pH using 10N NaOH until the pH is between 5-9. If the pH

exceeds 9, add the original preserved sample drop wise to bring the pH back down into range.

10.2 Aliquot 5.0mL of each aqueous sample or previously prepared solid sample extract (including associated QC samples) into a designated auto sampler tube. If the aqueous sample or extract contains suspended solids, filter through a 0.45µm pore-diameter membrane filter.

10.3 Prepare the aqueous Method Blank (MB) by aliquoting 5.0mL of DI water into an auto sampler tube. One method blank must be prepared for each batch of twenty (or fewer) aqueous matrix environmental samples processed together as a unit. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. An MB should also be prepared and analyzed each time there is a change in reagents.

10.4 Prepare the aqueous Laboratory Control Samples (LCS) similar to the ICV standard by using 0.10mL of 50mg/L Ammonia as N Intermediate Standard Solution, *2nd source*, to create 5.0mL of LCS in DI water. One LCS must be prepared for each batch of twenty (or fewer) aqueous matrix environmental samples processed together as a unit. The LCS is analyzed to measure the accuracy of the method. The concentration of the LCS is expected to be 1.00mg/L.

10.5 Prepare a Matrix Spike (MS), Matrix Spike Duplicate (MSD) set as follows: Select a representative sample of the batch. To two 5.0mL representative aliquots of selected sample, add 0.10mL of 50mg/L Ammonia as N Intermediate Standard Solution, *1st source*. One MS/MSD set should be prepared for each batch of twenty (or fewer) aqueous matrix environmental samples processed together as a unit. Matrix spiked samples are analyzed as a means of determining the effect of matrix on target analyte detection; the matrix spiked sample is prepared in duplicate to serve as a laboratory duplicate, which is analyzed to measure the precision of the analysis. The concentration of the MS and MSD is expected to be 1.00mg/L.

11. GENERAL LACHAT OPERATION AND MAINTENANCE PROCEDURES

11.1 LACHAT INSTRUMENT SET UP

11.1.1 Turn on power to auto sampler, pump and the sample processing module by switching on the power strip. Turn on the computer.

NOTE: The auto sampler will automatically perform an operation check by lifting the probe out of the rinse reservoir and advancing the sample cartridges by one position. The sample processing module will open and shut each of the two valves, the LED of the heater control will display the current temperature of the block, and the lamp will come on.

11.1.2 Install the proper manifold for the analysis to be conducted (e.g., ammonia nitrogen analysis).

11.1.3 Place the appropriate interference filter into the upper slot of the detector.

11.1.4 Connect the "sample loop" to ports one and four of the injection valve.

11.1.5 Connect the "carrier" line to port two of the injection valve.

11.1.6 Place the manifold on to the sample processing module and connect the "to manifold" line to port three of the injection valve.

11.1.7 Connect the heating unit tubing to the manifold (if necessary).

11.1.8 Insert each pump tube into a pump tube cartridge and place on the pump. Adjust the tension levers to maximum tension. **Be sure that the pump tubes are seated correctly in the cartridges. This will prevent pinching of the tubes, which may restrict flow.**

NOTE: When preparing for any analysis that requires a column, make sure the column is in the **off-line** position at this time.

11.1.9 This is a heated procedure. Set the heat controller temperature to the required setting, 60°C, by pressing the "on" button. To adjust the temperature, press the "up" and "down" buttons. Press the "on" button again to lock in the setting.

NOTE: Be sure to turn the heat controller off at the end of the run!

11.1.10 Prepare the calibration standards (Section 7.0) and place them in the auto sampler in order of decreasing concentrations. Complete filling the sampler tray using the prepared samples to be analyzed.

11.1.11 After flushing the lines with deionized water, place the reagent lines into the proper reagent solutions and begin pumping reagent through the system.

NOTE: Some chemistries require a certain sequence in which reagents are introduced. Check the LACHAT operator's manual.

11.1.12 This chemistry does not require use of a column.

11.1.13 Allow the reagents to be pumped through the entire system for at least 3-5 minutes.

11.1.14 Set up the computer as described in Section 11.2 below. Once the computer is set up, the system is ready to be started to begin calibration and data collection. *Note that system shut down procedures are addressed in Section 14.*

11.2 COMPUTER SET UP PROCEDURE

11.2.1 From the Program Manager in Windows, double click on the "Lachat Instruments" icon. Then double click on the "Omnion FIA" icon. Click "OK" in the Omnion data system window.

NOTE: The sample probe will return to the wash reservoir and the injection valves will open and close.

11.2.2 Type your user name and password then click "OK". Click on the "Flow Injection Analysis" icon. If a user name and password has not been assigned, have the System Manager assign one, or refer to the installation section of the *Quickchem 8000 Continuum Series Automated Ion Analyzer Omnion FIA Software Installation and Tutorial* manual.

11.2.3 Load the method for the analyte(s) you want to run. From the menu bar, click on "File", then "Open Method". The path for Channel 2 is c:\Omnion\methods\methodtemp\nh3temp2.met. A new "Method" is created for each analysis each day of use. Each day's data are stored in an analyte subdirectory named for the year, using a mmdd format (e.g., c:\Omnion\methods\nh3\2004\1128nh.met). This method pathway refers to ammonia nitrogen run on 11/28/2004.

11.2.4 Load the master trays for the analyte(s) you want to run. From the "File" option on the menu bar, click on "Open Tray". Select the appropriate tray. The path for the default tray is c:\Omnion\trays\traytemp\nh3temp.tra. Fill in the sample identifications and dilution factor and save the tray by clicking "File", then "Save Tray As".

Each day's analysis data are stored in a subdirectory named for the year using a mmdd format (e.g., c:\Omnion\trays\nh3\2004\1128nh.tra).

11.2.5 Check the calibration curve information by clicking on the "Review" icon, or pull down the "Method" menu and click on "Review Analyte Calibration Curve". If calibration curve data appears, clear the previous data by pulling down the "Method" menu and clicking on "Calibration Clear".

NOTE: You must clear the previous calibration curve before analyzing calibration standards.

11.3 MANIFOLD CLEANING PROCEDURE
If the baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure:

11.3.1 Place all reagent lines in deionized water and pump 2-5 minutes to clear the lines of all residual reagents.

11.3.2 Place the reagent lines and carrier in 1M hydrochloric acid (i.e., 82.6mL concentrated HCl brought to a final volume of 1L using DI water). Allow the pump to run for several minutes to flush and clean the lines.

11.3.3 Place all the flushed lines in deionized water and pump until the HCl is thoroughly washed out.

11.3.4 Reattach all the reagent lines and resume pumping the reagents.

12. PROCEDURE

NOTE: When particulate matter is present, the sample must be filtered prior to analyses. The sample may be centrifuged in place of filtration.

12.1 Prepare the calibration standards as described in Section 7. Set heat to 60°C on the Lachat analyzer.

12.2 Prepare the samples as described in Sections 9 and 10.

12.3 Fill the autosampler tubes with the appropriate standards and samples (including QC); load the auto sampler as described in Step 11.1. and per the run sequence depicted below:

(1) 5.00mg/L NH_3-N calibration standard
(2) 2.00mg/L NH_3-N calibration standard
(3) 1.00mg/L NH_3-N calibration standard
(4) 0.50mg/L NH_3-N calibration standard
(5) 0.20mg/L NH_3-N calibration standard
(6) 0.10mg/L NH_3-N calibration standard
(7) 0.00mg/L NH_3-N calibration standard
(8) ICV (second source)
(9) ICB (Initial Calibration Blank)

(10) Method Blank (MB)

(11) Laboratory Control Sample (LCS)

(12) maximum of 8 Field Samples (including MS/MSD)

(22) CCV (Section 7.)

(23) CCB (DI water blank)

(24) maximum of 10 Field Samples

(34) CCV

(35) CCB

(36) repeat steps 10 through 22

NOTES: It is often helpful to refer to your tray as a guide to ensure proper placement of standards and samples in the auto sampler.

No more than ten samples (including QC) may be analyzed between the ICV/ICB and first CCV/CCB.

No more than ten samples (including QC) may be analyzed between CCV/CCB sets.

A CCV/CCB set must be analyzed to close-out the run sequence.

See QC Table for QC sample acceptance limits.

12.4 Complete the proper instrument set up as described in Steps 11.1.11 through 11.1.14.

12.5 Make sure the method and tray pathways are correctly set up and that the previous calibration information has been cleared as described in Section 11.2.

12.6 Start the run by clicking on the "Run Tray" icon. Click "Catalogue". Save the run data catalogue in the proper path using a mmdd format (i.e., c:\Omnion\data\nh3\2004\1128nh.fdt). Click "Run" to begin the analysis process.

NOTE: The analysis may be paused or stopped in the middle of the run by clicking on the "Stop" icon. You can add samples or sample dilutions to your run by clicking on the "Tray" window and typing them in at the end of your saved tray. Save the updated information by first clicking "File", then "Save Tray". Restart the run by clicking "Resume". If you edit your tray by deleting standards or samples, you must "Save Tray As" by using the original file name with a "b" ("c", "d", etc.) added; example: 1128nhb.tra. Restart the analysis by renaming the data file in the same manner; example: 1128nhb.fdt.

13. CALCULATIONS AND REPORTING RESULTS

13.1 After the analysis is complete, print a copy of the following analyzer reports (access proper menu, "Open", "Print"), and deliver them to the Reporting Group:

- Tray Table(s) with any written comments and handwritten date and initials of analyst.
- Run Time Report(s); must be hand dated and initialed by the analyst.
- Custom Report(s) with just header information.

13.2 The analyzer data is directed to a designated network directory from which the Reporting Group imports it into LIMS. All sample calculations are performed in LIMS.

13.2.1 Sample quantitation is accomplished using a standard curve, which is generated by plotting the peak areas of the processed standards against their known concentrations. The linear regression analysis of the standard curve must yield a correlation coefficient (r^2) value $\geq$0.995 to be acceptable.

13.2.2 The representative sample calculation for NH3 as N in soil samples is as follows:

$$\text{Concentration (mg/L)} = \frac{A \bullet D \bullet V}{W_{dry}}$$

where:

A = mg/L NH_3 as N (calculated from the sample peak area using the standard curve equation)

D = Dilution factor (if applicable)

V = Extract volume (mL); (100 mL if this SOP is followed without deviation)

W_{dry} = Dry weight (g) of soil extracted (see equation below)

$$W_{dry} = \frac{W_{moist} \bullet \%\ solids}{100}$$

where:

W_{moist} = moist weight of soil extracted

13.2.3 Note that sample results are adjusted for dilutions and/or % solids, as applicable.

13.2.4 Percent recoveries and RPD values for QC sample analyses are also calculated (see Section 15 for further details).

14. SYSTEM SHUT DOWN PROCEDURE

NOTE: Some methods require certain reagents to be removed last. Check the LACHAT operator's manual.

14.1 Make sure the appropriate files are saved, then exit and log off from the current Omnion session. Exit Windows and shut down the computer.

14.2 If applicable, turn the pump setting down then switch the column to the "off-line" position.

14.3 Remove the reagent lines from each reagent and place into deionized water. Turn the pump setting up so that the DI water is pumped through. Continue to run the system and allow the transmission lines to rinse for 5-10 minutes. ***This is a critical step in preventive maintenance of the manifolds.***

14.4 Release the cartridge tension on the transmission line to the sipper bath and remove the line from the deionized water. Turn the heat controller off (if required).

14.5 Remove the reagent transmission lines from the deionized water and allow all liquid to be pumped out of the manifold by pumping air through the lines.

14.6 Turn off the pump, auto sampler and manifold unit by switching off the power strip.

14.7 Release the pump tube cartridges tension completely to avoid the tubing from becoming crushed.

14.8 To remove the manifold, follow the Lachat set up procedure (Section 11.1) in reverse order, starting with Step 11.1.8.

15. QUALITY CONTROL

Various types of quality control (QC) samples such as method blank (MB), laboratory control sample (LCS) and matrix spike/matrix spike duplicate (MS/MSD) are discussed previously in Sections 9 and 10. Acceptance criteria for these samples are shown in the QC Check Summary Table presented at the end of this SOP.

15.1 LABORATORY CONTROL SAMPLE

LCS results obtained are compared to results expected using the equation presented below:

$$\text{Percent Recovery (\%R)} = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Expected}}} \times 100$$

where:

$Conc_{Found}$ = analyte concentration found in the LCS

$Conc_{Expected}$ = anticipated analyte concentration based on known amount spiked

15.2 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE

Analyte recovery for the MS/MSD is calculated as shown below:

$$\%R = \frac{Concentration_{Found} - Concentration_{Sample}}{Concentration_{Target}} \times 100$$

where:

$Conc_{Found}$ = analyte concentration found in the MS or MSD

$Conc_{Sample}$ = analyte concentration found in the native field sample

$Conc_{Target}$ = analyte concentration anticipated based on known amount spiked

Precision is evaluated as the Relative Percent Difference (RPD) between the sample and it's duplicate. RPD is calculated as shown below:

$$RPD\ (\%) = \frac{|Result_x - Result_{Dup}|}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

15.3 LINEARITY STUDY

A linear calibration range (LCR) study must be performed at minimum, every six months, or whenever there is a significant change in operator, background or instrument response. The study must consist of a blank and a minimum of three standards. The range of the linearity study is broader than that defined as the linear calibration range, since the purpose of the linearity study is to verify the instrument's overall capabilities. All verification data must agree within ±10% of expected values.

15.4 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study shall be performed as needed and at a minimum, every six months.

16. DEVIATIONS FROM METHODS

16.1 Section 6.1 of Method 350.1 and Section 3a of Method SM4500-NH_3 H state that all solutions must be made in ammonia-free water and discusses the use of treated distilled water. Paragon uses deionized (DI) water generated by the in-house laboratory deionization system. It has been demonstrated, through the analysis of MDL studies, PT samples, etc., that Paragon's DI water is ammonia-free and meets ASTM Type I and II standards.

16.2 Section 6.4 of Method 350.1 states that due to the instability of the sodium hypochlorite solution, storage over an extended period should be avoided. It is Paragon's policy to store this solution up to one year. Successful analysis of PT samples has indicated no negative impact from this practice.

16.3 Both Methods 350.1 and SM4500-NH_3 H refer to use of a wash water solution. Because the type of automated flow injection analyzer used by Paragon provides a constant flow of reagents through the system, the use of a separate wash water solution is not required.

16.4 Section 6.6 of Method 350.1 and Section 3f of Method SM4500-NH_3 H directs the creation of a 0.05% sodium nitroprusside reagent (0.5g sodium nitroprusside to 1L using DI water). Paragon creates a 7 times stronger solution by dissolving 3.5g sodium nitroprusside in 1L of DI water. Sodium nitroprusside reagent is used in this procedure to intensify color development.

Section 7.1 of Method 350.1 and Section 1b of Method SM4500-NH_3 H state that the color intensity is pH dependent and recommends that standards should also be acidified in cases where acid-preserved samples are analyzed. Paragon does not acidify the standard solutions. Instead, Paragon uses a strong basic EDTA buffer to unify the pH of samples and standards as part of the analysis process. Further, this buffered pH adjustment reduces the interferences caused by over-acidified samples.

16.5 Paragon dilutes stock standards and creates calibration standards in concentrations that differ from those described in Section 6.0 of Method 350.1 and referenced in Method SM4500-NH_3 H. Both Methods 350.1 and SM4500-NH_3 H cite approximately 0.01 to 2.0mg/L NH_3 as N as the Method's operational range; Paragon standards bracket a range of approximately 0.10 to 5.0mg/L NH_3 as N.

16.6 Section 9 of this SOP describes a solid preparation procedure. Paragon notes that Method EPA 350.1 is applicable to the determination of ammonia in drinking, surface and saline waters, domestic and industrial wastes (Section 1.1).

17. SAFETY, HAZARDS AND WASTE DISPOSAL

17.1 SAFETY AND HAZARDS

17.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

17.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

17.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples),

handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

17.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

17.1.5 All flammable compounds must be kept away from ignition sources.

17.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name; NFPA Health, Flammability, and Reactivity ratings, and date.

17.1.7 Food and drink are prohibited in all lab areas.

17.2 WASTE DISPOSAL

17.2.1 Solid filtrate residues and any other solid residues shall be disposed of in the Contaminated Soils and Solids Waste satellite collection vessel.

17.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

17.2.3 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Waste Compliance Officer will address the disposition of these samples.

18. REFERENCES

18.1 U.S. Environmental Protection Agency, EPA-600/R-93-100, Methods for Determination of Inorganic Substances in Environmental Samples, Method 350.1, "*Nitrogen, Ammonia. (Colorimetric, Automated Phenate)*".

18.2 A.P.H.A., A.W.W.A. and W.P.C.F., 1989. Standard Methods for the Examination of Water and Wastewater, 20th edition, Revised 1998, Method 4500-NH_3 H. Automated Phenate Method.

18.3 Lachat Automated Ion Analyzer Methods Manual, Method Number 10-107-06-1-C, Determination of Ammonia Nitrogen.

18.4 Keeny, D.R. and D.W. Nelson, 1982. Methods of Soil Analysis, Part 2, Agronomy 9:649, American Society of Agronomists, Madison, WI. "Nitrogen - Inorganic Forms".

DOCUMENT REVISION HISTORY

7/26/05: Program Specification references added.

11/6/07: It is not necessary to 'matrix match' calibration standards and QC samples (not required in any referenced method, comparison of QC samples shows it's not warranted). Consequently, all matrix-matching text (i.e., 2M KCl for solids calibration, QC) was removed. Updated EDTA Buffer NaOH strength, Section 6.5, and pH adjustment discussion Section 10. Clerical corrections throughout. Revamped and combined CALCULATIONS and REPORTING RESULTS Sections 13, 15 (updated from spreadsheets to LIMS). Added DOCUMENT REVISION HISTORY section.

Analytical Method: EPA 350.1; SM4500-NH_3 H	**Parameter:** Ammonia-Nitrogen		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point (plus blank)	As needed (i.e., at on-set of analyses or repeated when continuing calibration does not meet criteria)	Correlation coefficient (r^2) for linear regression must be $\geq$0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification (ICV); second source; at or below midpoint	Once after each initial calibration	Response must agree within $\pm$10% of expected value	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Blanks: Method Blank (MB), Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	The MB may be run initially as part of the calibration curve; the ICB is run following the calibration curve. CCBs are run following the CCV (after every ten samples), and to close an analytical run sequence	Ammonia-nitrogen content of the blank must not exceed analyte reporting limit (RL)	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Laboratory Control Sample (LCS)	Matrix specific. One LCS must be prepared and analyzed per $\leq$20 environmental samples of similar matrix	Results must agree within $\pm$10% of expected values for aqueous sample analyses; within $\pm$15% for solid matrix extract analyses, or as otherwise specified in the applicable LIMS program specification	Check all calculations. If no computation errors are found, prepare a fresh LCS and analyze. If criteria are still not met, system must be recalibrated and all samples associated with the failed LCS must be reanalyzed.
Continuing Calibration Verification (CCV); first source; at or below midpoint	Run after every ten samples and to end any run sequence (must be followed by a CCB analysis)	Response must agree within $\pm$10% of expected value	Check that calculations and preparation are correct, evaluate/ correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must also be reanalyzed.
Matrix Spike (MS)	One per batch of $\leq$20 field samples of similar matrix	Recoveries should meet advisory limits of $\pm$25% of the expected values; client-specified criteria may apply	Compare with LCS results and check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike (laboratory) Duplicate	One per batch of $\leq$ 20 field samples of similar matrix	(See MS recovery criteria above). RPD advisory limit is $\leq$ 20; client-specified criteria may apply	(See MS recovery criteria above). For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.

Analytical Method: EPA 350.1; SM4500-NH_3 H	**Parameter:** Ammonia-Nitrogen		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Linearity check; minimum of three standards and a blank; run to verify the range of capability of the instrument	At minimum every six months; whenever a significant change in operator, background, or instrument response occurs	All verification data results must agree within ±10% of expected values	Evaluate/correct instrument malfunction; reanalyze until acceptable results are generated.
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	At minimum every six months; whenever a significant change in operator, background, or instrument response occurs	Positive result < the analyte reporting limit (RL).	Determine the reason for failure and fix problem with the system. Repeat the MDL study. If criteria still not met, discuss with QA Manager (RL may be adjusted if required).

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1130 REVISION 5

TITLE: **DETERMINATION OF NITROGEN, NITRITE (AS NO_2^--N) IN WATER AND SOIL BY COLORIMETRIC SPECTROPHOTOMETRIC DETERMINATION -- EPA METHOD 354.1 AND STANDARD METHOD SM4500-NO_2 B**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER Steve Wolfman DATE 7/21/08

QUALITY ASSURANCE MANAGER Dot Schenk DATE 7/20/08

LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: NEW, 8/12/02; Rev1, 12/11/02; Rev2, 2/13/04 and 12/15/04 (re-released without revision); Rev3, 7/26/05; Rev4, 4/10/06; Rev5, 7/20/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) references USEPA Method 354.1 and Standard Method (SM) 4500-NO_2 B for the determination of native nitrite content in environmental water samples. Soil samples may also be analyzed using these methods following rotary tumbler extraction with deionized water.

2. SUMMARY

To determine native nitrite (NO_2^--N) content, an aliquot of an unpreserved sample or extract is developed using a color reagent. The resultant color is read using a UV spectrophotometer. Values are reported as NO_2^--N.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the ability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of a proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any

errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these methods to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 This colorimetric procedure requires an optically clear sample. Sample color that absorbs at approximately 543nm interferes with the colorimetric determination. This interference may be corrected by diluting the sample or by analyzing an aliquot of sample without the addition of color reagent (an initial absorbance reading can thus be obtained). The sample's corrected absorbance reading is then calculated by subtracting the initial absorbance reading from the final absorbance reading to obtain a corrected absorbance reading.

Since nitrite is found in a soluble form, the sample should be pre-filtered through a 0.45μm pore diameter membrane filter.

4.2 There are very few known interferences at concentrations less than 1,000 times that of the nitrite, however, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity (> 600mg/L) will give low results due to a shift in pH.

5. APPARATUS AND MATERIALS

5.1 UV/VIS Spectrophotometer, Sequoia - Turner Model 340, or equivalent. Capable of absorbance measurements at 543nm

5.2 Spectrophotometer cuvettes, optical glass, 1" diameter (path length) and 150mm tall. VWR Cat No. 22366-006, No. 33-17-82 or equivalent

5.3 Analytical balance, 0.0001g sensitivity, verified per SOP 305

5.4 Syringe, outfitted with a 0.45μm filter disk

5.5 Volumetric dispensers, Eppendorf™ or equivalent, capable of dispensing 0.01-10.0mL, operated per SOP 321 requirements

5.6 TCLP-type mechanical tumbler, capable of 1 hour soil extraction by agitation

5.7 Centrifuge, capable of sustaining approximately 3500rpm

5.8 Centrifuge tubes, disposable, 50mL volume

5.9 Vortex mixer

5.10 Volumetric flasks, various sizes, Class A

5.11 pH paper, suitable of determining pH 6

6. REAGENTS

NOTE: Only ACS grade or better chemicals and reagents may be used. Reagents and solutions may be stored in either plastic or glass containers.

6.1 Deionized (DI) Water

6.2 Hydrochloric Acid (HCl) Solution: Slowly and cautiously add a measured volume of concentrated HCl to two equal volumes of DI water (1:3 dilution). *Shelf life = 1 year.*

6.3 Color reagent: To 250mL degassed DI water, add 50mL concentrated Phosphoric Acid (H_3PO_4) and 20.0g sulfanilamide. After dissolving the sulfanilamide completely, add 1.0g N-(1-naphthyl)-ethylenediamine dihydrochloride. Mix to dissolve, then dilute to 500mL with degassed deionized water. *Store refrigerated in an amber container. Shelf life = 6 months.*

6.4 Ottawa sand. *Keep container sealed tightly. No special storage or shelf life considerations.*

6.5 Sodium Nitrite ($NaNO_2$), reagent grade: First and second sources purchased from separate vendors. Used to create the first and second source NO_2^--N Stock Solutions. *Shelf life = 5 years. Oven dry for about 1hr then cool in desiccator before use.*

7. NITRITE CALIBRATION STANDARDS

7.1 Nitrite (NO_2^--N) Stock Solutions, 1000mg/L: Created from $NaNO_2$ reagent grade salts, first and second sources. Used to create the first and second source NO_2^--N 20mg/L Intermediate Standards. Dissolve 0.4925g of $NaNO_2$ salt in 100mL DI water. Store at 4±2°C. *Shelf life = 1 month.*

7.2 Nitrite (NO_2^--N) Intermediate Standard, 200ppm (first source): Made by diluting 20.0mL of the first-source 1000mg/L NO_2^--N Stock Solution to a final volume of 100mL with DI water. This "First Source" Intermediate Standard is used to prepare the daily calibration standards and the continuing calibration verification (CCV) standards. Store at 4±2°C. *Shelf Life = 1 month.*

7.3 Nitrite (NO_2^--N) Intermediate Standard, 200ppm (second source): Made by diluting 20.0mL of the second-source 1000mg/L NO_2^--N Stock Solution to a final volume of 100mL with DI water. This second source intermediate standard is

used to prepare the initial calibration verification (ICV) standard and the Laboratory Control Sample (LCS) standard, which are identical. Store at 4±2°C. *Shelf Life = 1 month.*

7.4 NO_2^--N Calibration Standards (per Table below): Made in-house each day of use by dilution of the first source 200ppm NO_2^--N Intermediate Standard.

Note that DI water is used as the diluent to prepare calibration standards for aqueous sample analyses. The final volume of for all calibration standards is 20mL.

CONCENTRATION OF INITIAL SOLUTION (ppm)	VOLUME OF INITIAL STANDARD USED (mL)	CONCENTRATION OF FINAL SOLUTION (ppm)	FINAL VOLUME OF SOLUTION (mL)
200	0.050	0.50	20
200	0.020	0.20	20
200	0.010	0.10	20
200	0.010	0.05	40
0.05	8.0	0.02	20
0.05	4.0	0.01	20
0	0.0	0.0	20

7.5 Initial Calibration Verification Standard (ICV), 0.10ppm: Made in-house each day of use by diluting 0.01mL of the "second source" NO_2^--N Stock Solution (1000ppm) to 100mL, using DI water or 0.010mL of 200ppm second source standard into 20mL DI water.

7.6 Continuing Calibration Verification Standard (CCV), 0.20ppm: Made in-house each day of use by diluting 0.02mL of the "first source" 200ppm NO_2^--N intermediate standard to 20mL using DI water.

8. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

8.1 All samples should be collected according to an approved sampling plan.

8.2 Sampling and storage of samples in glass bottles or in plastic bottles is permissible. Samples should be kept cool at 4±2°C.

8.3 For nitrite (NO_2^--N) analysis, aqueous samples must be analyzed within 48 hours after collection. There is no promulgated holding time for soil samples.

9. AQUEOUS EXTRACTION OF SOLID SAMPLES AND ASSOCIATED QC SAMPLE PREPARATION

9.1 Weigh 4.0g moist samples into a 50mL disposable polypropylene centrifuge tube.

9.2 Method Blank: Weigh 4.0g clean Ottawa sand into a 50mL disposable polypropylene centrifuge tube.

9.3 Prepare NO_2^--N Laboratory Control Sample (LCS) as follows: Weigh 4.0g clean silica sand into a 50mL disposable polypropylene centrifuge tube. Spike with 0.02mL of 200mg/L NO_2^--N intermediate standard (second source). Creates a 0.1mg/L LCS extract.

9.4 Prepare NO_2^--N Matrix Spike (MS), Matrix Spike Duplicate (MSD) samples as follows: For one of the samples in the batch, spike two duplicate 4.0g aliquots with 0.02mL of 200mg/L NO_2^--N intermediate standard (first source). Creates a 0.1mg/L MS/MSD sample.

9.5 To all of the above, add 40.0mL DI water.

9.6 Shake samples for 1 hour on the TCLP tumbler.

9.7 Centrifuge for about 15min @ 3500rpm.

10. PREPARATION OF AQUEOUS FIELD AND ASSOCIATED QC SAMPLES

10.1 Place a 20mL aliquot of sample into a clean spectrophotometer cuvette. If the sample is colored or turbid, treat as described in Section 4.1.

10.2 Place 20mL of DI water into a clean spectrophotometer cuvette to serve as the aqueous Method Blank.

10.3 Prepare NO_2^--N Laboratory Control Sample (LCS) as follows: Place 20mL of the aqueous ICV Solution (see Section 7.4) into a clean spectrophotometer cuvette. Used as the 0.1mg/L (second source) LCS standard or 0.010mL of 200ppm second source standard to 20mL DI water.

10.4 Prepare NO_2^--N Matrix Spike (MS), Matrix Spike Duplicate (MSD) samples as follows: For one of the samples in the batch, spike two duplicate 20mL aliquots with 0.01mL of 200mg/L NO_2^--N intermediate standard (first source). Creates a 0.1mg/L MS/MSD.

11. PROCEDURE FOR DETERMINING NITRITE CONTENT

NOTE: If the sample has a pH greater than 10 or total alkalinity in excess of 600mg/L, adjust to approximately pH 6 with 1:3 HCl, otherwise, there is no pH adjustment for NO_2^--N analysis.

11.1 COLOR DEVELOPMENT

11.1.1 Aliquots of standards, aqueous sample or solid sample extract are developed colorimetrically and read using a UV spectrophotometer.

11.1.2 Prepare calibration standards, solid sample extracts and aqueous samples as discussed previously. All aliquots are to be contained in optically-matched cuvettes.

11.1.3 Add 0.480mL of color reagent to each cuvette. Mix each using the vortex mixer.

11.1.4 Allow color to develop for at least 10 minutes (absorbance must be read within 2 hours).

11.2 ESTABLISHING THE CALIBRATION CURVE

11.2.1 Read each calibration standard at 543nm using the UV spectrophotometer. Record each reading in the LIMS interface spreadsheet.

11.2.2 Using LIMS, compute a linear regression for the calibration standard absorbance readings. The correlation coefficient (r^2) must be $\geq$0.995.

11.2.3 After an acceptable calibration curve has been established, analyze the second source check standard (ICV). The ICV result must agree within $\pm$10% of the known value when quantitated using the initial calibration.

11.2.4 Analyze an Initial Calibration Blank (ICB) following the ICV standard. The ICB must be free of analyte concentration above the analyte reporting limit. Sample analyses cannot proceed until an acceptable calibration curve has been verified and an acceptable ICB has been generated.

11.3 ANALYZING SAMPLES

11.3.1 The absorbance of each sample/extract is read at 543nm. Begin sample analysis with the batch Method Blank (MB), followed by the LCS. The MB must be free of analyte concentration above the analyte reporting limit, and the LCS must generate results within ±10% of the expected value for aqueous sample analysis, and within ±20% of the expected value for solid sample extracts analysis. Sample analyses cannot continue unless these acceptance criteria are met.

11.3.2 Begin analyzing the prepared samples (including the batch MS and MSD). A continuing calibration verification (CCV) standard must be analyzed after every tenth cuvette reading. The CCV analysis must yield results within ±10% of the initial calibration. If this criterion is not met, reanalyze the CCV (make sure calculations and preparation is correct). If the CCV still fails, analyses must be halted and a new calibration curve must be generated. All samples analyzed after the last acceptable CCV must be reanalyzed.

11.3.3 The analysis of a continuing calibration blank (CCB) must follow CCV analysis. The CCB must not yield results greater than the analyte reporting limit.

NOTE: The CCV/CCB combination must be analyzed after every ten environmental matrix samples, and to close any analytical run sequence.

12. QUALITY CONTROL (QC) SAMPLES

12.1 DEFINITION OF ANALYSIS BATCH

An analysis batch is defined as a group of twenty (20) or less field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike, and matrix spike duplicate (MS/MSD). All QC samples must be carried through all stages of the sample preparation and measurement steps.

12.2 BLANKS

Method blanks (MBs) are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Initial Calibration Blanks (ICBs) and Continuing Calibration Blanks (CCBs) are run to demonstrate that the analytical system remains free of artifacts and carryover. All blanks must be free of positive analyte results greater than the analyte reporting limit.

12.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. The results obtained are compared to results expected. To be acceptable, the LCS recovery must be between 90% and 110% of the expected concentration for aqueous sample analyses, and between 80% and 120% of the expected concentration for solid matrix extract analyses.

LCS results obtained are compared to results expected using the equation presented below:

$$\text{Percent Recovery (\%R)} = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Expected}}} \times 100$$

where:

$\text{Conc}_{\text{Found}}$ = analyte concentration found in the LCS

$\text{Conc}_{\text{Expected}}$ = anticipated analyte concentration based on known amount spiked

12.4 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE

Matrix spikes (MS/MSD) consist of field samples into which known concentrations of target analytes are added and analyzed as a means of determining the effect of matrix on target analyte detection. The matrix spike

duplicate (MSD) serves as a laboratory duplicate analysis. Analyte recovery for the MS/MSD pair is calculated as shown below:

$$\%R = \frac{Concentration_{Found} - Concentration_{Sample}}{Concentration_{Target}} \times 100$$

where:

$Conc_{Found}$ = analyte concentration found in the MS or MSD sample
$Conc_{Sample}$ = analyte concentration found in the field sample
$Conc_{Target}$ = target (anticipated) analyte concentration based on amount spiked

The advisory quality control limits in water and soil for MS/MSD recovery are set at 75-125%. Some clients may specify particular MS/MSD control limits.

The laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. For this procedure in water and soil, the Relative Percent Difference (RPD) between a sample and its duplicate should not be greater than 20%. RPD is calculated as shown below:

$$RPD\ (\%) = \frac{|\ Result_x - Result_{Dup}\ |}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

Advisory acceptance criteria for all spikes and duplicates should be met. If MS/MSD recovery or RPD criteria are not met, check calculations, spike preparation, and freshness of the standard used for spiking. Narrate if sample matrix interference is suspected as the cause of the MS/MSD advisory criteria not being met.

12.5 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study should be performed as needed and at minimum, annually.

13. DEVIATIONS FROM THE METHODS

13.1 Section 6.1 of Method 354.1 cites the use of distilled water for preparing all reagents and standards. Paragon uses laboratory-generated deionized (DI) water, which is equivalent to distilled water. The DI water system is monitored daily and meets ASTM Type I and II standards.

13.2 The reagent recipe as given differs between Section 6.2 of Method 354.1 and Section 3b of SM4500-NO_2 B for the creation of the color reagent. Paragon uses phosphoric acid (not HCl) based on the reagent recipe cited in SM4500-NO_2 B. However, Paragon creates a stronger color reagent than that described by using twice the ratioed amount of sulfanilamide and N-(1-naphthyl)-ethylenediamine

dihydrochloride. Additionally, though not described in either referenced method, Paragon degasses the DI water used to create this reagent. Per SM4500-NO_2 B, Paragon does not add sodium acetate as a buffer to the color reagent.

13.3 Per Section 3e of SM4500-NO_2 B, Paragon creates a stronger nitrite stock solution at a concentration of 1000mg/L, not 100mg/L as described in Section 6.3 of Method 354.1. SM 4500-NO_3^- I reagent citations, and Section 6.3 of Method 354.1 call for the preservation of nitrite stock standards with chloroform. Paragon closely monitors the performance of and assigned shelf life of the nitrite stock solution and does not preserve this standard with chloroform. Paragon does not standardize this reagent by titration.

Also, the concentration of Paragon's nitrite intermediate standard solution (200mg/L) is stronger than the nitrite standard solutions described in the referenced methods. However, the range of subsequent nitrite calibration standards used by Paragon (0.01–0.50mg/L) falls within the applicable analytical range cited by both methods.

13.4 Paragon uses a 20mL aliquot of standard or sample (or extract) for color development instead of the 50mL aliquot described in Section 7 of Method 354.1 and Section 4b of SM4500-NO2 B. Also, Paragon uses approximately half the ratioed amount of color reagent cited by the methods. Per SM4500-NO2 B, absorbance is read at 543nm (540nm cited in Method 354.1).

13.5 Section 9 of this SOP describes a solid preparation procedure. Paragon notes that Method EPA 354.1 is applicable to the measurement of nitrite in drinking, surface and saline waters, and domestic and industrial wastes (Section 1.1).

14. SAFETY, HAZARDS AND WASTE DISPOSAL

14.1 SAFETY AND HAZARDS

14.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

14.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

14.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area..

14.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

14.1.5 All flammable compounds must be kept away from ignition sources.

14.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

14.1.7 Food and drink are prohibited in all lab areas.

14.2 WASTE DISPOSAL

14.2.1 Solid filtrate residues and any other solid residues shall be disposed of in satellite the Contaminated Soils and Solids Waste collection vessel.

14.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

14.2.3 Certain clients may require that the samples and residues from their analyses be returned. The Waste Compliance Officer addresses these sample returns.

15. REFERENCES

15.1 A.P.H.A., A.W.W.A. and W.P.C.F. Standard Methods for the Examination of Water and Wastewater, 20th edition.

15.2 Keeny, D.R. and D.W. Nelson, 1982. Methods of Soil Analysis, Part 2, Agronomy 9:649, American Society of Agronomists, Madison, WI. "Nitrogen - Inorganic Forms".

15.3 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes. Method 354.1, "Determination of Nitrite", issued 1971.

DOCUMENT REVISION HISTORY

7/26/05: Added reference Program Specification directive in "Responsibilities".

4/10/06: Added as item 13.4 of "Deviations" that Paragon does not add chloroform as a preservative to nitrite stock solutions. Added DOCUMENT REVISION HISTORY.

7/20/08: Minor clerical corrections and procedural clarifications. Added 'oven-dry' to sodium nitrite reagent 6.5. Updated Standard Method reference 15.1 from 17th to 20th edition.

Analytical Method: EPA 354.1, SM\4500-NO2 B	**Parameter:** Nitrite in water and soil		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point (plus blank); first source	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria)	Correlation coefficient (r^2) for linear regression must be $\geq$0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Independent Calibration Verification (ICV); second source	Once after each initial calibration	Response must agree within $\pm$10% of initial calibration	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Blanks: Method Blank (MB), Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	The MB may be run initially as part of the calibration curve, the ICB is run following the calibration curve. CCBs are run following the CCV (after every ten samples), and to close an analytical run sequence	NO_2^--N content of the blank must not exceed analyte reporting limit (RL)	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All samples run since the last acceptable blank must also be reanalyzed.
Laboratory Control Sample (LCS)	One LCS must be run per 20 environmental samples	Results must agree within $\pm$10% of expected values for aqueous sample analyses; within $\pm$ 20% for solid matrix extract analyses	Check all calculations. If no computation errors are found, prepare a fresh LCS and analyze. If criteria are still not met, system must be recalibrated and all samples run since the last acceptable LCS must be reanalyzed.
Continuing Calibration Verification (CCV); first source	Run after every ten samples and to end any run sequence (must be followed by a CCB analysis)	Response must agree within $\pm$10% of initial calibration	Check that calculations and preparation are correct, evaluate/ correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Matrix Spike (MS)	One per batch of $\leq$20 field samples	Recoveries should meet advisory limits of $\pm$25% of the expected values; client-specified criteria may apply	Compare with LCS results and check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike (laboratory) Duplicate	One per batch of $\leq$20 field samples	(See MS recovery criteria above). RPD advisory limit is $\leq$20; client-specified criteria may apply	(See MS recovery criteria above). For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/ Project/QA Managers.
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	As needed; at minimum annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with the system. Repeat the MDL study. If criteria still not met, discuss with QA Manager (RL may be adjusted if required).

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1132 REVISION 3

TITLE: SEDIMENT LOAD

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/6/07

QUALITY ASSURANCE MANAGER _____ DATE 2/6/07

LABORATORY MANAGER _____ DATE 2-9-07

HISTORY: Was DRAFT, Rev0, 10/2/03; Rev1, 2/25/04 and 3/29/05 (format updated); Rev2, 7/26/05 (Program Spec. reference added); Rev3, 2/2/07.
re-release w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes procedures for the separation of the aqueous phase and the sediment phase of a sample in order to determine the sediment load of the sample. This procedure may be performed as a stand-alone determination, or as a physical preparation prior to subsequent analytical preparation and testing.

2. SUMMARY

A measured volume of an aqueous sample containing sediments is separated into solid and liquid phases. Separation techniques may consist of centrifuging and decanting, filtration, and/or drying. The solid phase is weighed after separation, and Sediment Load is calculated and reported as mg/L. The separated phases may then be subjected to analytical testing, as requested.

3. RESPONSIBILITIES

3.1 The Paragon Project Manager is responsible for providing project instruction as needed.

3.2 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review.

3.3 Analysts must demonstrate the capability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of a proficiency test sample.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard

criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the processing of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Filter congestion can occur during filtration, which increases separation time. If sediment levels visually look high, use a different method of separation or use multiple, staged filters, if appropriate.

5. APPARATUS AND MATERIALS

5.1 wash bottle

5.2 centrifuge, capable of 3500rpm

5.3 centrifuge tubes with caps, disposable, 250mL

5.4 graduated cylinders, 100-1000mL

5.5 peristaltic pump, and inert tubing dedicated to only one sample

5.6 filter capsules, 0.45µm, Pall/Gelman #12176, or Aqua Prep 600, or other equivalent; alternatively, glass fiber filters, 47mm, Gelman A/E or Whatman Grade 934AH

5.7 filter funnel assembly (e.g., funnel, glass-fritted filter base, funnel clamp, vacuum source, 1L vacuum flask)

5.8 polypropylene containers, 250mL-4L

5.9 weighing pans, aluminum

5.10 top loading balance, 0.01g sensitivity

5.11 analytical balance, 0.0001g sensitivity

5.12 drying oven, set at ~100°C

5.13 drying oven, set to maintain 103-105°C

5.14 desiccator, with color indicating desiccant

5.15 forceps and/or heat resistant oven gloves

5.16 vortex mixer

5.17 sample containers with caps, various sizes and materials

6. REAGENTS

Deionized (DI) water, obtainable from the laboratory's deionized water system

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 All samples should be collected according to an approved sampling plan.

7.2 Sampling and storage of samples in plastic bottles, such as polyethylene or cube containers, is permissible. **Note that, as applicable, the container requirements of subsequent analytical methods must be met.**

7.3 **Samples should not be chemically preserved prior to sediment load determination. If required by a requested subsequent analytical method, appropriate chemical preservative may be added after sediment load determination is made.**

7.4 There is no maximum holding time allowance established for sediment load determination. However, if the sample is to be analytically tested subsequently, sediment load determination must be conducted within the analytical method's maximum holding time allowance.

8. PROCEDURE

8.1 SEPARATION OF AQUEOUS PHASE AND SEDIMENT PHASE

NOTE: The entire contents of a particular container must be used if possible. Subsampling a container can introduce significant bias, due to rapid settling.

- Due to client requirements (i.e., further analyses on separate phases), sediment state (settled vs mixed, dried vs undried) and sediment levels, the separation techniques used in sediment load determination can vary. This SOP addresses the most stringent methods - full separation with siphoning, centrifuging, and/or filtering. **The analyst must consult project instructions and the associated LIMS program specification for project-specific direction.**
- Any or all separation techniques may be applicable to a set of client samples. Be sure to document on the network spreadsheet, and in the data package narrative, what steps were required for the separation of the samples, as well as any extra steps taken to complete the separation.
- When the separation is complete, the separated phases are given a new Paragon sample ID. Hazard labels are applied, if necessary, and the

samples are returned to the appropriate storage area.

NOTE: It is important to maintain the separated phases in a condition such that they may be analyzed for any requested analysis.

8.2 SETTLED SOLIDS

8.2.1 If left undisturbed, some samples will separate into two phases with the sediment on the bottom and a clear aqueous layer on the top. Pour or siphon (with peristaltic pump and dedicated tubing) the clear aqueous phase from the sample container, **without disturbing or transferring any of the settled solid phase**, into an appropriately sized graduated cylinder. **Leave some liquid in the original container for mixing.** Measure the volume and record in the network spreadsheet.

8.2.2 Next, transfer the measured aqueous phase into a clean container of appropriate size. Label the container with the sample ID and "Aqueous Phase", and place it in proper storage.

8.2.3 The remaining liquid with sediment in the original container can now be processed. Mix the sediment and remaining liquid by swirling the container. Be sure that all solids are loosened and then…

8.2.3.1 …pour directly into an appropriate sized graduated cylinder. Measure the volume and record in the network spreadsheet. Next, quantitatively transfer the material to a **labeled, pre-weighed glass container with cap**. Use a wash bottle filled with DI water to rinse the sides of the graduated cylinder and the original sample container to remove any remaining sediment, adding the rinse directly into the pre-weighed glass container with cap.

8.2.3.2 **OR**, …pour directly into a **pre-weighed 250mL disposable centrifuge tube with cap**, and separate by means of centrifuging. Decant the aqueous phase into another **labeled, pre-weighed 250mL disposable centrifuge tube with cap**. Then, quantitatively transfer the sediment phase to a **labeled, pre-weighed glass container with cap**. Use a wash bottle filled with DI water to rinse the sides of the sample container to remove any remaining sediment, adding the rinse directly into the pre-weighed glass container with cap.

NOTE: The aqueous and sediment phase measurements added together become the sample's "Total Volume" in mLs.

8.2.4 DRYING SOLID MATERIALS

8.2.4.1 Dry the sediment phase (Step 8.2.3) by placing the labeled glass container(s) in a drying oven set at ~100°C. Let the sediment phase sit in the oven overnight to evaporate off all remaining liquid.

8.2.4.2 Move the sediment container(s) to a drying oven set to maintain 103-105°C and allow the sediment to bake for at least one hour.

8.2.4.3 Remove the sediment container(s) from the oven and store in a desiccator until cooled to room temperature.

8.2.4.4 Weigh the glass container (and cap); record weight in the network spreadsheet.

8.2.4.5 Repeat Steps 8.2.4.2 to 8.2.4.4 (drying, cooling, weighing) until a consistent weight is achieved (i.e., difference between weighing is ≤4%, or when the weight change is less than ±0.5mg).

8.2.5 Calculate sediment load (Section 8.5) using the last weight recorded.

8.3 SUSPENDED SEDIMENT

If the sample contains a large amount of suspended sediment that will not settle out, the entire sample must be serially centrifuged.

8.3.1 Pour the sample (or aliquot thereof) into an appropriate-sized graduated cylinder, measure and record the volume on the network spreadsheet.

8.3.2 Transfer an aliquot of sample into a 250mL centrifuge tube.

NOTE: If wet weight is required, pre-weigh the tube (and cap) and record.

8.3.3 Place the tube in the centrifuge and spin for ~15 minutes at 3500rpm.

8.3.4 Decant the top aqueous phase into a clean, labeled (sample ID and "Aqueous Phase") appropriate-sized container.

8.3.5 Repeat Steps 8.3.1 to 8.3.4, recording measurements and adding aliquots to the same tube and decanting to the same aqueous phase container, until the entire sample is centrifuged. **DO NOT pour off any of the settled solid phase!** Put the container of aqueous phase in proper storage.

8.3.6 Next, the sediment phase of the sample can be addressed. Dislodge the sediments in the centrifuge tube by carefully squirting with DI water, cap, then vortex. Quantitatively transfer the contents of the centrifuge tube, using DI water to rinse the sides of the tube, to a **labeled, pre-weighed glass container with cap**.

8.3.7 Dry the solid materials per Section 8.2.4 above.

8.3.8 Calculate sediment load (Section 8.5) using the last weight recorded.

8.4 LOW SEDIMENT LEVELS

If sediment levels are visually low, the entire sample can be filtered through a pre-washed, pre-weighed glass fiber filter.

8.4.1 FILTER PRE-TREATMENT

Begin by assembling the filtration apparatus (vacuum source, vacuum flask, filter base, funnel and clamp). Pre-wash filter by placing it on the filter assembly and passing 100mL of DI water through it (discard rinsate). Move the rinsed filter to labeled aluminum weighing dish, and place the dish with filter in an oven set to maintain 103-105°C, for approximately 1hr. Remove the dish with filter from the oven and place in a desiccator to cool to room temperature. Weigh the dish with filter using an analytical balance, record weight.

8.4.2 Select a pre-treated filter (Step 8.4.1) and center it in the funnel. Turn on the vacuum. Pre-wet the filter using a small amount of DI water to ensure a good seal.

8.4.3 Label a suitable container with sample ID and "Aqueous Phase", and use the container as a sample-specific collection flask.

8.4.4 Measure a volume of sample into a clean graduated cylinder; record on network spreadsheet. Pour the sample volume through the filter, and collect in the labeled container (Step 8.4.3). Repeat until all the sample has been filtered and collected. Then cap and place the filtered aqueous portion of the sample in proper storage.

NOTE: All measurements added together become the sample's "Total Volume" in mLs.

Multiple filters may be required if filtration rate slows or stops due to congestion.

The filter(s) and contents must be retained (i.e., each filter must be carefully returned to it's labeled aluminum weighing dish).

8.4.5 Next, the sediment portion of the sample that was captured by the filter(s) can be addressed. Place the filter and dish into a drying oven set to maintain 103-105°C, for at least 1hr. Remove the filter and dish from the oven and place in a desiccator until cooled to room temperature. Weigh the filter and dish and record on the network spreadsheet.

8.4.6 Repeat drying, cooling and weighing, as described in Step 8.4.5 above, until a consistent weight is achieved (i.e., difference between weightings is ≤4%, or when the weight change is less than ±0.5mg).

8.4.7 Calculate sediment load (Section 8.5) using the last weight recorded.

8.5 CALCULATIONS

$$\text{Sediment Load (mg/L)} = (C_{residue} - C_{empty}) * 1000 / (V_{sample} /1000)$$

where:

$C_{residue}$ = Weight of container with dry residue (g)
C_{empty} = Weight of empty container (g)
V_{sample} = Measured volume of sample (mL)

9. QUALITY CONTROL

No method blank, duplicate or spiked samples are applicable to this procedure.

10. DEVIATIONS FROM METHOD

This procedure was developed at Paragon, based on client need, and is not based on any published method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Waste Manager will address the disposition of these samples.

12. REFERENCES

None.

DOCUMENT REVISION HISTORY

2/2/07: Updated LIMS program spec. language. Added DI water to REAGENTS. Augmented Section 7, pertaining to preservation and hold time. Reformatted PROCEDURES, added minor clarifications, referenced network spreadsheet for recording data and calculating sediment load. Updated HAZARDS. Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1133 REVISION 3

TITLE: ACIDITY BY TITRATION -- METHODS EPA 305.1 AND SM2310B

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/19/07
QUALITY ASSURANCE MANAGER _____ DATE 1/19/07
LABORATORY MANAGER _____ DATE 1-19-07

HISTORY: Was DRAFT, Rev0, 10/22/03; Rev1, 2/25/04 and 3/29/05 (format updated); Rev2, 7/26/05; Rev 3, 1/19/07. re-released without revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references – US EPA Method 305.1 and Standard Methods (SM) 2310B -- are used to determine acidity in environmental water and wastewater samples, and other waters containing ferrous iron or other polyvalent cations in a reduced state.

This method covers the range from approximately 10-1000mg/L as $CaCO_3$, using a 100mL sample volume. The acidity of a water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end point pH used in the determination. Strong mineral acids, weak acids (i.e., carbonic and acetic acid) and hydrolyzing salts such as iron or aluminum sulfates may contribute to the measured acidity according to the method of determination.

2. SUMMARY

Acidity is determined by adding a small amount of 30% hydrogen peroxide to an acidified sample (pH 4 or less) and the sample is then brought to a boil. After the sample cools, it is titrated to the endpoint (pH 8.2) with 0.02N NaOH. The results are calculated from the volumes and normalities of the acid and base used as well as the sample volume titrated. The results of the analysis are expressed as mg $CaCO_3$/L.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or by the successful analysis of a proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the data spreadsheet or analytical review sheets indicate that this review for precision, accuracy and completeness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to correct the errors that were found.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Soaps, oily matter, suspended solids, or precipitates may cause a sluggish response with the pH meter. It may be necessary to allow additional time between titrant additions to let the electrode come to equilibrium.

NOTE: The sample may not be altered in any way to remove interferences because they may contribute to its acidity.

5. APPARATUS AND MATERIALS

5.1 beakers, Pyrex™, 150mL. Use an appropriate beaker size that keeps the air space above the solution to a minimum.

5.2 pipettes, plastic transfer

5.3 volumetric flasks, Class A, 500mL and 1L

5.4 top loading balance capable of reading to 0.01g

5.5 Accumet pH/mV Meter 50, or equivalent, capable of reading to 0.05 pH units

5.6 pH electrode, glass, combination style with reference electrode contained within probe body

5.7 hot plate, large

5.8 magnetic stir plate

5.9 magnetic stir bars, Teflon™-coated

5.10 Eppendorf™ pipette or equivalent, adjustable, capable of delivering 1.0mL

5.11 graduated glass pipets for H_2SO_4 addition

6. REAGENTS

6.1 Deionized (DI) water.

6.2 pH Buffers (4.01, 7.00, 10.01): Orion, 910104, 910107, 910110 or equivalents. Store in polypropylene. *Shelf life = 1 year.*.

6.3 Hydrogen peroxide (H_2O_2), 30% solution: Mallinckrodt, 5240 or equivalent. Store in polypropylene. *Shelf life = 1 year.*

6.4 Standardized sulfuric acid (H_2SO_4), 0.02N: EMD, SX1244-5 or equivalent. Purchased from a commercial vendor or made in-house by diluting 1.0mL of 50% H_2SO_4 to 900mL DI water. Standardization of this solution is carried out for each usage by titrating against the standard base (i.e., 0.20N Na_2CO_3). Store in polypropylene. *Shelf life = 1 year or until degradation is evident.*

6.5 Standardized sodium hydroxide (NaOH), 0.02N: JT Baker, 3722-07 or equivalent. Purchased from a commercial vendor or made in-house by diluting 80mL of 0.25N NaOH to 1L of DI water. Standardization of this solution is carried out for each usage by titrating against the standard acid (i.e., 0.02N H_2SO_4). Store in polypropylene. *Shelf life = 1 year or until degradation is evident.*

6.6 Sodium hydroxide solution, 0.25N: Dissolve 10g NaOH in a final volume of 1L using DI water. Shelf Life = 1 year.

6.7 Hydrochloric Acid (HCl), 0.02N: JT Baker, 9530-33 or equivalent. Purchased from a commercial vendor or made in-house by diluting 200mL of 0.1N HCl to 1L with DI water. Standardization of this solution is carried out for each usage by titrating against the standard base (i.e., THAM). Store in polypropylene. *Shelf life = 1 year or until degradation is evident.*

6.8 Hydrochloric Acid (HCl), 0.1N: JT Baker, 9530-33 (concentrated) or equivalent. Purchased from a commercial vendor or made in-house by diluting 8.3mL of concentrated HCl to 1L with DI water. Store in polypropylene. *Shelf life = 1 year or until degradation is evident.*

6.9 Tris(hydroxymethyl)aminomethane (THAM), 0.20N: JT Baker, 4099-06 or equivalent. Dry about 15g primary standard THAM at about 100°C for 1-2 hours and cool in a desiccator. Transfer 12.114g of the dried THAM to a 500mL volumetric flask. Add 200-300mL of DI water to the flask and swirl to dissolve the salt. Fill to the mark with DI water and mix thoroughly. Store in polypropylene. *Shelf life = 1 year.*

6.10 Phenolphthalein indicator solution: VWR, Cat. No. VW3341-2 or equivalent. Store in polypropylene. *Shelf life = 1 year.*

6.11 Bromocresol green indicator solution: EM Science, 2800 or equivalent. Dissolve 0.5g of bromocrescol green sodium salt in 500mL DI water. Store in polypropylene. *Shelf life = 1 year.*

6.12 Sodium carbonate standard solution (Na_2CO_3), 0.20N: JT Baker, 3604-01 or equivalent. Dry about 10g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Transfer 5.300g of the dried Na_2CO_3 to a 500mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in polypropylene. *Shelf life = 1 year.*

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples may be collected in either plastic or glass containers and must be collected according to an approved sampling plan. The sample containers should be filled as full as possible to minimize headspace.

7.2 Water samples should be kept refrigerated (0-6°C) from the time of collection and analyzed as soon as possible. The samples must be analyzed within 14 days after collection.

8. PROCEDURE

8.1 CALIBRATION OF pH METER

Calibrate the pH meter according to manufacturer's instructions by using pH buffers 4.01, 7.00 and 10.01. On the Accumet 50 pH meter, push "standardize" and select choice #2, "clear existing standards". Place the probe in first pH buffer, push "standardize" and select choice #1, "update or add standard". Enter buffer value and push enter. Let the probe sit in the buffer solution for 1-2 minutes, then push enter. Repeat these steps for next two buffers concentrations. Discard the buffer aliquots after each day's use.

8.2 HOT PEROXIDE TREATMENT

8.2.1 Place a 150mL beaker on the top loading balance. Tare the balance. Gravimetrically pipet a 100mL aliquot of sample (or less if a smaller sample size is required) into the beaker. Record the sample volume in the data spreadsheet. If less than a 100mL aliquot of sample is used, bring to a final gravimetric volume of 100mL with DI water.

8.2.2 Measure the pH of the sample. If the pH is above 4.0, add standard sulfuric acid (Section 6.3) in 5.0mL increments to lower the pH to 4.0 or less. If the initial pH of the sample is less than 4.0, the incremental addition of sulfuric acid is not required.

8.2.3 Add 5 drops of hydrogen peroxide.

8.2.4 Heat the sample to boiling and continue boiling for 2 to 5 minutes. In some instances, the concentration of ferrous iron in a sample is such that an additional amount of hydrogen peroxide and a slightly longer boiling time may be required.

8.2.5 Laboratory Duplicate (DUP): Select one sample per batch of 20 or less field samples processed as a unit, and prepare a second aliquot of that sample to serve as the laboratory duplicate. Process as described in Steps 8.2.1 through 8.2.4 above.

8.2.6 Method Blank (MB): Aliquot 100mL of DI water into a 150mL beaker to be processed as the batch method blank. MBs are run to demonstrate that interferences from the analytical system, glassware and reagents are under control. Process as described in Steps 8.2.1 through 8.2.4 above.

8.2.7 Laboratory Control Sample (LCS): Prepare this check sample by transferring 10.0mL of 0.02N HCl standard solution to a 150mL beaker containing a stir bar; dilute to 100mL with DI water. One LCS is to be prepared for each batch of samples processed. The LCS is run at the beginning of each day's analysis following standardization of the titrant, as a measure of the accuracy of the method. Process as described in Steps 8.2.1 through 8.2.4 above.

8.3 STANDARDIZATION OF THE ACID TITRANT

8.3.1 Pipette 1.00mL of 0.20N Na_2CO_3 (Section 6.7) and approximately 2mL of bromocresol green indicator into a 150mL beaker containing 100mL DI water. Add a stir bar and place the beaker + contents on the laboratory balance and tare the balance.

8.3.2 Place the beaker + contents on a stir plate. Adjust the stir plate control so that the beaker's contents mixes slowly.

8.3.3 Place the pH probe in the beaker. Using the pH meter and color indicator as reference points, titrate to a pH of 4.0 by adding 0.02N H_2SO_4 dropwise. When the color of the solution turns from blue to green, the endpoint has been reached. Place the beaker + titrated contents on the balance and record the weight of the titrant used in the data spreadsheet.

8.3.4 Repeat Steps (8.3.1 - 8.3.3) twice more for a total of three standardization replicates. Calculate the average of the standardization results to determine the titrant's concentration.

8.4 STANDARDIZATION OF THE BASE TITRANT

8.4.1 Pipette 10.0mL of standardized 0.02N H_2SO_4 (Section 6.3) and approximately 1 to 2 drops of phenolphthalein solution into a 150mL beaker containing 100mL DI water. Add a stir bar and place the beaker + contents on the laboratory balance and tare the balance.

8.4.2 Place the beaker + contents on a stir plate. Adjust the stir plate control so that the beaker's contents mixes slowly.

8.4.3 Place the pH probe in the beaker. Using the pH meter and color indicator as reference points, titrate to a pH of 8.2 by adding 0.02N NaOH dropwise. When the color of the solution turns pink, the endpoint has been reached. Place the beaker + titrated contents on the balance and record the weight of the titrant used in the data spreadsheet.

8.4.4 Repeat Steps (8.4.1 - 8.4.3) twice more for a total of three standardization replicates. Calculate the average of the standardization results to determine the titrant's concentration.

8.5 TITRATION OF SAMPLES

The samples prepared previously in Section 8.2 must be allowed to cool to room temperature before titrating. Titrate as follows:

8.5.1 Add stir bar and 1-2 drops of phenolphthalein solution to the sample beaker.

8.5.2 Move the sample beaker to the stir plate and submerge the pH probe in the sample solution. Adjust the stir control so that the beaker's contents mix slowly.

8.5.4 Add 0.02N NaOH dropwise until the sample turns pink or the pH meter reads 8.2. Place the beaker with titrated sample on the top loading balance and record the amount of titrant used in the data spreadsheet.

NOTE: Rinse the pH probe with DI water between each sample immersion.

8.6 ANALYTICAL RUN SEQUENCE

Perform the acidity determinations in the following sequence:

1. MB
2. LCS
3. DUP
4. 17 field samples

If a second batch of samples are to be analyzed, the sequence repeats beginning with a MB, LCS, DUP, 17 field samples, etc.

8.7 CALCULATIONS

8.7.1 SULFURIC ACID TITRANT, 0.02N

$$C_{H_2SO_4} = \frac{(C_{Na_2CO_3})(V_{Na_2CO_3})}{V_{H_2SO_4}}$$

where:

$C_{Na_2CO_3}$ = concentration of Na_2CO_3 titrant, N or eq/L (equals 0.20N if preparation is followed without deviation)

$V_{Na_2CO_3}$ = volume (mL) of Na_2CO_3 standard titrated; equals 1.0mL if SOP is followed without deviation)

$V_{H_2SO_4}$ = volume (mL) of H_2SO_4 titrant required to reach endpoint

therefore:

$$C_{H_2SO_4} = \frac{(0.20N)(1.0mL)}{V_{H_2SO_4}}$$

Average the results of the three replicate standardizations to calculate the H_2SO_4 titrant concentration.

8.7.2 NAOH TITRANT, 0.02N

$$C_{NaOH} = \frac{(C_{H_2SO_4})(V_{H_2SO_4})}{V_{NaOH}}$$

where:

$C_{H_2SO_4}$ = concentration of H_2SO_4 titrant, N or eq/L (normality is calculated from the standardization of the acid)

$V_{H_2SO_4}$ = volume (mL) of H_2SO_4 standard titrated; equals 10.0mL if SOP is followed without deviation)

V_{NaOH} = volume (mL) of NaOH titrant required to reach endpoint

therefore:

$$C_{NaOH} = \frac{(\text{calculated normality})(10.0\ mL)}{V_{NaOH}}$$

Average the results of the three replicate standardizations to calculate the NaOH titrant concentration.

8.7.3 CALCULATION OF ACIDITY

$$\text{acidity as mg/L CaCO3} = \frac{[\ (A \times B)\ -\ (C \times D)\ ] \times\ 50{,}000}{\text{mL of sample titrated}}$$

where:

A = Concentration of NaOH

B = Volume of NaOH

C = Concentration of H_2SO_4

D = Volume of H_2SO_4

50,000 = conversion factor (eq/L to mg $CaCO_3$/L)

9. QUALITY CONTROL (QC)

9.1 Various types of QC samples such as method blank (MB), laboratory duplicate (DUP) and laboratory control sample (LCS) are discussed previously in Section 8.2. Acceptance criteria for these quality control measures are shown in the QC Summary Table at the end of this SOP.

9.2 LABORATORY CONTROL SAMPLE RECOVERY

Results obtained for the LCS are compared to results expected. The mathematical evaluation is expressed as Percent Recovery (%R), and is calculated as follows:

$$\%R = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Target}}} \times 100$$

To be acceptable, percent recovery must be between 85% and 115% of the expected concentration.

9.3 LABORATORY DUPLICATE PRECISION

The laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. The duplicate results are compared mathematically (shown below), with the precision expressed as Relative Percent Difference (RPD):

$$\text{RPD (\%)} = \frac{|\ \text{Result}_x - \text{Result}_{\text{Dup}}\ |}{\frac{(\text{Result}_x + \text{Result}_{\text{Dup}})}{2}} \times 100$$

For this procedure, the RPD should not be greater than 15%.

10. DEVIATIONS FROM METHOD

There are no known deviations from the methods.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The aqueous solution left over from the titration shall be disposed of in the Aqueous Laboratory Waste satellite collection vessel.

11.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs; all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

11.2.3 Certain clients may require that the samples and residues from the analysis of their samples are segregated and returned to the client's location. The Waste Compliance Officer will address the disposition of these samples.

12. REFERENCES

12.1 U.S. Environmental Protection Agency, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, 1983. Method 305.1, "Acidity (Titrimetric)".

12.2 A.P.H.A., A.W.W.A. and W.P.C.F., Standard Methods for the Examination of Water and Wastewater, 20th edition, pp 2:24-26, 1998. Method 2310B, "Acidity".

DOCUMENT REVISION HISTORY

7/26/05: Program specification reference added, Section 3.

1/19/07: Language of program specification reference updated. Added 0.25NaOH and 0.1N HCl recipes to Section 6. Added DOCUMENT REVISION HISTORY.

Analytical Method: EPA 305.1; SM 2310B	**Parameter:** Acidity		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Calibration: analyte content is determined by direct concentration (obtained by calculation from titration)	The titrants are standardized each day of use	Titrant should calculate to be between 0.18-0.22N	If titrant does not meet concentration criteria; prepare fresh and standardize via three replicate analyses.
Method Blank (MB)	One MB per each batch of ≤20 field samples and each time a reagent is changed	No blank's acidity may exceed the reporting limit (RL); usually 10mg $CaCO_3$/L	Check all calculations. If no computation errors are found, prepare a fresh blank and analyze. All associated samples must also be reanalyzed.
Laboratory Control Sample (LCS)	One per batch of ≤20 field samples	Results obtained must be within 85-115 % of that expected	Check calculations and preparation for documentable errors. If no errors are found, remake and reanalyze. All associated samples must also be reanalyzed.
Laboratory Duplicate (DUP)	One per batch of ≤20 field samples	RPD must be ≤15%	Check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 127 REVISION 9

TITLE: PROCUREMENT OF SUPPLIES AND MATERIALS, INCLUDING RADIOACTIVE MATERIALS, AND EVALUATION OF PURCHASED ITEMS RECEIVED

FORMS: PURCHASE REQUISITION FORM

APPROVED BY:

TECHNICAL MANAGER _____ DATE 10/2/07
QUALITY ASSURANCE MANAGER _____ DATE 10/2/07
LABORATORY MANAGER _____ DATE 10/4/07

HISTORY: Rev0, 11/16/92; Rev1, 1/14/94; Rev2, PCN #125, 2/1/94, Rev3, PCN #315, 1/3/95; Rev4, 7/15/99; Rev5, 12/31/01; Rev6, 2/14/0; Rev7, combined with SOP 128, 2/9/04, format updated 3/24/05; Rev8, 9/11/06; Rev9, 10/2/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) defines the procedures to be followed for completing and managing procurement requests, as well as those procedures to be used for evaluating the acceptability of the purchased items received.

Also defined herein are the requirements for items that are purchased (e.g., standards, solvents, reagents, laboratory supplies and equipment), including radioactive materials, and for vendors that are approved for use. These requirements are established to ensure that all items used by Paragon are of acceptable quality, and that the purchase of radioactive materials meets Paragon's licensing requirements.

2. SUMMARY

All supplies and materials ordered must meet all applicable technical requirements as established by the appropriate Department Manager, and the Radiation Safety Officer (RSO), as applicable. Only vendors deemed suitable for use, as defined by the appropriate Department Manager and RSO, as applicable, shall be purchased from.

A Purchase Requisition Form is used to request all supplies and materials. Signatures signifying appropriate Departmental and financial approval must be obtained prior to submitting the completed form to Paragon's Purchasing Agent.

Paragon's Purchasing Agent then generates a Purchase Order Form (created electronically within the DataChem accounts system), and completes the acquisition process. All required documentation shall be maintained by the Purchasing Agent.

An initial inspection of all incoming materials upon receipt is performed by the Purchasing Agent or designee. The ongoing evaluation of suppliers used and the acceptability of the materials received from them is the responsibility of the Department Manager, and RSO as applicable.

3. RESPONSIBILITIES

3.1 It is the responsibility of Paragon's Purchasing Agent to provide guidance regarding the procurement protocols to be followed, to process procurement requests in a timely manner, to manage vendor accounts in conjunction with the appropriate Department Manager(s), retain purchasing records as required, and maintain a supply of requisition forms.

3.2 The Department Manger is responsible for establishing and enforcing the quality requirements for all standards, reagents, materials and supplies ordered, as well as evaluating the acceptability of these materials after receipt (evaluative training shall be provided to delegated staff, as applicable). The requirements established for these materials shall be based on method requirements, equipment requirements, quality guidances, and client criteria and user needs, as applicable.

The Department Manager is responsible for directing the purchase of materials and supplies only from suitable vendors. Certification documents may be applicable to some materials and supplies ordered; the Department who purchased the materials is responsible for retaining these records.

The Department Manager, or designee, shall record purchased materials information in the Paragon Standards and Solutions database, as applicable, per LQAP and SOP 300 directives.

3.3 The RSO (or designee) is responsible for the purchase of all radioactive materials. Because of licensing constraints, the RSO must know the quantities of radioactive materials that are present in the laboratory at all times. Therefore, it is appropriate that the RSO be responsible for all radioactive materials purchases.

3.4 The Quality Assurance Department is responsible for providing general support as needed, and for oversight of conformance to the purchase of materials and verification system requirements.

3.5 It is the responsibility of all personnel to perform these procedures according to this SOP and to complete all documentation required for review.

4. PROCEDURE

4.1 All items purchased must meet the applicable technical requirements as defined by the Department Manager. Only vendors deemed suitable for use, as defined by the appropriate Department Manager and RSO, as applicable, shall be purchased from. The following areas may be evaluated when assessing the suitability of a supplier:

- Paragon's experience with the supplier.
- Supplier's product specifications and technical literature.
- Paragon's evaluation of supplier's quality assurance program.

- Supplier's support and service.
- Supplier's referrals and recommendations.
- Results of Paragon's inspection and testing of materials by the appropriate Department.
- Price.

The suppliers that Paragon uses and the materials acquired from them are evaluated on an ongoing basis. If a performance issue occurs, the supplier is contacted for resolution. If the matter cannot be resolved, an acceptable alternate supplier is used.

4.2 The requestor shall completely fill out the Purchase Requisition Form as prompted by the lines indicated, including the desired vendor to be used. The Form shall then be submitted to the appropriate Department Manager or RSO, as applicable.

4.3 All radioactive materials shall be ordered through the RSO. The appropriate Department Manager/designee or RSO shall review the completed Purchase Requisition Form for completeness and accuracy and shall sign and date the Form to signify financial approval for the items to be ordered. Financial approval from an appropriate Senior Manager must also be obtained, as applicable, before submitting the completed Purchase Requisition Form to Paragon's Purchasing Agent.

4.4 Paragon's Purchasing Agent will review the requisition for completeness and correctness, including the approval signatures obtained. The Purchasing Agent is responsible for generation of a purchase order, documenting the date the materials are ordered, managing the acquisition of any items that may be backordered, and maintaining the required documentation associated with the materials' purchase and receipt.

4.5 Sample Receiving personnel notify the Purchasing Agent when incoming materials have arrived. If the materials are radioactive, Sample Receiving staff will first perform a radioactive material contamination survey (SOP 008), and then will contact both the RSO and the Purchasing Agent to notify them that the radioactive material has arrived. The radioactive material contamination survey results must not exceed the limits of contamination as prescribed in Colorado RH 17.15.8 (see Table 5.1 of SOP 008).

4.6 Before accepting any materials, the Purchasing Agent or designee shall perform an initial inspection consisting of the following:

- Verify that materials were not damaged in transit.

- Compare the materials to the Purchase Order and/or Requisition Form and the supplier's packing slip.

As applicable, the RSO shall verify that the removable contamination is within acceptance limits and shall accept the material for distribution.

4.7 The end user is then notified that the materials ordered have arrived and have been accepted.

4.8 The materials are kept in the area received until the Department who ordered them relocates the items. This is done to avoid misplacement or loss and potential contamination, as well as to keep the items segregated should further evaluative testing need to be conducted before the items are released to the laboratory for use.

4.9 Per Departmental direction, further inspection or testing of the acceptability of materials received may be conducted (e.g., review of Certificates of Cleanliness received for VOA vial shipments; lot analysis of Trace Metals grade HNO_3, verification of radioanalytical standards). Associated documentation, including materials certificates received, shall be retained by the applicable Department.

NOTE: Where additional evaluation practices exist, staff are **not** permitted to use the materials until the evaluation has been completed successfully.

4.10 Should any purchased items be deemed damaged (e.g., initial receipt inspection) or unacceptable (e.g., additional review or testing), resolution shall be pursued by the Department Manager in conjunction with the Purchasing Agent. The QA Department shall be notified, as appropriate.

4.11 For solvents and reagents, Departmental end users are responsible for labeling the individual bottles with date of receipt and initials. Other information (e.g., date of expiration) must also be entered into Paragon's Standards and Reagents database, as applicable (see LQAP and SOP 300).

5. SAFETY, HAZARDS AND WASTE DISPOSAL

5.1 SAFETY AND HAZARDS

5.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

5.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), or when handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

5.2 WASTE DISPOSAL
Not Applicable.

6. REFERENCES

Current NELAC standard
Applicable client quality assurance documents

DOCUMENT REVISION HISTORY

9/11/06: Augmented RESPONSIBILITIES and procedural requirements; added DOCUMENT REVISION HISTORY; attached Form.

10/2/07: Combined with SOP 011 – PURCHASE OF RADIOACTIVE MATERIALS (retired).

DATA CHEM LABORATORIES, INC.

Purchase Requisition

Number: 64446

P.O. Number: _____

Date: _____

Recommended Supplier: _____

Contact Name & Phone: _____

Items needed by: _____

Deliver to: _____

Break Down	Account or Activity	Task or Division	Activity	Dept.

	Quantity	Catalog Number	Description	Estimated Unit Cost
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
			Estimated Total Cost	

Requestor _____ Date _____

Purchasing/Financial _____ Date _____

Manager _____ Date _____

Other _____ Date _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 132 REVISION 6

TITLE: BUILDING SECURITY

FORMS: 155 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 12/11/06
QUALITY ASSURANCE MANAGER _____ DATE 12/6/06
LABORATORY MANAGER _____ DATE 12-12-06

HISTORY: Rev0, 3/10/92; Rev1, 3/10/93; Rev2, 5/18/01; Rev3, 4/29/02; Rev4, 2/9/04; Rev5, 3/10/05; Rev6, 12/7/06. re-released w/o revision 1/14/07 DAS

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes procedures used to provide a secure environment for staff, equipment, materials, and samples.

2. OVERVIEW

The building is equipped with an alarm system and motion sensors, which are monitored by a contracted security vendor. Each employee is made aware of the current alarm code and is issued an alarm quick reference card. The laboratory's ~~the~~ front office area is separated from the operational area and access is controlled via doorways that require pass code entry. All employees are made aware of the current internal pass code. All visitors, with the exception of previously exempted repair/maintenance personnel (Section 5.3), are required to read the Visitor Orientation Guidelines, sign the Visitor log, and obtain a "VISITOR" badge, which must be worn prominently while in the facility. Visitors must sign out and return the "VISITOR" badge upon exit. All non-exempted visitors must be escorted by a Paragon employee at all times while in the facility.

DAS 12/14/06

3. RESPONSIBILITIES

3.1 All employees are responsible for maintaining the facility in a secure manner. Doorways shall not be propped open and left unattended. Access and pass codes shall remain confidential.

3.2 It is the responsibility of the last staff member leaving the building for the night to properly arm the alarm system.

3.3 The Facilities Manager and designee(s) are responsible for the issuance and maintenance of security codes, for interfacing with the security system vendor, for addressing security issues should they arise, and for enforcing compliance with the procedures outlined in this SOP. The Facilities Manager and designee(s) are available by cell and/or home phone during non-business hours. If a security risk is identified, the security codes shall be changed immediately.

3.4 Paragon's Health & Safety Officer (HSO) is responsible for maintaining the content and availability of the Visitor Orientation Guidelines.

3.5 The Quality Assurance Department provides clerical support to the HSO and Facilities Manager as needed by issuing the Visitor log and maintaining an adequate supply of Visitor badges.

4. APPARATUS AND MATERIALS

4.1 "VISITOR" badges

4.2 Visitor log

4.3 Visitor Orientation Guidelines

4.4 Alarm system

4.5 Employee quick reference cards

4.6 Doorway keycode entry devices

5. PROCEDURE

5.1 All visitors are required to read the Visitor Orientation Guidelines, which is located next to the Visitor log.

5.2 The Visitor log (Form 155) and "VISITOR" badges are maintained in the front lobby area. All visitors who do not have prior permission from an authorized Paragon individual to conduct work on the premises (see 5~~.4~~3 below) are required to sign in. Upon sign in, each visitor must acquire a "VISITOR" badge and wear it prominently at all times while in the facility. Each "VISITOR" badge is numbered, and the number of the badge used must be recorded in the Visitor log. 1/14/07 DAS

5.3 All visitors must be escorted by a Paragon employee or other authorized individual at all times. Exception: Selected vendors are allowed access without continuous escort in order to facilitate maintenance, repairs or deliveries.

5.4 All visitors are required to sign out and to surrender the "VISITOR" badge upon exit.

6. SAFETY AND HAZARDS

See Paragon Analytics Chemical Plan (CHP) and Radiation Protection Plan (RPP), current revisions.

7. REFERENCES

Paragon Analytics Emergency and Contingency Plan (ECP), current revision.

DOCUMENT REVISION HISTORY

12/7/06: Expanded Responsibilities Section and added reference to the Visitor Orientation Guidelines (Sections 2, 4, and 5). Changed 'front desk' references to front lobby area. Added DOCUMENT REVISION HISTORY and Form.

PARAGON ANALYTICS

VISITORS LOG

VISITORS: For conformance with *Paragon's Safety Program*, please see **adjacent postings** for pertinent information. You **must** check the 'Acknowledged' box below, indicating your receipt/awareness of this information, before you can conduct your business onsite at this facility.

DATE	NAME (Please Print)	COMPANY	COMPANY LOCATION	TO SEE	SAFETY INFO. ACKNOWLEDGED	BADGE NO. USED	TIME IN	TIME OUT

Business use; does not require pagination. EXEMPT FROM REVIEW. Form 155r3.xls (10/8/2007)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1400 REVISION 6

TITLE: PROCESS SOFTWARE VALIDATION

FORM: 1403 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/8/07

QUALITY ASSURANCE MANAGER _____ DATE 1/8/07

LABORATORY MANAGER _____ DATE 1-8-07

HISTORY: Rev0, 5/23/97; Rev1, 10/8/99; Rev2, 8/25/00; Rev3, 3/28/02; Rev4, 3/28/03; Rev5, 2/13/04 and 7/26/05 (re-released without revision); Rev6, 1/8/07. re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the validation of a software process that has been created or modified for the purpose of processing laboratory data, manipulating data, or reporting data to our clients in either an electronic format or a report (hardcopy) format. This procedure is applicable for all such software applications or processes that are used throughout the laboratory for the purposes described above.

2. SUMMARY

Paragon uses various types of computer software to collect data, perform calculations on data, and report data to clients. Some of the software used to collect the data is created by the various instrument manufacturers and these software applications are specific to a certain instrument or a particular instrument model number. Upgrades or changes to this kind of software are provided, via software maintenance agreements, by the instrument manufacturers. However, software that is used to manipulate data, perform calculations, and report data, is either purchased by Paragon from other vendors, or it is created by Paragon's Information Systems (IS) Department staff.

Changes may be made to software for one or more of the following reasons:

- An improvement to the way the software performs its particular task is requested;
- Client specification or request requires a slight modification to a particular software process;
- New tests or procedures added to the data handling system; or
- Custom reports or EDD generation are requested.

Each of the items listed above may encompass varying levels of detailed changes to a software process. Whenever these changes, as defined in the Procedures Section of this SOP, are made to a software process, the process must be validated to ensure that the change was made successfully. This validation is documented on a Software Process Validation (SPV) form (Form 1403), that is then retained by the IS Department

indefinitely.

3. RESPONSIBILITIES

3.1 Paragon's Information Systems (IS) Department will maintain the verification/ validation records generated during the performance of this SOP. IS Department staff shall ensure that an SPV form is used and shall verify that the form is appropriately and completely filled out.

3.2 Laboratory Reporting Group staff involved in this process are required to adhere to the requirements of this SOP as they perform the necessary validation/ verification steps. Upon completion of the required documentation, the Reporting Group staff shall return the documentation to the IS Department, along with any supplemental records needed to demonstrate successful completion of this procedure.

4. PROCEDURES

4.1 DEFINITIONS

The following definitions apply exclusively to this SOP. While other SOPs may use some of the same text within their documentation, the meaning of the terms described below must be defined here in order to interpret this procedure properly.

- **Application:** A software program that may serve as a specific tool for data retrieval, processing, manipulation, and reporting.
- **Software Process:** A programming element of an application that performs a specific task within that application.
- **Process Validator:** An individual who has been designated to test a Process Change in order to validate its effectiveness and accuracy.

4.2 PROCESS CHANGES TO SOFTWARE

Process Changes to software are defined as any change that may affect the final result or any supporting flag conventions that were used to report results to clients. The following are examples of Process Changes that would initiate the software process validation procedures discussed in this SOP:

- A change in an equation or equations that are used to obtain a result.
- A change in the logic structure of the program that is used to access equations.
- A change in the logic structure of the program used to flag associated results with any particular set of flagging criteria, including client specific criteria.
- A change in any part of the application process that affects both retrieval and manipulation of data from instruments, or the process of hand data entry.

- A change that may alter or modify the use of a variable (one that is either calculated or logical) in a data process.

4.3 Examples of issues or items that are *not* regarded as Process Changes under the above definitions and descriptions and, therefore, *will not* initiate the software process validation procedure include:

- A change to a field width on a report.
- A change to fonts that are used on a report.
- A change to properties of a field relating to user access and/or privileges.
- Cosmetic changes to the user interface and other supporting screens.
- Adding test codes, client names, or other supporting information to an application.

4.4 When a Process Change, as described above, is made to an application, an SPV form must be issued to a Process Validator who works with the Department(s) for whom the Process Change affects. This Process Validator will verify that the Process Change works as intended and shall complete the SPV form within three (3) working days. The SPV form will then be returned to the IS Department for archival.

4.5 If, however, the Process Change does not perform as expected, the Process Validator shall mark the SPV form with an entry in the appropriate section for an unsuccessful Process Change, and shall initial and date this entry. The SPV form will then be returned to the IS Department who will first correct the problems with the Process Change, then re-issue the same SPV form for re-evaluation. These steps will repeat as necessary until the Process Change can be validated.

5. PROCESS SUMMARY

The following is a summary of the steps required to satisfy the requirements of this SOP:

- A Process Change, as defined in herein, is requested, and is made according to the procedures discussed above.
- A Software Process Validation (SPV) form is issued by the IS Department to a Process Validator for completion.
- The Process Validator tests the Process Change. If the Process Change is successful, all required documentation is returned to the IS Department and the IS Department retains the SPV form indefinitely.
- If the Process Change is unsuccessful, the Process Validator marks an entry indicating such on the SPV form and initials and dates the entry. The SPV form and all support information is given to the IS Department.
- The IS Department makes the appropriate corrections and re-issues the SPV form

to the Process Validator.

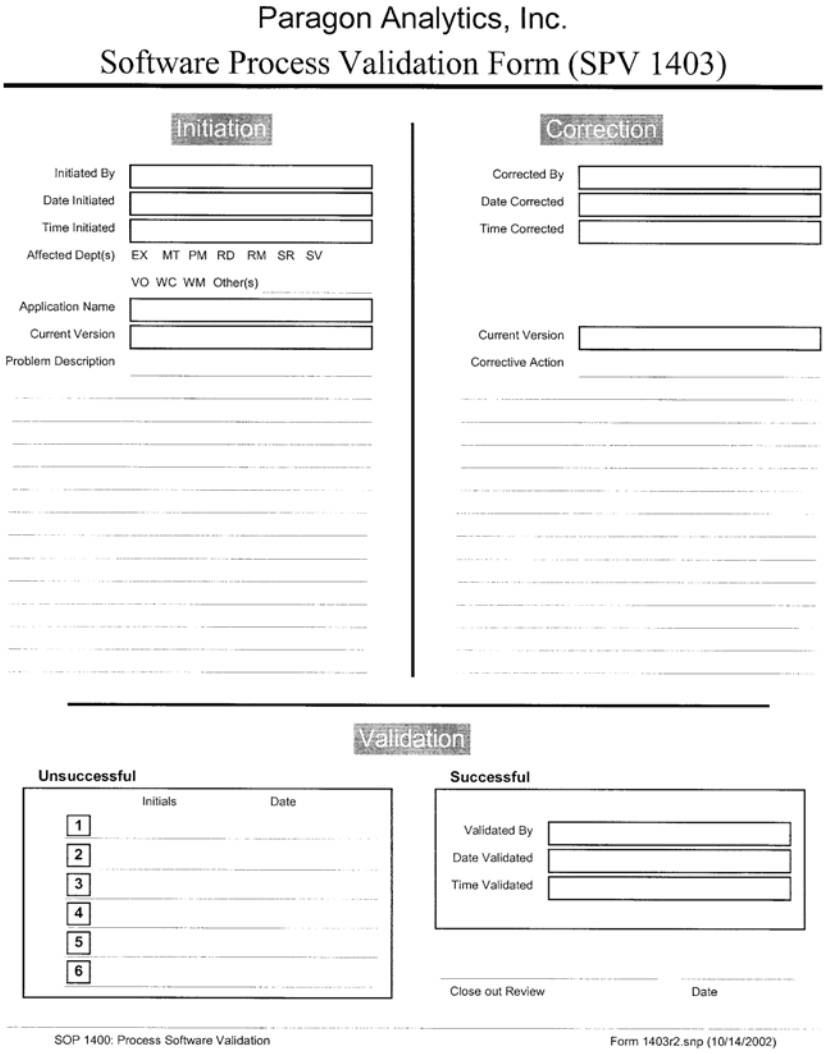
- The cycle of circulation of the SPV form between the IS Department and the Process Validator is repeated until the Process Change is successful.

6. REFERENCES

None.

DOCUMENT REVISION HISTORY

1/8/07: Added Form.



Paragon Analytics, Inc.

Software Process Validation Form (SPV 1403)

Initiation

Initiated By
Date Initiated
Time Initiated
Affected Dept(s) EX MT PM RD RM SR SV
VO WC WM Other(s)
Application Name
Current Version
Problem Description

Correction

Corrected By
Date Corrected
Time Corrected
Current Version
Corrective Action

Validation

Unsuccessful

	Initials	Date
1		
2		
3		
4		
5		
6		

Successful

Validated By
Date Validated
Time Validated

Close out Review Date

SOP 1400: Process Software Validation Form 1403r2.snp (10/14/2002)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1401 REVISION 5

TITLE: COMPUTER AND LIMS BACKUP AND RESTORATION PROTOCOLS

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1-8-07

QUALITY ASSURANCE MANAGER _____ DATE 1/8/07

LABORATORY MANAGER _____ DATE 1-8-07

HISTORY: Rev0, 11/15/99; Rev1, 8/25/00; Rev2, 3/28/02; Rev3, 3/28/03; Rev4, 2/13/04 and 3/9/06 (re-released without revision; Rev5, 1/8/07. re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes procedures for backing up network servers and instrument PC hard drives. Archiving of backup tapes and restoration of files is also discussed.

2. SUMMARY

The Information Systems (IS) Manager routinely backs up all instrument computer systems and network files. The files are verified as they are backed up and re-verified subsequently to ensure restorability. Key backup tapes are stored in an off-site bank vault.

3. RESPONSIBILITIES

3.1 The IS Department is responsible for establishing and following procedures regarding backup of network files, and for overseeing PC hard drive backup efforts. The IS Department shall determine what devices and supplies are suitable for accomplishing backups and restorations, and shall maintain these devices and availability of the necessary supplies. Management of archived file information is the responsibility of the IS Department. The IS Department is responsible for file restoration efforts as they become necessary, or when requested.

3.2 Laboratory staff are responsible for coordinating instrument backup with the IS Department in accordance with established schedules.

3.3 It is the responsibility of all personnel who work with these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. PROCEDURES

Several aspects of routine network operations (including backup) are highlighted below:

- The network is scanned constantly for viruses.

- The network is completely backed up every night, with the exception of Saturday and Sunday. Monday through Thursday tapes are kept on-site. Each tape can accommodate three weeks of backup. The IS Manager maintains the tape archive. Friday tapes are stored off-site in a bank vault.
- Database files maintained on the network are backed up three times daily. The files are verified each time they are backed up. LIMS, reporting databases, and accounting databases are all backed up in this manner.
- Patches and upgrades from both Microsoft and Netware are checked for weekly. If found, patches and upgrades are installed during the off-hours so as not to impact laboratory productivity. Laboratory personnel are notified via e-mail of any upcoming network maintenance.
- Most instrument PCs are network interfaced. Stand-alone instrument PC systems and files are backed up periodically, as needed, prompted by the laboratory Department Manager or other applicable staff.

5. REFERENCES

None.

DOCUMENT REVISION HISTORY

1/8/07: Updated RESPONSIBILITIES. Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

See various amendments page 2 (i.e., further details provided).
3/9/09 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 1402 REVISION 6

TITLE: **LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS) VERSION CONTROL**

FORMS: ~~NONE~~

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/5/07

QUALITY ASSURANCE MANAGER _____ DATE 11/4/07

LABORATORY MANAGER _____ DATE 11/5/07

HISTORY: Rev0, 3/3/98; Rev1, 8/25/00; Rev2, 3/28/02; Rev3, 3/28/03; Rev4, 2/13/04 (format update) and 7/26/05 (re-released without revision); Rev5, 1/8/07; Rev6, 11/4/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes procedures for tracking and controlling release iterations of LIMS software.

2. SUMMARY

The Laboratory Information Management System (LIMS) is a Microsoft Windows® based product that was developed in-house. The LIMS is maintained and customized by the LIMS Manager as the needs of the laboratory and clients require. Any changes that are made to the LIMS, or portions of the LIMS, are documented and maintained by the LIMS Manager in a version control database. The version control database contains the following information:

- Old version number;
- Name of object that was changed;
- Type of object changed;
- Description of the item changed within the object;
- Date the change was made;
- Detailed description of what function the change addresses or performs ;
- New version number.

3. RESPONSIBILITIES

3.1 The LIMS Manager is responsible for the maintenance and continued development of LIMS. The LIMS Manager is responsible for maintaining a library of changes made to LIMS. The LIMS Manager shall determine what LIMS training is required contingent upon functional position, and shall oversee the employee's receipt of appropriate LIMS training.

(by means of use of discrete data sets; limited application before full release, etc.) 3/9/09 DAS

3.2 All LIMS hardware and communications components changes are proposed and performed by IS/LIMS management staff, with the concurrence of the Laboratory Director. All changes are fully tested before being implemented throughout the laboratory. The acceptance criteria is that the change adequately addresses the need, and provides accurate data/processing.

are

the correct information is referenced or captured, 3/9/09 DAS

All employees shall adhere to IS and LIMS policies as they are directed, and as expressed in Paragon's IS and LIMS policy statements, for which each employee receives annual refresher training.

3.4 It is the responsibility of all personnel who work with these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. PROCEDURES

The LIMS Manager retains a "working copy" of the LIMS -- this copy is used to make any changes to the LIMS. After these changes have been made, the LIMS Manager documents the changes, as described above, and "releases" the newest version of LIMS. A sequence of steps describing the process of making a change in LIMS is shown below:

- The LIMS Manager changes objects (portions) in LIMS as needed.
- The changes are documented in the version control database (as described above).
- The changes are tested by the LIMS Manager prior to release.
- The LIMS Manager releases the newest version of the LIMS to the laboratory.
- LIMS upgrades are automatically installed prompted by a small program that has been incorporated into the network login process.
- The LIMS Manager maintains an archive of version updates.

(i.e., is the outcome independently verifiable), and does the software task run from start to finish without 'freezing' or other glitch (e.g., no error messages) 3/9/09 DAS

5. REFERENCES

None.

DOCUMENT REVISION HISTORY

1/8/07: Updated RESPONSIBILITIES. Added DOCUMENT REVISION HISTORY.

11/4/07: Updated RESPONSIBILITIES to include IS/LIMS management staff with the concurrence of the Laboratory Director, regarding all LIMS hardware and communications components changes. Also noted that the acceptance criteria for these changes is that the change adequately addresses the need, and provides accurate data/processing.

The LIMS Manager is responsible for maintaining documentation of software testing, including the evaluation of test results. 3/9/09 DAS

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 143 REVISION 4

TITLE: **NEW EMPLOYEE QUALITY ASSURANCE ORIENTATION AND TRAINING**

FORMS: **159, 162, 921, 977**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7/18/05
QUALITY ASSURANCE MANAGER _____ DATE 7/18/05
LABORATORY MANAGER _____ DATE 7-19-05

HISTORY: Rev0, 3/28/95; Rev1, 8/23/00; Rev2, 4/17/02; Rev3, 9/22/03; Rev4, 7/20/05.
re-released w/o revision 10/15/07 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) provides an overview of the Quality Assurance (QA) training received by new employees. The scope and content of the Health & Safety and waste disposal training also received by new employees is not addressed in this SOP.

2. OVERVIEW

QA training is given to new employees in five phases: (1) General Introduction and Initial QA Training, (2) Departmental Orientation and SOP Review, (3) On-the-Job Training, (4) Initial Demonstration of Capability (IDOC), and (5) supplemental QA and Department Training sessions, as topical needs arise. Health & Safety and waste disposal training are managed and conducted by the Health & Safety and Facilities Departments.

3. RESPONSIBILITIES

3.1 Only staff that have previously demonstrated competency in the area for which training is to be conducted are permitted to train.

3.2 Management of training content, scheduling, and documentation of training conducted is the responsibility of the appropriate Department Manager.

3.3 The QA Department is responsible for the oversight and maintenance of all QA and skills training records.

3.4 The Health & Safety and Facilities Departments are responsible for the oversight and maintenance of all Health & Safety and waste disposal training records.

4. PROCEDURE

4.1 A representative of the QA Department meets with each new employee, usually on their first day of hire. Specific employee information (name, employee number, title, group assignment, etc.) is entered into the SOP and Training Records database. Preliminary SOP assignments are also made in the database. An employee folder is created on the network to receive images of the employee's training records.

4.2 The QA Department representative then performs the following steps as part of the General Introduction and Initial QA Training:

- an overview of Paragon's quality culture and training to be received is given.
- The employee's initials and signature are obtained (Form 977, Ongoing Signature and Initials File).
- Signed Professional Conduct (Form 162) and IS and LIMS Policies ethics statements are acquired.
- The employee is informed of obligations and protection under "Whistleblower Protection for Contractor Employees", USDOE General Provision DEAR 952.203.70 (Form 921, Waste, Fraud and Abuse Notification).
- Copies of the employee's resume and degree, transcript or diploma are requested if not already available.

4.3 Credits for the above information are entered into the SOP and Training Records database. Preliminary SOP assignments are made and a printout of the employee's assigned SOPs is provided. The following SOPs, *which must be read and signed-off within two weeks of hire*, are discussed with the new employee:

- Control and Format of Laboratory Logbooks (SOP 303)
- Internal Chain-of-Custody (SOP 318)
- Review, Revision and Distribution of Controlled Documents (SOP 926)
- Issuing and Tracking of Non Conformance Reports (SOP 928)

4.4 The Laboratory Quality Assurance Plan (LQAP) is identified and stipulated as required reading *within the first month of hire.*

4.5 Images of information obtained above, as applicable, are posted to the employee's folder on the network.

4.6 The new employee is then routed to the Health & Safety Manager or Facilities Manager or designee to receive their initial Health & Safety and waste disposal Training.

4.7 Following initial Health & Safety and waste disposal training, the appropriate Department Manager oversees the Departmental Orientation and SOP Review Training received by each new employee. Employee SOP review is managed via the SOP module of the SOP and Training Records database. Dates for each SOP that were read by the new hire are entered into the database by the Department Manager, and the new employee signs a report printout attesting to the SOPs read and understood. The signed SOP report is forwarded to the QA Department for retention.

4.8 Departmental skills are learned by the new employee during On-the-Job Training with appropriate supervision. After sufficient competency has been gained in a particular area or with regard to a specific technical SOP, the new hire substantiates his/her skill via an Initial Demonstration of Capability (IDOC). IDOC summary data, reviewed and signed by the Department Manager, is submitted to the QA Department for tracking and retention.

4.4 Supplemental QA and Department Training (continuing education) is provided to employees via topical training sessions, as the need arises. The QA Department maintains these training files (credits the training in the database, posts documentation images).

5. REFERENCES

None.

Must Discard 30 Days from _____ (date printed)

See change page 9, Section 7.7.4.2 Note, re: metals, mercury and some RAD samples whose pH was adjusted must be held for a minimum of 24hrs (not 16!) before processing. 1/16/08 DAS

Note Section 7.3.6 amendment, and addition of Operator's Aid with same content. 12/24/08 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 202 REVISION 10

TITLE: LOGIN AND DISTRIBUTION OF SAMPLES AND WORKORDERS

FORMS: 008, 201, 214, 319 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 12/11/06

QUALITY ASSURANCE MANAGER _____ DATE 12/11/06

LABORATORY MANAGER _____ DATE 12-12-06

HISTORY: Rev0, 12/23/94; Rev1, 5/22/97; Rev2, 1/6/99; Rev3, 11/24/99; Rev4, 1/17/00; Rev5, 8/14/01; Rev6, 1/24/02; Rev7, 4/17/02; Rev8, 3/19/03; Rev9, 2/9/04 and 7/18/05; Rev10, 12/7/06.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes procedures for the acceptance and login of samples received by Paragon. Samples are received and processed in a manner that minimizes both exposure risk to laboratory personnel and potential for sample contamination.

Radiation survey, login procedures, workorder folder initiation, sample temperature upon receipt (where applicable), sample identity and condition verification, discrepancy resolution, temporary storage, Project Manager review, and distribution of samples within the laboratory are discussed. Sample chain-of-custody procedures are addressed in SOP 318. SOP 207 addresses sample packaging for subcontracted analysis.

2. SUMMARY

All sample shipping containers are surveyed for external radiation (SOP 008). For chilled samples, cooler temperature is determined. The contents of each shipping container are inspected for breakage, then the cooler is unpacked. A workorder number is assigned and a workorder folder initiated. General sample information is entered into the Laboratory Information Management System (LIMS), and Paragon sample labels are generated and applied to each sample bottle. Where appropriate, samples are prescreened (SOP 703) to roughly determine the nature and level of radioactivity. Where applicable, samples are checked for pH and/or residual chlorine. The samples are then grouped (for future segregated sample storage), but held together in temporary storage pending ~~release by the Project Manager. Samples are not released for~~ distribution to the laboratory areas ~~for processing until additional login steps are completed and the Project Manager has reviewed the workorder folder.~~ 1/7/07 DAS

3. RESPONSIBILITIES

3.1 Only personnel who have been trained regarding Department of Transportation (DOT) survey and the procedures outlined in this SOP will be responsible for

sample receipt and workorder preparation.

3.2 Sample Receiving staff are responsible for observing required sample handling protocol, including secondary containment (SOP 023), and for managing the contents and operation of the cooling units in use in the Sample Receiving area.

3.3 Paragon's Radiation Safety Officer (RSO), in conjunction with the Sample Receiving Department Manager, are responsible for properly maintaining the radiation survey equipment, ensuring that calibration requirements are met and retaining associated documentation, and for keeping an appropriate supply of associated materials (e.g., check standards, wipes, etc.).

3.4 The Quality Assurance Department is responsible for providing verified thermometers, including infrared temperature devices, for use by Sample Receiving staff and for issuing temperature verification logbooks as needed.

3.5 The Sample Receiving Department Manager is responsible for ensuring that all personnel are properly trained in LIMS and all tasks described in this SOP, and for ensuring that the proper equipment and consumables (e.g., labels, acids, bases, test kits, disposable pipets, etc.) needed to perform these tasks are readily available.

3.6 The Project Manager is responsible for communicating all necessary information to Sample Receiving staff, for interfacing with the client to resolve discrepancies, for reviewing all login information, and for releasing the samples electronically in LIMS once the workorder review has been completed, so that the work may begin.

3.7 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.8 It is the responsibility of all personnel who work with these procedures to note any anomalies or out-of-control events. Any discrepancies must be documented and corrective action taken and documented.

4. INTERFERENCES

4.1 Samples are received and entered into the laboratory system through the Sample Receiving area. This area is not designated for sample preparation, waste disposal, or solvent/reagent storage or any other practice that could pose undue

risk of contamination of samples during login processes. A fume hood is used when sample shipping containers are initially opened. Benchtop areas used for sample container inspection and staging for labeling are frequently wiped down. With the exception of required pH and/or chlorine residual check, sample containers are to remain closed during login.

4.2 Segregated (e.g., standards vs samples, volatiles only, etc.) cooling units (i.e., refrigerators, freezers) are maintained throughout the laboratory and their temperatures are controlled within method-required limits (SOP 326). Samples for volatile analysis (VOAs) are transferred from temporary (RU#20) storage to the appropriate volatiles laboratory (e.g., GC/Fuels or GC/MS-VOAs) storage units, as quickly as possible to avoid potential cross-contamination. A volatiles refrigerator blank program (SOP 512) is observed by Paragon to monitor potential volatile sample contamination. Samples requiring preparation for organic, inorganic and/or radiochemical analysis are likewise transferred to their designated storage areas.

5. APPARATUS AND MATERIALS

5.1 Radiation Exposure Rate Survey Meter, Ludlum Model 19 or Model 192 MicroRoentgen meter or Ludlum Model 3 Survey Meter with Geiger-Mueller Detector or other equivalent, and appropriate check standards

5.2 Filter Paper, Whatman #42 (47 mm), Rad-Wipe Smears, or other equivalent

5.3 Pre-printed “Radioactive Materials” stickers

5.4 Infrared temperature device, Oakton InfraPro2 or equivalent
(Operation and daily check procedures for this device are detailed in SOP 210)

5.5 File folders, 8½ x 11 size, various designated colors

5.6 Barcode label printer, Seiko Instruments Model 220 or equivalent

5.7 Labels, Seiko SLP-2RLH, 28mm x 89mm, self-adhesive or equivalent

5.8 pH paper: narrow range, acidic (for reading pH<2), narrow range, basic (for reading pH>9), wide range (for reading pH 0-14)

5.9 Pasteur pipette, glass, disposable

5.10 Eppendorf (or equivalent) pipettor, 5mL, and disposable tips

5.11 Specimen cups, disposable, polypropylene

6. REAGENTS

6.1 pH Adjustment:

Nitric Acid (HNO_3), concentrated, trace metals grade

Hydrochloric Acid (HCl), concentrated, reagent grade

Sulfuric Acid (H_2SO_4), 50%, reagent grade

Sodium Hydroxide, NaOH, 20%, reagent grade

6.2 Chlorine Residual Testing and Adjustment:
DPD dispenser, IDEXX Laboratories #WDPD5FD, or equivalent
Sodium Thiosulfate ($Na_2S_2O_3$), 0.008%, reagent grade

7. PROCEDURE

7.1 Inspect the cooler's custody seals, if present, and note presence/intactness on Sample Receipt Form 201.

7.2 DOT SURVEY
All sample shipping containers must be surveyed for external radiation upon receipt. Complete the DOT survey per SOP 008. Document the survey results on Sample Receipt Form 201 (Comments Section) or Form 008 (in cases where a more extensive survey is required). As necessary, notify the Sample Receiving Department and Project Managers of any discrepancies or non-compliance with DOT 49 CFR and IATA regulations.

NOTE: Due to radioactive material license limitations, Paragon will not accept radioactive material packages that require a Radioactive II or III DOT Warning label. Neither will Paragon accept Radioactive Material - Low Specific Activity, N.O.S. packages with more than 0.5 mR/hour surface radiation exposure rate.

7.2.1 Coolers yielding survey results less than two times (2x) laboratory background levels will be processed for normal login.

7.2.2 Samples will be provisionally logged in and routed for prescreening (SOP 703) if:

- the client is listed in LIMS as "Requires Prescreen"
- the samples are from a Department of Energy (DOE) client
- the cooler has been shipped as a radioactive material per 49 CFR or IATA regulations
- the cooler survey yields results greater than two times laboratory background levels.

7.2.3 If the samples were shipped as radioactive materials, or the cooler survey yields results >2X background (see Step 7.2.2 above), the following steps are also performed (SOP 008):

- the outside of the cooler is swiped

- the inside of the cooler is swiped
- a composite swipe of the bottles is done

7.3 INSPECTION AND VERIFICATION
TEMPERATURE DETERMINATION (CHILLED SAMPLES)

7.3.1 If applicable, retrieve the associated Incoming Project Notice (IPN; Form 214), LIMS program specification directives, or any prior communication notes.

7.3.2 Under a fume hood, open the sample shipping container (cooler) and remove all paperwork.

7.3.3 Initially inspect the cooler's contents for breakage. After the initial inspection is complete, the cooler may be unpacked outside of the hood, as appropriate. If it is noted that a sample is broken, the broken sample must be secured appropriately before unpacking the cooler.

7.3.4 Following procedures outlined in SOP 210, obtain a representative temperature of chilled samples as promptly as possible (within two hours of receipt); record result on Form 201. Coolers that are chilled should yield temperatures between 0.1-6 °C. Note on Form 201 if iced samples are received near to the time they were obtained, and have not yet had enough time to cool to required temperature. Notify the Project Manager as soon as possible if temperature is not within specified limits.

7.3.5 Unpack the cooler, further inspecting each sample for integrity (e.g., lid not cracked, no headspace where required to be headspace-free, etc.) Note issues observed on Form 201.

7.3.6 ~~Arrange the sample bottles on a bench top in groups according to client sample ID, and in the order they appear on the client chain-of-custody (COC) form.~~ See amendment on page following 12/24/08 DAS

7.3.7 ~~Verify sample bottle label information against the information given on the client COC. Record discrepancies noted on Form 201. Notify the Project Manager of any documentation discrepancies, missing information, or problems with sample integrity. Complete the field COC form by adding the signature of the receiving technician and the date and time of laboratory sample receipt.~~

7.3.~~8~~10 As applicable, remove the shipping label from the sample cooler and place it in the workorder folder (see Step 7.9).

7.3.6 **Line the samples up on the benchtop, based on presented COC order. Double check the line up and multiple bottle position against the COC. This step is to be performed after the initial line up and after all samples and associated bottles have been placed in the proper order. This step provides for a double check and must include all associated bottles in the sample set.**

7.3.7 Verify sample bottle label information against the information given on the client COC. Record discrepancies noted on Form 201. Notify the Project Manager of any documentation discrepancies, missing information, or problems with sample integrity. Complete the field COC form by adding the signature of the receiving technician and the date and time of laboratory sample receipt.

7.3.8 **Assign laboratory IDs in the sequence of the sample listing on the COC; create labels (see 7.4.3 below).**

7.3.9 **While applying the labels (see also 7.4.3.5 below), verify the label ID against the laboratory ID on the COC, and the client ID number. Make sure that all numbers match accordingly, and that all samples and their associated bottles are in the listed order on the COC. It is strongly encouraged to ask for an independent double check randomly, and for difficult sample sets (e.g., long or convoluted client IDs), while labeling.**

7.4 PRELOGIN

Paragon LIMS is a relational database that was developed in-house and is a proprietary product. Information regarding the structure and function of LIMS may only be viewed by Paragon employees and may <u>not</u> be provided to any non-employee (e.g., client, auditor, validator).

7.4.1 Go to the 'PRELOGIN' section of LIMS, and create a workorder number. Indicate the assigned Paragon workorder number on the field COC and on all other workorder paperwork.

<u>NOTE</u>: The work order number format is based on date (YYMMNNN), with NNN indicating ascending workorder, starting at 001 each month.

For example: The first batch of samples received in January 2007 would be assigned the work order number 0701001.

7.4.2 Enter the following sample information into LIMS:

- client name
- date and time samples received
- number of samples received
- matrix (e.g., soil, water, oil, liquid, solid, filter, wipe)
- preservative used
- number of bottles per sample
- sample storage area designation (upon distribution)
- note if there is a limited volume

7.4.3 Individual sample designations and barcode labels will now be generated:

7.4.3.1 Each sample designation within the workorder is assigned a unique "dash" number (-XX), that is an incremental extension of the workorder number.

For example: The first sample designation within the first batch of samples received in January 2007 would be assigned 0701001-01.

7.4.3.2 The laboratory assigned sample designations (Paragon ID) may be marked on the field COC next to the corresponding

client ID.

7.4.3.3 Multiple containers of the same sample designation receive the same "dash" number, followed by an incremental container number (-N).

For example: The 3rd bottle provided for the first sample designation within the first batch of samples received in January 2007 would be assigned 0701001-01-3.

7.4.3.4 Print the Paragon barcode labels, which also contain text as described above, for all samples in the workorder.

7.4.3.5 Take care to carefully affix each Paragon label to the proper client sample and bottle. To the extent possible, affix the Paragon labels such that no information already present on the sample container is obscured. If necessary, wipe the outside of the containers dry prior to labeling.

7.5 APHIS DESIGNATION

All soil samples that require U.S. Department of Agriculture (USDA) Animal and Plant Health Inspection Service (APHIS) Foreign Soil Quarantine, will be labeled with the APHIS Quarantine Label (available from the Health & Safety Manager). These are soil samples from foreign countries and most states south of Colorado. These samples will require heat treatment (SOP 001) prior to disposal.

7.6 PRESCREEN

If samples do not require prescreening, skip to Step 7.7. Perform the following steps for samples that are only to be provisionally logged in (i.e., that are to remain in prelogin status) to allow for radioactivity prescreening before sample acceptance:

7.6.1 Store the samples in the Sample Receiving walk-in cooler (RU#20).

7.6.2 Enter the sample information (Paragon ID, matrix, etc.) onto the "Prescreen Log" (Form 319). This form serves as both a work request and temporary chain-of-custody documentation.

7.6.3 Copy the field COC on bright pink (or some other eye-catching color) paper. If not all samples listed on the COC are to be prescreened, indicate the ones that *are* to be prescreened by circling them.

7.6.4 Give the prescreen paperwork directly to the Prescreen Analyst or clip it to the Prescreen clipboard located near the doorway of the Prescreen Lab.

7.6.5 Prescreen personnel use the Form 319 to sign out the designated samples from RU#20, aliquotting them for analysis (SOP 703), then returning and signing the samples back into RU#20.

When available, the prescreening results are given to the Sample Receiving Department Manager (or designee) for entry into LIMS. The LIMS evaluation will classify the samples, generate special handling instructions as applicable, and generate additional sample labels as appropriate, based on the prescreen results.

NOTE: Samples designated for prescreening are considered to be 'On Hold' and cannot be removed from 'Hold' status until the special handling instructions have been completed and the samples are released in LIMS (see Section 7.12). **Note that some samples may require RSO approval for release based on the level of radioactivity.**

A copy of the prescreen results, and special handling instructions as applicable, is placed in the workorder folder.

7.6.6 Apply any additional labels provided to the appropriate sample containers, as directed by the special handling instructions.

7.7 pH CHECK

Where applicable, the pH of non-volatile, non-biological aqueous samples is verified (the fume hood may be used when performing this task). *Do not verify the pH of urine samples received*:

7.7.1 Stage several portions of the appropriate pH paper (e.g., narrow range acidic for samples preserved with acid; narrow range basic for samples preserved with NaOH; etc.) for testing.

7.7.2 Use a clean glass Pasteur pipette to remove a *small* aliquot of sample from its container. Dispense the aliquot by spreading a few drops over a piece of pH paper. Dispose of the used pipette properly.

7.7.3 Read the pH paper immediately, and record results on Form 201:

7.7.3.1 the strip must read ≤2 for samples that are acid preserved and whose pH should measure ≤2.

7.7.3.2 the strip must read ≥9 for samples that are base-preserved and whose pH should measure ≥ 9. **Note that the required pH for base preserved samples varies from ≥9 to ≥12, depending on method requirements.**

7.7.3.3 the strip should read approximately 7 (use wide range pH paper), for samples that are non-preserved and whose pH should be neutral.

7.7.4 ***DO NOT** adjust the pH of a sample unless directed to do so by the Project Manager! Notify the PM immediately of any sample pH outside the acceptance limit.* The PM will contact the client for direction on how to proceed.

7.7.4.1 If the PM instructs Sample Receiving personnel to add preservative to the sample, record the sample ID, initial pH, type and amount of preservative used, lot or standard number, new pH, and date and time of addition on Form 201.

7.7.4.2 Label the sample bottle adjusted with the amount and type of preservative used, date and initials of the individual who adjusted the pH.

NOTE: Metals, mercury and various radiochemistry method requirements dictate that samples preserved (or pH adjusted) at the laboratory, must be held for a minimum of ~~16~~ 24 hours in the original sample container before aliquotting for analysis. 1/16/08 DAS

7.8 CHLORINE RESIDUAL DETERMINATION

Some samples, to be analyzed by 600-series (wastewater) methods, may require that a chlorine residual check be performed upon sample receipt. **Perform this task only when directed to do so by the Project Manager:**

7.8.1 Using a 5mL Eppendorf-type pipettor, and a clean pipette tip for each sample container, take an aliquot of sample from its container and dispense it into a labeled plastic specimen cup. Recap the sample container.

7.8.2 Shake the EZ DPD dispenser. Remove the cap and dispense one aliquot of the reagent into each specimen cup by depressing the button.

7.8.3 Gently swirl the specimen cup and watch for any color change.

NOTE: In the event of a color change indicating the presence of residual chlorine, notify the Project Manager immediately. ***DO NOT ADD SODIUM THIOSULFATE OR PROCEED WITHOUT THE PROJECT MANAGER'S PERMISSION!***

7.8.4 If the PM, per client instruction, instructs Sample Receiving personnel to proceed with login of samples containing residual chlorine, check the appropriate box and list the affected samples on page 2 of Form 201.

7.9 FOLDER INITIATION

Initiate a workorder folder. Various colors of file folders are used for easy visual indication:

- red folders are for workorders containing samples that require prescreening
- gray folders are used to indicate normal considerations and turnaround times
- orange folders denote a "RUSH" order

Select the appropriately colored folder and mark the workorder number and client name on the folder's tab. Place all workorder paperwork (e.g., shipping label, IPN, Form 201, field COC, etc.) inside the folder.

7.10 STORAGE, LOGIN, DISTRIBUTION

7.10.1 Regroup the samples based on analysis type, place the samples in bins (SOP 023), and put the bins in RU#20 for temporary storage until the workorder (and special handling instructions resulting from prescreen analysis, if applicable), are released by the PM.

At the discretion of the PM, short-hold or RUSH samples not held for prescreen may be delivered to the appropriate laboratory area.

7.10.2 Check that all paperwork is present in the workorder folder, and forward it to the PM (or designee) for login and subsequent review.

7.10.2.1 Login of the samples is completed by adding additional information (e.g., client sample IDs, date sampled, appropriate test codes for analyses requested, turnaround time, etc.) into LIMS.

7.10.2.2 Various printouts (workorder, cross-reference Table, etc.) are added to the workorder folder. Any notes regarding atypical sample retention or disposal requirements (such as neutralization of quarantine samples per SOP 001) are also placed in the workorder folder, if not already present.

7.10.2.3 The LIMS login information and contents of the folder are then reviewed. Any discrepancies noted are corrected, and

the workorder is electronically released and distributed in LIMS.

7.10.3 Once released by the PM, distribute the remaining samples to the appropriate laboratories observing internal chain-of-custody procedures as outlined in SOP 318. If not already delivered, prioritize delivering short-hold and RUSH samples first.

If a single container is provided for multiple lab analyses, distribute according to the following priority list:

- If volatile organics by GC/MS are requested, deliver to the VOAs lab **or**
- If BTEX or GRO are requested, deliver to the FUELS lab **or**
- If any analysis is requested which requires cold storage, deliver to the cooling unit associated with the shortest hold analysis **or**
- Deliver to the location which has the most analyses designated for that sample.

8. SAFETY, HAZARDS AND WASTE DISPOSAL

8.1 SAFETY AND HAZARDS

8.1.1 The building is equipped with safety showers, eyewash stations, fire extinguishers, fire blankets, and first aid kits. All laboratory personnel must be trained in the use and location of these items.

8.1.2 Read the MSDSs before using any solvents or reagents for the first time.

8.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals, or within a laboratory area

8.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents.and acids).

8.1.5 All flammable compounds must be kept away from ignition sources.

8.1.6 Any non-original containers used to hold reagents (e.g., wash bottles, automatic dispenser bottles, etc.) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

8.1.7 Food and drink are prohibited in all lab areas.

8.2 WASTE DISPOSAL

All empty solvent bottles, pipets and contact wastes are disposed of according to the appropriate SOPs. All labels and markings must be defaced from reagent bottles or the bottles labeled as 'Empty' prior to disposal.

9. REFERENCES

40 CFR 139

49 CFR

IATA DGR (1997) or current year

Paragon LIMS Guide -- *Confidential*

DOCUMENT REVISION HISTORY

7/18/05: Re-released without revision.

12/7/06: Combined with SOP 201-- Laboratory Information Management System (LIMS) Entry of Sample Receipt Information and Distribution of Workorders (SOP 201 retired). Augmented Title to address both samples and workorders. Changed references to 'Sample Control' Department, to Sample Receiving Department throughout. Streamlined Summary (Section 2), expanded Responsibilities (Section 3), reworded Interferences (Section 4). Reordered and augmented Apparatus and Materials (Section 5), revamped Reagents (Section 6). Restructured, reworded and added more details to Procedure (Section 7) as needed. Made sure all acronyms were defined, added task identification headers. Use of Sample Login Book was deleted and replaced with PRELOGIN steps. Use of barcodes added. Additional References added to Section 9. DOCUMENT REVISION HISTORY Section was added; Forms were attached.

See various amendments

Paragon Analytics

SAMPLE LOGIN / DOT SURVEY

Client _____ Workorder No. _____ Project/Site _____

Shipping Container ID ____ ____ ____ ____ ____ ____ ____ ____

External Micro R Meter Reading (μ R/hr) ____ ____ ____ ____ ____ ____ ____ ____

Background Micro R Meter Reading (μ R/hr)_____ Date _____ Initials _____

Notify RSO immediately if shipping container's meter reading is more than twice background reading!!

Samples received from clients designated as "always prescreen" must be routed through the prescreening process (see SOP 202).

If twice background is exceeded, RSO or designee will complete the following Table:

CLIENT SAMPLE ID	CONTAINER DESIGNATION	EXPOSURE RATE (μ R/hr)

Further action (e.g., prescreening, wipe testing per SOP 008, etc.) will be directed by the RSO. As applicable, sample disposition will be communicated via LIMS Project Specifications.

Where applicable, attach LB5100 prescreening and/or wipe testing results.

Form 008r6.doc (6/26/04)

Paragon Analytics

CONDITION OF SAMPLE UPON RECEIPT FORM

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

1.	Does this project require any **special handling** in addition to standard Paragon procedures?		YES	NO
2.	Is **pre-screening** required per SOP 008?		YES	NO
3.	Are custody **seals** on **shipping containers** intact?	N/A	YES	NO
4.	Are custody **seals** on **sample containers** intact?	N/A	YES	NO
5.	Is there a **COC (Chain-of-Custody) present** or other representative documents?		YES	NO
6.	Is the **COC** (if applicable) **complete and legible**?	N/A	YES	NO
7.	Are **bottle IDs legible** and in **agreement** with **COC sample IDs**?	N/A	YES	NO
8.	Is the COC in agreement with samples received? (**# of samples, # of containers, matrix**)	N/A	YES	NO
9.	Were **airbills** present and/or removable?	N/A	YES	NO
10.	Are all **aqueous samples** requiring preservation **preserved correctly**? (excluding volatile organics)	N/A	YES	NO
11.	Are all aqueous **non-preserved samples** at the **correct pH**?	N/A	YES	NO
12.	Is there **sufficient sample** for the requested analyses?		YES	NO
13.	Were all samples placed in the **proper containers** for the requested analyses?		YES	NO
14.	Are all samples within **holding times** for the requested analyses?		YES	NO
15.	Were all sample containers received **intact**? (not broken or leaking, etc.)		YES	NO
16.	Are all samples requiring no headspace (volatiles, reactive cyanide/sulfide, radon), headspace free? **Size of bubble**: ____ < green pea ____> green pea	N/A	YES	NO
17.	Were samples checked for and free from the presence of **residual chlorine?** (Applicable when PM has indicated samples are from a chlorinated water source; note if field preservation with sodium thiosulfate was not observed.)	N/A	YES	NO
18.	Were the sample(s) **shipped on ice**?	N/A	YES	NO
19.	Were cooler temperatures measured at 0.1-6.0°C?	N/A	YES	NO

***IR gun used** *(circle one)*: **#2** - Oakton InfraPro II, SN2922500201-0066; **#4** - Oakton InfraPro II, SN2372220101-0002

Cooler #'s								
Temperature (°C)								
No. of custody seals								
DOT Survey/ Acceptance Information: External µR/hr reading								

Background µR/hr reading _____

Were external µR/hr readings ≤ two times background and within DOT acceptance criteria? **YES / NO** (If no, see Form 008.)

Additional Information: PROVIDE DETAILS BELOW FOR A NO RESPONSE TO ANY QUESTION ABOVE EXCEPT #1 AND #2

_____

_____

_____

_____

_____

_____

If applicable, was the client contacted? **YES / NO / NA** Contact Name:_____ Date/Time:_____

Project Manager Signature/ Date: _____

Form 201r18.xls (6/26/04)

Kit: Y / N **Rush?** Y / N **Prescreen?** Y / N ***Paragon Analytics***

INCOMING PROJECT NOTICE

Date: _____ **Copy to:** Sample Control

Initiator: _____

Date(s) expected: _____

Client: _____ Assigned PM: _____

Address: _____ Client Contact: _____

_____ Phone: _____

Report to: _____ Fax: _____

Proj. Name/Number: _____

# Samp	Matrix	Analysis/Method	Price	Sub Lab	# x Cont. Type	Preserv.	Tot. Bottles
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		

QC Level: _____ Disposal or handling? $5 / $10 / $15 / $_____ / RTC

Report Level: _____ TAT (working days): 20 / 15 / 10 / 5 / 3 / 2 / 24hr /____

EDD: N / Y Format: Report: Wet Weight / Dry Weight / As Received

Kit to:

Date kit needed: _____ **am / pm**

Attention: _____

Company: _____

Address: _____

_____

Phone: _____

Potential Radioactivity:

Do the samples contain radioactive materials?	Y / N
Are any samples potentially mixed hazardous materials?	Y / N
Are any samples from a known RAM site?	Y / N

Additional Special Handling:

Include: COC(s) Bubble Wrap Labels Seals Blue Ice Temp. Blks

Comments: Rush Special Test Special Analyte Special Charge Detection Limits (see attached)

Kit Prepared by: _____ Date: _____ Picked up by: _____ Date: _____

i:\oprtns\misc\forms\IPN_Form214r5.xls (10/29/03)

PRE-SCREEN CHAIN-OF-CUSTODY LOGBOOK *Paragon Analytics*

WORKORDER # And SAMPLE ID #	# Of Containers	Sample Matrix	Date & Time	Reliq. By	LOG Initials	OUT Date/Time	LOG Initials	IN Date/Time	Delivered By Initials/Date

ALL SAMPLES STORED IN RU20

Form 319r2.xls (12/15/99)

Sample Receipt Self-Check Steps

1.) **Inspect each sample for integrity while unpacking cooler (note issues on Form 201).**

2.) **Line up samples on benchtop per listed COC order.**

3.) **Double check line up and multiple bottle position against COC for all samples/bottles.**

4.) **Verify bottle label ID against COC ID, record discrepancies on Form 201, and notify Project Manager. Sign and date COC.**

5.) **Assign laboratory IDs in the sequence of the sample listing on the COC.**

6.) **Create labels.**

7.) **While applying labels, verify the label ID against the laboratory ID on the COC, and the client ID number.**

8.) **It is strongly encouraged to ask for an independent double check randomly, and for difficult sample sets, while labeling.**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 205 REVISION 8

TITLE: **PREPARATION OF BOTTLE ORDERS, SHIPPING SAMPLE KITS AND MAINTAINING INVENTORY OF BOTTLES, PRESERVATIVES, AND LABELS**

FORMS: **202, 214, 216** **(use current iteration)**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 11/20/06
QUALITY ASSURANCE MANAGER _____ DATE 11/20/06
LABORATORY MANAGER _____ DATE 11-21-06

HISTORY: Rev0, 2/13/92; Rev1, 10/20/92; Rev2, PCN #27, 11/15/93; Rev3, PCN #305, 12/23/94; Rev4, 2/13/02; Rev5, 2/10/03; Rev6, 9/22/03, Rev7, 3/24/05; Rev8, 11/20/06.
re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes procedures for preparing bottle orders (i.e., kit requests), shipping the prepared sample kits to the client, and maintaining an adequate inventory of bottles, preservatives, and labels.

2. OVERVIEW

Kit requests are generated by the Project Manager (PM) and are submitted to the Sample Receiving Department using an Incoming Project Notice (IPN), Form 214 or equivalent (e-mail, etc.). Sample Receiving personnel assemble the number and types of containers, associated paperwork, custody seals, labels and packing material, as needed to fill the request.

Preservatives are added to the containers, as applicable, per the bottle and preservative reference chart (Form 216), which references the sample container preservation limitations stipulated in 40 CFR 136.3, Table II.

The sample kit is then packaged (usually in coolers) and shipped to the client. Paragon chain-of-custody (COC) forms (Form 202) may also be provided with the shipment. The completed IPN (equivalent), is retained by the Sample Receiving Department. After the samples have been collected, the client ships the containers to Paragon for analysis.

Sample Receiving personnel maintain an approximate two-week supply of bottles, preservatives and labels.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 Paragon's LIMS program specification system and associated project analyte

nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

4. APPARATUS AND MATERIALS

4.1 vials, bottles and jars (various materials, sizes and closures), purchased as clean from the manufacturer.

NOTE: Bottle lot numbers and manufacturer's lot analysis information are retained on file by the Sample Receiving Department.

4.2 reagent dispensers (e.g., 0.5mL, 5mL, 25mL, as needed)

4.3 pipets, glass, disposable

4.4 pH paper, narrow range, acidic (pH <2), EMD #1.09580 or equivalent

4.5 pH paper, narrow range, basic (pH >10), EMD #1.09585 or equivalent

4.6 packing material (e.g., foam blocks, bubble wrap, styrofoam peanuts)

NOTE: Per Paragon's Health & Safety Manager, use of vermiculite is not permitted.

4.7 packaging tape

4.8 custody seals

5. REAGENTS – only reagent grade or better chemicals shall be used, only trace metals grade nitric acid shall be used!!

5.1 Sulfuric Acid (H_2SO_4), concentrated, approximately 98%

5.2 Hydrochloric Acid (HCl), approximately 36%

5.3 Nitric Acid (HNO_3), 20% (v/v), **trace metals grade only!!**

5.4 Sodium Hydroxide (NaOH), approximately 20%

5.5 Sodium Thiosulfate ($Na_2S_2O_3$), 10%

5.6 Zinc Acetate, $Zn(C_2H_30_2)_2$, 2N

5.7 Trip Blank Water, unpreserved -- prepared by the GC/MS-Volatiles laboratory, as requested -- preserved in Sample Receiving Department with HCl as needed -- not stored for future use.

6. PROCEDURE

6.1 The PM initiates a kit request (IPN, Form 214 or equivalent), and submits it to the Sample Receiving Department with as much advance notice as possible (a minimum of 3 days prior notification is preferred).

6.2 Generally, the number and types of bottles and preservatives needed are indicated on the IPN (client-specific requests/requirements may apply). A bottle and preservative reference chart (Form 216) is available in the Sample Receiving Department for consultation. The proper amount of preservative is added to the containers, as applicable, after Sample Receiving personnel compile the required sample containers. Preserved bottles are labeled with specific reagent stickers or color-coded labels, indicating the presence of a particular preservative.

NOTE: All dispensing of preservatives is to be done in the fume hood, while wearing safety glasses, latex gloves, and a lab coat.

6.3 Trip Blanks may be requested by clients sampling for Volatile Organic Analytes (VOAs). The number of Trip Blank sets needed, and whether or not the Trip Blanks are to be sent unpreserved or preserved with HCl, is stipulated by the client and indicated on the IPN/equivalent. Trip Blanks are prepared as follows:

6.3.1 Each set of Trip Blanks consists of two 40mL, certified-clean, VOA vials completely filled (i.e., no headspace present) with prepared Trip Blank water (see Section 5.7).

6.3.2 For Trip Blanks that are to be preserved with HCl, a container of Trip Blank water is adjusted to pH <2 with 36% HCl. The pH of the acidified water is verified to be <2 using low range pH paper and a clean Pasteur pipette. The acidified Trip Blank water is then used to fill the VOA Trip Blank vials (headspace free).

6.4 The sample kit is assembled and packaged (usually in coolers) by Sample Receiving personnel. Foam blocks, bubble wrap, styrofoam peanuts, etc. are used to cushion the containers. All preserved containers are placed in secondary containment (i.e., plastic bags). An absorbent pad is placed in the bottom of all coolers that contain preserved bottles. Paragon chain-of-custody forms (Form 202) if requested, and other associated paperwork (i.e., seals and labels) are placed in a Ziploc bag and put on top of the supplies placed inside the cooler. If any of the sample containers were preserved, a "Preservative Warning" statement and appropriate MSDSs are also placed in a Ziploc bag and arranged in such a way that when the cooler is opened, the "Preservation Warning" statement is visible.

6.5 The cooler is sealed with chain-of-custody seals and packaging tape and is shipped to the client with DOT-compliant labeling, as appropriate.

NOTE: Different carriers require different labeling for exempt material.

6.6 The completed IPN/equivalent) is retained in Sample Receiving Department files.

6.7 Per Paragon protocol (SOP 127), Sample Receiving personnel order supplies as needed to maintain an approximate two-week supply of bottles, preservatives and labels.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

7.1.1 The building is equipped with safety showers, eyewash stations, fire extinguishers, fire blankets, and first aid kits. All laboratory personnel must be trained in the use and location of these items.

7.1.2 Read the MSDSs before using any solvents or reagents for the first time.

7.1.3 All handling of acids and bases and other chemicals with a Threshold Limit Value (TLV) (see Section 8.2) of less than 50ppm will be conducted in the fume hood. Safety glasses, latex gloves and a lab coat must be worn when handling all acids and bases.

7.1.4 Stock acids and bases are to be appropriately segregated for storage in the cabinets underneath the fume hood.

7.2 WASTE DISPOSAL

Empty acid and base containers are to be triple-rinsed with tap water before disposal. All container labels must be defaced. Sample Receiving personnel are to contact Waste Management staff if any chemicals require disposal.

8. REFERENCES

8.1 Code of Federal Regulations, Part 40, Chapter 136.

8.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

11/20/06: Changed ‘Sample Control Department’ to Sample Receiving Department, and the term ‘chain-of-custody seal’ to custody seal throughout. Added reference to LIMS program specifications in Section 3.2. Removed statements regarding provision of ‘blue ice’, Sections 4 and 6.4. Added DOCUMENT REVISION HISTORY and Forms. No update to the Operator Aide (Form 216) was required, the posting was checked and found to be accurate, legible and protected.

Paragon Analytics
A Division of DataChem Laboratories, Inc.

225 Commerce Drive Fort Collins, CO 80524
800-443-1511 or (970) 490-1511 (970) 490-1522 Fax

Accession Number (LAB ID) _____

Chain-of-Custody Date _____ Page ___ of ___

Originator: Retain pink copy!

Project Name/No.: _____ **Sampler(s):** _____ Turnaround (circle one): **Standard** or **Rush (Due** _____ **)** Dispose: **Date** _____ or **Return to Client**

Report To:
Phone:
Fax:
E-mail:
Company:
Address:

Circle method (right); provide additional information as needed (comments).

Sample ID	Date	Time *	Lab ID	Matrix	Preservative (indicate type... HCl, etc.)	No. of Containers	VOCs SW8260B	BTEX (only) SW8021B	SVOCs SW8270C	OC Pesticides SW8081A	PCBs SW8082	Herbicides SW8151A	Explosives SW8330	TCLP Organics SW1311 SW8260B 8270C 8081A 8151A	TCLP Metals SW1311 Hg SW6010B 7470	Total Metals by ICP Hg SW6010B 7470 7471 E200.7	Dissolved Metals by ICP Hg SW6010B 7470 E200.7	Total Metals by ICP/MS SW6020A E200.8	Dissolved Metals by ICP/MS SW6020A E200.8	Hexavalent Chromium SW7196A Alkaline Digest? Y / N	Inorganic Anions SW9056 E300.0 (specify in comments)	Solids: Total E160.3 TDS E160.1 TSS E160.2	pH SW9040B SW9045C	TPH SW8015B GRO DRO (circle one or both)	Gross Alpha / Beta SW9310 E900.0	Actinides by Paragon SOP Pu / U / Am / Th / Cm / ___	Tritium E906.0	Total Alpha-Emitting Radium SW9315 E903.0	Radium 226 E903.1	Radium 228 SW9320 E904.0	Strontium 90 (Total RadioSr) D5811-00	Gamma Isotopes E901.1	Radon 222 SM7510Rn				

* **Time Zone:** EST CST MST PST **Matrix Key:** O = oil, S = soil, NS = non-soil solid, W = water, L = liquid, E = extract, F = filter

Comments:

Form 202r6.xls (6/16/06)

Relinquished By: (1)	*Relinquished By:* (2)
Signature _____	Signature _____
Printed Name _____	Printed Name _____
Date _____ Time _____	Date _____ Time _____
Company _____	Company _____
Received By: (1)	*Received By:* (2)
Signature _____	Signature _____
Printed Name _____	Printed Name _____
Date _____ Time _____	Date _____ Time _____
Company _____	Company _____

Kit: Y / N **Rush?** Y / N **Prescreen?** Y / N ***Paragon Analytics***

INCOMING PROJECT NOTICE

Date: _____ **Copy to:** Sample Control

Initiator: _____

Date(s) expected: _____

Client: _____ Assigned PM: _____

Address: _____ Client Contact: _____

_____ Phone: _____

Report to: _____ Fax: _____

Proj. Name/Number: _____

# Samp	Matrix	Analysis/Method	Price	Sub Lab	# x Cont. Type	Preserv.	Tot. Bottles
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		

QC Level: _____ Disposal or handling? $5 / $10 / $15 / $_____ / RTC

Report Level: _____ TAT (working days): 20 / 15 / 10 / 5 / 3 / 2 / 24hr /____

EDD: N / Y Format: Report: Wet Weight / Dry Weight / As Received

Kit to:

Date kit needed: _____ **am / pm**

Attention: _____

Company: _____

Address: _____

_____

Phone: _____

Potential Radioactivity:

Do the samples contain radioactive materials?	Y / N
Are any samples potentially mixed hazardous materials?	Y / N
Are any samples from a known RAM site?	Y / N

Additional Special Handling:

Include: COC(s) Bubble Wrap Labels Seals Blue Ice Temp. Blks

Comments: Rush Special Test Special Analyte Special Charge Detection Limits (see attached)

Kit Prepared by: _____ Date: _____ Picked up by: _____ Date: _____

Sample Container Preservation Limitations As Per 40CFR136.3 Table II

Preservative	Concentration	Container Size	Volume of Preservative (ML)
NOTE: The limits shown below are specified in a memorandum of understanding between the United States Department of Transportation and the United States Environmental Protection Agency in 40CFR136.3. These limits apply to water samples being shipped with an acid or base preservative. Ordinarily, these would be classified as a hazardous material for transportation requiring full U.N. Specification packaging, however, the memorandum of understanding allows water samples preserved with acids or bases to not be considered as a hazardous material for transportation, providing that acid or base concentration does not exceed maximum weight percent concentration specified.			
Sulfuric Acid	98%, Conc.	125 ml	0.2
Sulfuric Acid	98%, Conc.	250 ml	0.25
Sulfuric Acid	98%, Conc.	500 ml	0.5
Sulfuric Acid	98%, Conc.	1000 ml	1.0
Nitric Acid	20%	125 ml	0.75
Nitric Acid	20%	250 ml	1.5
Nitric Acid	20%	500 ml	3
Nitric Acid	20%	1000 ml	6
Nitric Acid	20%	1 Gallon	22
Hydrochloric Acid	36%, Conc.	40 ml VOA	0.05 ml
Hydrochloric Acid	36%, Conc.	500 ml	0.5
Hydrochloric Acid	36%, Conc.	1000 ml	1
Sodium Hydroxide	20%	500 ml	1.5
Sodium Hydroxide	20%	1000 ml	3
NOTE: USDOT restrictions are not applicable to the following two preservatives:			
Zinc Acetate (Total Sulfides Analysis) *	2 N	500 ml	2 ml *
Sodium Thiosulfate	10%	125 ml to 40 ml ** (VOAs); 1000 ml ** (SVOCs)	4 drops (0.2 ml) (VOAs); 0.8 ml (SVOCs)

* Sample bottles supplied for Total Sulfides are to be preserved with both 1.5 ml Sodium Hydroxide and 2 ml Zinc Acetate.

** Proper sample collection must be observed by the client in the field in order to obtain the proper preservation. For Volatile Organics Analytes (VOAs), approximately 4 drops of 10% Sodium Thiosulfate reagent is to be added to each 125 ml amber bottle collection bottle supplied to the client. The client is to collect the sample in the 125 ml amber bottle (without overflow), swirl the contents of the bottle, then decant the sample into two 40 ml VOA vials (headspace free). Contingent upon client requirements, each 40 ml VOA vial may require preservation with 36% Hydrochloric Acid. The Project Manager is responsible for ensuring that the client is aware of the appropriate sample collection procedure.

Form 216r1.frm (2/4/2002)

This page posted as an Operator's Aide in Sample Receiving; following page contains same information plus some additional regulatory information.
11/21/06 DAS

Sample Container Preservation Limitations As Per 40CFR136.3 Table II

Preservative	Concentration	Container Size	Volume of Preservative (ML)	Target pH	Wt% Acid or Base	Maximum Allowed Wt % Acid or Base
NOTE: The limits shown below are specified in a memorandum of understanding between the United States Department of Transportation and the United States Environmental Protection Agency in 40CFR136.3. These limits apply to water samples being shipped with an acid or base preservative. Ordinarily, these would be classified as a hazardous material for transportation requiring full U.N. Specification packaging, however, the memorandum of understanding allows water samples preserved with acids or bases to not be considered as a hazardous material for transportation, providing that acid or base concentration does not exceed maximum weight percent concentration specified.						
Sulfuric Acid	98%, Conc.	125 ml	0.2	1.53	0.29%	0.35%
Sulfuric Acid	98%, Conc.	250 ml	0.25	1.74	0.18%	0.35%
Sulfuric Acid	98%, Conc.	500 ml	0.5	1.74	0.18%	0.35%
Sulfuric Acid	98%, Conc.	1000 ml	1.0	1.74	0.18%	0.35%
Nitric Acid	20%	125 ml	0.75	1.69	0.13%	0.15%
Nitric Acid	20%	250 ml	1.5	1.69	0.13%	0.15%
Nitric Acid	20%	500 ml	3	1.69	0.13%	0.15%
Nitric Acid	20%	1000 ml	6	1.69	0.13%	0.15%
Nitric Acid	20%	1 Gallon	22	1.70	0.13%	0.15%
Hydrochloric Acid	36%, Conc.	40 ml VOA	0.05 ml	1.93	0.04%	0.04%
Hydrochloric Acid	36%, Conc.	500 ml	0.5	1.93	0.04%	0.04%
Hydrochloric Acid	36%, Conc.	1000 ml	1	1.93	0.04%	0.04%
Sodium Hydroxide	20%	500 ml	1.5	12.26	0.073%	0.08%
Sodium Hydroxide	20%	1000 ml	3	12.26	0.073%	0.08%
NOTE: USDOT restrictions are not applicable to the following two preservatives:						
Zinc Acetate (Total Sulfides Analysis)	2 N	500 ml	2 ml *	N/A	N/A	N/A
Sodium Thiosulfate	10%	125 ml to 40 ml **	4 drops (0.2 ml)	N/A	N/A	N/A

* Sample bottles supplied for Total Sulfides are to be preserved with both 1.5 ml Sodium Hydroxide and 2 ml Zinc Acetate.

** Proper sample collection must be observed by the client in the field in order to obtain the proper preservation. For Volatile Organics Analytes (VOAs), approximately 4 drops of 10% Sodium Thiosulfate reagent is to be added to each 125 ml amber bottle collection bottle supplied to the client. The client is to collect the sample in the 125 ml amber bottle (without overflow), swirl the contents of the bottle, then decant the sample into two 40 ml VOA vials (headspace free). Contingent upon client requirements, each 40 ml VOA vial may require preservation with 36% Hydrochloric Acid. The Project Manager is responsible for ensuring that the client is aware of the appropriate sample collection procedure.

Form 216r1.frm (2/4/2002)

Must Discard 30 Days from _____ (date printed)

Correction: The two IR guns currently in use in Sample Receiving are 2 & 4.
12/12/06 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 210 REVISION 6

TITLE: **USE AND CALIBRATION VERIFICATION OF INFRARED TEMPERATURE GUNS**

FORMS: **201, 209, 352** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/20/06

QUALITY ASSURANCE MANAGER _____ DATE 11/20/06

LABORATORY MANAGER _____ DATE 11-21-06

HISTORY: Rev0, 2/4/94 and 12/23/94; Rev1, 1/18/99; Rev2, 1/10/00; Rev3, 4/17/02; Rev4, 3/6/03; Rev5, 10/17/03 and 3/23/05; Rev6, 11/20/06.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes procedures for the daily calibration verification and use of infrared (IR) temperature devices (guns).

2. SUMMARY

IR temperature guns provide a means of measuring temperatures rapidly and non-invasively. Two IR guns, clearly marked as gun "1" and gun "2", are used by Sample Receiving staff to measure the temperature of incoming samples that require thermal preservation. Radiochemistry Department personnel uses a third, dedicated, IR gun to measure the temperature of silica gel samples undergoing evaporation. A functional check, prior to use, is performed per the procedures detailed in this SOP, on each IR gun each day the device is used. The Quality Assurance (QA) Department performs an in-house, NIST-traceable verification of each IR gun, annually, and maintains records of these verifications (SOP 923).

3. RESPONSIBILITIES

3.1 It is the responsibility of all technicians to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 All personnel who work with these procedures are responsible for documenting any anomalies or out-of-control events. Appropriate corrective actions must be taken and documented.

3.3 The QA Department is responsible for verifying the calibration and accuracy of each IR gun annually and for maintaining the annual verification records.

4. PROCEDURES FOR THE CALIBRATION VERIFICATION AND USE OF SAMPLE RECEIVING IR GUNS

4.1 CALIBRATION VERIFICATION CHECK

Per NELAC (and method) requirements, coolers containing samples requiring thermal preservation should be received chilled but not frozen (i.e., ~ 0.1°C to 6°C). Temperature blanks kept in Sample Receiving walk-in cooler RU#20, which is maintained at 4±2°C (SOP 326), are used to provide a one-point verification check of each Sample Receiving IR gun, each day before use.

4.1.1 Obtain, and record on Form 209, a reading from the annually-verified thermometer (SOP 923) assigned to/kept in RU#20.

4.1.2 Select a Sample Receiving IR gun. Remove the one-liter amber water check bottle from the refrigerator. Holding the bottle away from your body and down toward the floor, aim the IR gun at the center of the bottle and obtain a temperature reading. Record this reading on Form 209.

NOTE: Each IR gun is operated at the distance of 1-2 inches from the object, and in the manner prescribed by the manufacturer's instructions.

Repeat this Step using the other Sample Receiving IR gun.

4.1.3 Return the amber water check bottle to RU#20 and remove the 40mL VOA water check vial. Holding the vial away from your body and down toward the floor, aim the IR gun along the length of the vial, and obtain a temperature reading. Record this reading on Form 209.

Repeat this Step using the other Sample Receiving IR gun.

4.1.4 Compare the IR gun readings to the reading obtained from the refrigerator's interior thermometer (Step 4.1.1). The IR gun temperature readings must agree within ±2°C. ***Notify the QA Department immediately if this criterion is not met, so that prompt, appropriate corrective actions may be taken.***

4.1.5 Once the Sample Receiving IR guns have been successfully verified, they may be used to determine representative cooler temperatures, as applicable, per the procedure described below.

4.2 USING SAMPLE RECEIVING IR GUNS TO DETERMINE REPRESENTATIVE COOLER TEMPERATURES

This procedure pertains to coolers containing samples that require thermal preservation (i.e., chilling). It is Paragon's policy to determine the representative temperature for these coolers of samples within 2 hours of receipt. Per NELAC (and method) requirements, coolers containing chilled samples should be received at temperatures between just above freezing (i.e., ~ 0.1°C) to 6°C.

4.2.1 After inspecting the cooler's custody seals for intactness (SOP 202), open the cooler's lid and select a sample container representative of the cooler's contents (i.e., representative of container types present, and representative of container position within the cooler, relative to the ice or ice packs). If a designated temperature blank was provided in the cooler, this sample container may be selected so long as it was packed, relative to the ice or ice packs, in a manner that is representative of the other samples present in the cooler.

4.2.2 Remove the selected container from the cooler and hold it away from your body and down toward the floor. Aim an IR temperature gun at the container and obtain a reading using the technique described in Steps 4.1.2 and 4.1.3 above.

Based on professional judgment, a second representative sample container may be selected and measured to ensure that the temperature measurement obtained, is representative of the cooler's contents. Record the representative temperature determined for each cooler on Form 201, and note the identity of the IR gun that was used to obtain the temperature. ***Notify the Project Manager immediately if the representative cooler temperature determined, is outside the just above freezing (i.e., ~ 0.1°C) to 6°C acceptance limits.***

5. PROCEDURES FOR THE CALIBRATION VERIFICATION AND USE OF THE RADIOCHEMISTRY IR GUN

5.1 CALIBRATION VERIFICATION CHECK

A calibration verification check of the Radiochemistry IR gun is to be performed per the procedure described below, prior to use, each day this IR gun is used. Data from this calibration verification check are recorded in the Radiochemistry IR Gun Verification Check logbook (Form 352).

5.1.1 Oven #3 is located in the Low Level Actinides Lab. Determine the oven's current temperature by reading the annually-verified thermometer (SOP 923) that is kept inside this oven. Record this reading as "Thermometer" (i.e., reference) temperature, on Form 352.

5.1.2 Hold the Radiochemistry IR gun about 1-2 inches in front of, and at the center of, the bottle that holds the oven's assigned interior thermometer. Depress the IR gun trigger and record the reading obtained as "IR Gun" (i.e., check or test) temperature on Form 352.

5.1.3 The normal point of use and accuracy requirement for the Radiochemistry IR gun (SOP 791) is 200±20°C. Oven #3 is maintained at 100-110°C. Use of Oven #3 as a test condition, has been determined to be the closest to the Radiochemistry IR gun's point of

use, that can be readily and accurately verified.

For purposes of the Radiochemistry IR gun verification, the temperature obtained via the IR Gun in Step 5.1.2 above, must agree within ±10°C of the temperature obtained via the thermometer in Step 5.1.1 above, to be acceptable. ***Notify the QA Department immediately if the IR gun fails the verification test, so that prompt, appropriate corrective action may be taken.***

5.2 DETERMINATION OF SILICA GEL EVAPORATION TEMPERATURES
Follow the procedures detailed in SOP 791.

6. SAFETY, HAZARDS AND WASTE DISPOSAL

No special hazard precautions.

7. REFERENCES

7.1 NELAC standard, current revision.

7.2 Operating Instructions, Manufacturer of IR Temperature Device.

DOCUMENT REVISION HISTORY

11/20/06: Changed reference from 'Sample Control Department' to Sample Receiving Department throughout. The term 'Chain-of-Custody' seal was changed to Custody seal, Section 4. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

Infrared (IR) Temperature Gun and RU#20 Daily Check Log

Record the Current, Max and Min temperatures below, then press Memory Clear to reset memory.

		CURRENT ELECTRONIC THERMOMETER #22061893			BOTTLE TEMPERATURE (°C) (1)				
DATE	**TIME**	**TEMPERATURE (°C)(1)**	**MAX TEMP. (°C)(1)**	**MIN TEMP. (°C)(1)**	BOTTLE	**Gun #2(2)**	**Gun #4(3)**	**INITIALS**	**COMMENTS**
					LITER				
					VOA				
					LITER				
					VOA				
					LITER				
					VOA				
					LITER				
					VOA				
					LITER				
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					VOA				
					LITER				
					VOA				
					LITER				
					VOA				
					LITER				
					VOA				

(1) **Acceptance ranges**: RU#20 cooler temperature must be within 4±2 °C.

IR gun readings (*of temperature check water bottles*) must agree within ±2°C of current temperature electronic thermometer reading.

Notify QA Staff immediately if measured temperatures exceed these ranges !!

(2) **IR Gun #2:** Oakton, Model InfraPro II, SN 2922500201-0066 **(red trigger)**
(3) **IR Gun #4:** Oakton, Model InfraPro II, SN 2372220101-0002 **(black trigger)**

Reviewed by / date ________________________

Paragon Analytics

CONDITION OF SAMPLE UPON RECEIPT FORM

Client: _____ Workorder No: _____

Project Manager: _____ Initials: _____ Date: _____

1. Does this project require any **special handling** in addition to standard Paragon procedures?		YES	NO
2. Is **pre-screening** required per SOP 008?		YES	NO
3. Are custody **seals** on **shipping containers** intact?	N/A	YES	NO
4. Are custody **seals** on **sample containers** intact?	N/A	YES	NO
5. Is there a **COC (Chain-of-Custody) present** or other representative documents?		YES	NO
6. Is the **COC** (if applicable) **complete and legible**?	N/A	YES	NO
7. Are **bottle IDs legible** and in **agreement** with **COC sample IDs**?	N/A	YES	NO
8. Is the COC in agreement with samples received? (**# of samples, # of containers, matrix**)	N/A	YES	NO
9. Were **airbills** present and/or removable?	N/A	YES	NO
10. Are all **aqueous samples** requiring preservation **preserved correctly**? (excluding volatile organics)	N/A	YES	NO
11. Are all aqueous **non-preserved samples** at the **correct pH**?	N/A	YES	NO
12. Is there **sufficient sample** for the requested analyses?		YES	NO
13. Were all samples placed in the **proper containers** for the requested analyses?		YES	NO
14. Are all samples within **holding times** for the requested analyses?		YES	NO
15. Were all sample containers received **intact**? (not broken or leaking, etc.)		YES	NO
16. Are all samples requiring no headspace (volatiles, reactive cyanide/sulfide, radon), headspace free? **Size of bubble**: ____ < green pea ____ > green pea	N/A	YES	NO
17. Were samples checked for and free from the presence of **residual chlorine?** (Applicable when PM has indicated samples are from a chlorinated water source; note if field preservation with sodium thiosulfate was not observed.)	N/A	YES	NO
18. Were the sample(s) **shipped on ice**?	N/A	YES	NO
19. Were cooler temperatures measured at 0.1-6.0°C?	N/A	YES	NO

***IR gun used** *(circle one)*: #2 - Oakton InfraPro II, SN2922500201-0066; #4 - Oakton InfraPro II, SN2372220101-0002

Cooler #'s								
Temperature (°C)								
No. of custody seals								
DOT Survey/ Acceptance Information: External µR/hr reading								
Background µR/hr reading								

Were external µR/hr readings ≤ two times background and within DOT acceptance criteria? **YES / NO** (If no, see Form 008.)

Additional Information: PROVIDE DETAILS BELOW FOR A NO RESPONSE TO ANY QUESTION ABOVE EXCEPT #1 AND #2

If applicable, was the client contacted? **YES / NO / NA** Contact Name:_____ Date/Time:_____

Project Manager Signature/ Date: _____

Paragon Analytics

Radiochemistry IR Gun
Calibration Verification Check

Oven #3: Thermometer #8031 RadChem IR Gun: Raynger ST 2672490101-0045

DATE	TIME	INITIALS	Thermometer Temp. (°C)	RadChem IR Gun Temp. (°C)	Acceptable? (Y/N)	COMMENTS

Acceptance Limits: RadChem IR gun must agree within ± 10 °C of that day's Thermometer reading.

Notify QA Department immediately if RadChem IR gun fails verification check!

REVIEWED BY / DATE: _____

Must Discard 30 Days from _____ (date printed)

Amended 9/11/08: Two Operator's Aids added. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 300 REVISION 13

TITLE: STANDARDS, SOLVENTS, ACIDS, BASES AND REAGENTS MANAGEMENT IN THE LABORATORY

FORMS: 718

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3-17-08

QUALITY ASSURANCE MANAGER _____ DATE 3/17/08

LABORATORY MANAGER _____ DATE 3-17-08

HISTORY: Rev0, 12/17/91; Rev1, PCN #275, 9/28/94; Rev2, 4/09/96; Rev3, 2/18/98; Rev4, 11/20/98; Rev5, 12/2/99; Rev6, 2/10/00; Rev7, 3/2/00; Rev8, 10/8/01; Rev9, 3/2/2002; Rev10, 4/3/4; Rev11, 3/9/06; Rev12, 7/5/06. Rev13 (combined with SOP 798), 3/14/08.

1. SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to establish guidelines for the management of standards, solvents, acids, bases and reagents used throughout the laboratory. Guidance pertaining to receipt, records retention, labeling, documentation, containerization, storage and expiration of these materials is given.

All materials purchased by Paragon (SOP 127) are carefully selected based on the performance needs of their application. Records for certified materials (i.e., Certificates of Purity, Certificates of Assay or Analysis) are retained by the Department that uses the material.

Paragon's Standards & Solutions database, is the primary mechanism for logging-in the standards, solvents, acids and bases received, in readiness for their use. Reagents made from these materials are also documented in the Standards & Solutions database. While the Standards & Solutions database is used to catalog these intermediate standards/ solutions (e.g., ICV solutions; LCS and MS spiking standards; SUR spike solutions, radiochemical carriers, etc.), typically daily (working) standards documentation is accomplished by various other means, such as: direct entry into a LIMS datasheet, by use of the instrument run log, etc.

Some materials identified as 'quickly consumeables' [e.g., Methylene Chloride, Hexane, and Sodium Sulfate (Na_2SO_4)] are exempt from some labeling requirements, as described herein. No material is to be used beyond the manufacturer's expiration. Materials must be discarded sooner than manufacturer's expiration if contamination or degradation is evident. The expiration of intermediate materials is not to exceed that of the parent material. Re-verification of materials is permitted where possible/feasible. Also addressed by this SOP are procedures for preparing and verifying radioactive solutions, as well as the stable carriers that are used in radiochemical analyses. Note that these carriers must be verified before use.

Use of the PAR Standards & Solutions database helps to ensure good laboratory practices (GLP) by facilitating consistency in ordering and preparing standards, solvents, acids, bases and reagents, and also facilitates the traceability of these chemicals used. Some aspects of data reporting through the Laboratory Information Management System (LIMS), are also facilitated by interface with the Standards & Solutions database.

This SOP is intended to communicate a 'big picture view' of the policies/practices governing the management and use of standards, solvents, acids, bases and reagents used throughout the laboratory. **Should a conflict exist between the information provided in this SOP and that of a specific preparatory or determinative SOP, the guidance of the preparatory or determinative SOP takes precedence.**

2. SUMMARY

Chemical materials received, as well as the intermediate standards and reagents made from them, are catalogued and tracked in a manner that meets good laboratory practice. Paragon's Standards and Solutions database plays a key role in the management of these materials. This SOP provides an overview of the types of chemical materials used in the laboratories, and gives detailed guidance as to the receipt, records retention, labeling, documentation, containerization, storage and expiration requirements pertinent to the management of these materials.

Radioactive standards are prepared gravimetrically whenever possible, using the same diluent (basis) as the primary solution. The standard concentration is verified against an independent second source, if available. Depending on the nature of the standard, various methods are adapted to prepare the standard for analysis.

Stable (non-radioactive) carrier solutions are prepared according to the individual preparation SOPs. In some cases, verification of the final carrier concentration by ICP-AES analysis is required before use. All preparations for verification are done in triplicate. A reagent blank must accompany each batch. Another technician must witness the addition of tracing and spiking solutions.

3. RESPONSIBILITIES

3.1 Each Department Manager (DPM), in conjunction with their analytical staff, is responsible for ensuring that the management of all standards, solvents, acids, bases and reagents used within the Department, meets the criteria set forth in this SOP. The DPM, along with the Quality Assurance Manager (QAM) is responsible for providing adequate training and oversight pertaining to these requirements. The DPM or designee is responsible for performing a timely review (at minimum, monthly) of the information contained in the Standards & Solutions database. The DPM or designee is also responsible for maintaining certified materials records (e.g., Certificates of Purity/Assay/Analysis).

3.2 Because of the health, safety, cost and potential quality assurance impact of incorrectly prepared solutions, only trained staff members, approved by the Department Technical Manager, will be responsible for the preparation of

radioactive standards. It is the responsibility of the Department Manager to approve any deviations from this procedure. This approval may be noted on the documentation described below (Section 3.5).

3.3 It is the responsibility of the technician preparing the solutions to thoroughly review any pertinent Material Safety Data Sheets (MSDSs), and to follow the specific instructions provided in applicable SOPs. Any material with a TLV or PEL below 50ppm must be used in a fume hood.

3.4 It is the responsibility of the technician preparing the solution to check the stock materials for any applicable expiration dates. Do not prepare any solution using materials that have passed their expiration date.

3.5 It is the responsibility of the technician preparing the solutions to complete any applicable supporting documentation, such as the "RadChem Solutions Entry Form" in the Paragon LIMS system, or a controlled laboratory notebook. Any discrepancies, anomalies, or out-of-control events must be noted and corrective action taken and documented (SOP 928). The technician is also responsible for properly labeling the container of the solution made.

3.6 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data. Note that requirements for particular analytes, concentrations, etc. that differ from Paragon standard practices, may be contained in applicable LIMS program specifications.

3.7 IS Department staff are responsible for maintaining and augmenting the Standards & Solutions database as needed, and for assisting with the provision of necessary training to laboratory staff.

4. APPARATUS AND MATERIALS

4.1 See specific preparatory/determinative SOP. Necessary apparatus includes, but is not limited to: syringes; disposable or scrupulously-cleaned glassware; pipets; and balances. Note that pipets and balances must be operated as prescribed in their respective operational SOPs (321, 305). Where use of volumetric glassware is required (e.g., carrier preparation), only Class A volumetric glassware shall be used.

4.2 In general, Paragon purchases commercially-certified standards when available/feasible. Should standards need to be created in-house, only the highest

purity of materials should be used. For example, only 'Purge-and-Trap' grade methanol is used for creating volatile organics standards; 'Pesticide Residue' or 'HPLC' grade solvents may be used for making other organic standards and spiking solutions. Only 'Trace Metals' grade acids are used for inorganic standards, reagents and analyses.

4.3 Typically, semivolatile organic (SVOC) standards and spike solutions are made in methylene chloride. Standards and spikes used in ECD or FPD gas chromatographic analysis are typically made in hexane. Explosives standards and spike solutions are typically made in acetonitrile. Other organic standards and solutions may be made in methanol. Note that the solvent used for surrogates or other spiking solutions should generally be miscible with water (solubility issues may, however, preclude the use of water-miscible solvents in some procedures).

4.4 The laboratory's deionized (DI) water system is capable of producing water of sufficient quality to be used in laboratory preparations and analyses. See SOP 319 for details regarding Paragon's deionized water systems and requirements. Water used to prepare volatile organics (VOAs) standards will be DI water that has been heated and purged with inert gas to remove volatile substances (SOP 511). Where required by the method or good laboratory practices, HPLC grade water will be used for HPLC preparations and analyses.

Paragon purchases or creates only the necessary amount of standards and reagents in order to minimize waste. The concentrations of the standards and reagents used are also determined with this in mind, as well as method requirements. Note that client-specific criteria (LIMS program specification) may call for the use of standards or reagents that differ in composition from that of typical Paragon materials used. Factors such as limiting the number of dilutions required to obtain final working concentrations; inherent measurement error (i.e., no aliquots less than 5µL whenever possible); and the ratio of solvent to analyte (be sure, however, that sufficient volume of solvent (basis) is used to dissolve all standard materials) should also be considered when determining the volume of standard or reagent to prepare.

5. GENERAL PROCEDURES - ACIDS, BASES, SOLVENTS, REAGENTS

5.1 Retain any Certificates of Purity, Assay or Analysis received in Departmental records. Store materials in the designated area and in a manner that is consistent with manufacturer's recommendations. Materials should also be stored in a manner that facilitates 'first received, first used'.

5.2 Document the material's receipt in the Standards and Solutions database:

5.2.1 In the "Standards Database" application, select "Open Shipment Form".

5.2.2 Click on the tab 'Add New Shipment' and enter in the date the material was received by the lab.

5.2.3 Enter in "Received By".

5.2.4 A "Ship ID" will be assigned automatically.

NOTE: It is often useful to use the material's lot number as the material identification (or some portion thereof). This ensures that the 'ID" appears on the container label.

5.2.5 The "Inventory Item" will be the whole name of analyte (e.g., 'Hydrochloric Acid' or 'Plutonium-242'.

5.2.6 Enter the "Vendor Name", "Lot ID", as well as the "Catalog Number" and "Comments", as needed.

5.2.7 Enter the material's manufacturer's expiration. If no manufacturer's expiration is indicated on the material, apply the applicable duration indicated in the Table at the end of this SOP.

5.2.8 Click Save and Close.

5.3 **Date opened must be indicated on the container when first used.** If necessary, transfer the remainder of the material to another container that is suitable for the material, and that is of sufficient size to permit the proper labeling.

NOTE: In general, date received information is entered into the Standards & Solutions database, and is not marked directly on the material's container. In the case of 'quickly consumeables', the date received is marked on the transport carton, and not directly on the material container, in order to preserve the integrity of the carton structure for safe storage. Because 'quickly consumeables' are rapidly depleted, it is not necessary to mark 'date opened' on these containers.

5.4 The Standards & Solutions database contains the basic recipes for the standards and reagents used in Paragon analyses. Follow the recipes contained in the database, which were derived from the recipes contained in the preparatory and determinative SOPs, which in turn, are method based. Note that each preparation must be assigned a unique identification. **In some cases, it may be useful to incorporate the date made into the ID to assist in unique identification.** Be sure to complete all information (e.g., date, analyst, parent materials, lots, amounts, etc.).

5.5 Properly containerize (e.g., polypropylene bottle, amber glass, no headspace, etc.) the standard or reagent made, in a manner that is appropriate to the contents and method requirements.

5.6 Label or mark the container, at minimum, with the standard/reagent name and/or unique ID, basis (i.e., solvent, acid used) and date of expiration.

5.7 **No material is to be used beyond the manufacturer's expiration. The expiration of intermediate materials is not to exceed that of the parent material. Expirations for standards/reagents prepared from multiple sources shall coincide with the earliest expiration of the source materials used. Materials must be discarded sooner than manufacturer's expiration if contamination or degradation is evident. If no manufacturer's expiration is indicated on the material, apply the applicable duration indicated in the Table at the end of this SOP.**

5.8 **Re-verification of materials is permitted where possible/feasible (e.g., some inorganic source materials, metals standards).** Verifications must be demonstrated by acceptable method blank and laboratory control sample analysis results, or by other suitable means. **Document the material's re-verification in the Standards & Solutions database, and re-label the material appropriately.**

5.9 Store the container in a designated area under conditions that are appropriate to its contents and method requirements (e.g., ambient, refrigerator, freezer, desiccator). Use the Table at the end of this SOP as a quick reference. **Standards and reagents shall be stored separately away from samples. Hazardous materials storage rules shall be observed.**

5.10 All standards that are beyond their expiration shall be removed from the area, materials that cannot be re-verified shall be properly disposed (SOPs 003, 015, 024).

5.11 The Standards & Solutions database is maintained by analysts from each Department and undergoes regular (at minimum, monthly) peer or Supervisory entry review. This ensures that the database entries are accurate and complete.

6. STABLE CHEMISTRY STANDARDS, REAGENTS

Follow the general guidance of Section 5 above.

7. RADIOCHEMICAL STANDARDS, REAGENTS

Follow the general guidance of Section 5 above. **Note that for Radiochemistry Department standards, a Shipment Entry and Review Form (Form 718) must also be completed.** Specific considerations for radiochemical materials are given below.

7.1 PREPARATION AND VERIFICATION - NOMENCLATURE

7.1.1 **Reagents** and **carriers** are defined as those non-radioactive chemicals

whose preparations are described in the various preparation and analytical SOPs, as well as Section 5 above.

7.1.2 A **standard** is defined as a radioactive material, in which the concentration of radioactive analyte is used in the quantification of sample results. Standard Reference Material (SRM) is received directly from a manufacturer or supplier, such as the National Institute of Standards and Technology (NIST). The term Primary Standard applies to a standard that has not been diluted since receipt of the source Standard Reference Material. Generally, all other standards are prepared from the appropriate Primary Standard. The term Intermediate Dilution, applies to a dilution of a standard, in which the concentration of radioactive material is too high for routine laboratory use, and from which working standards are prepared. The term Working Standard applies to a dilute standard routinely used to spike client or quality control (QC) samples. Standards preparations are recorded in the Standards Preparation Logbook, which is kept in the Radiochemistry Instrument Lab, as well as the LIMS Standards Database. Standards are assigned unique and traceable ID's as described directly below:

7.1.2.1 Nuclear Inventory Log (NIL) numbers are assigned sequentially by the Radiation Safety Officer (RSO) upon receipt of radioactive materials in the laboratory.

7.1.2.2 The Standards ID number is generated in three parts. The first set of digits represents the NIL. The following four digits are the unique log number assigned by the QA Department to the particular Standards Preparation Logbook. The last two digits are the page number upon which the dilution/preparation of the standard is documented (e.g., 450.1284.25 is NIL 450, on page 25 of logbook #1284).

7.2 PREPARATION OF STANDARDS

7.2.1 All standards and calibration standards will be prepared only by, or under the close supervision of, a trained staff member.

7.2.2 All preparation steps will be recorded in the Standard Preparation Logbook. An entry must be made into this logbook, even if only transferring an aliquot into a new container. Meticulously record tares, aliquot start mass, finish mass or volume, aliquot units, dilution factor, starting and finishing activity, reference date, diluent, bottle description, etc. If converting between mass and volume, a density calculation should be performed and recorded in the Standard Preparation Logbook. The lot number of the diluent (normally a

diluted concentration of HCl or HNO_3), is recorded in the Standard Preparation Logbook.

7.2.2.1 The standard ID of the radioactive SRM(s) must be recorded. A description of the source material and the reference date for the activity must also be documented.

7.2.2.2 The source of all non-radioactive materials used in the preparation must be documented.

7.2.2.3 During the preparation, verify that all balances, pipettes and ovens, etc., are in control as defined by the appropriate QA SOPs. Record the pipette and balance numbers used in the preparation.

7.2.3 Upon completion of the preparation, calculate the final anticipated activity of the standard. Record these calculations in the logbook. Be sure to distinguish isotopic activity from total activity where applicable (e.g., $^{238}U/^{234}U$ activities vs. total activity of U).

7.2.4 Standards are normally diluted in the same diluent in which they were prepared by the manufacturer. In cases where the diluent is not documented, or where end use dictates that the solution matrix be changed, consult with the Radiochemistry Manager prior to dilution of the standard.

7.2.5 Use only tight-sealing bottles for storing radioactive standards. The useful life of a standard may be years, unless the solution integrity is compromised by evaporation. Nalgene® bottles, borosilicate vials (e.g., VOA vials), and tight-sealing bottles with rubber-lined caps are advisable choices for extended storage of standards. Liquid scintillation vials and specimen cups, etc., are NOT satisfactory containers for the storage of stock, primary, and intermediate standards.

7.2.6 The mass of stock, primary, and intermediate standards may be tracked to minimize the risk of uncontrolled, unnoticed evaporation. Discrepancies in solution mass between uses should be reported to the Radiochemistry Manager. Tracking standards mass often provides the opportunity to run a redundant check of solution aliquot versus mass removed. Discrepancies should be resolved prior to use of a dilution.

7.3 CREATING A STANDARD IN THE LIMS SOLUTIONS DATABASE

7.3.1 CHECKING FOR A PRIMARY SOLUTION

7.3.1.1 Click on ‘Open Rad Form’. The RadChem Solutions Entry Form will appear. If a shipment form was already created,

the parent standard may also already be entered. To check for this, do the following:

7.3.1.2 The number in the field "Solution ID" will be highlighted. Press <CTRL + F> to search the records. Enter the primary solution in the search field. If the primary solution has already been created, the primary solution will appear in the main form behind the search utility. Close the search box and proceed to Section 7.3.3.

7.3.1.3 If the primary solution has not been created, the message "search item not found" will appear. Close the search box and proceed to Section 7.3.2.

7.3.2 ADDING THE PRIMARY SOLUTION

7.3.2.1 Click the "Add" button. Type in the primary solution ID in the "Solution ID" field.

7.3.2.2 In the 'Sol Name' field, type the descriptive name of the standard (i.e., Am-241 Primary Standard).

7.3.2.3 Choose 'Type' as is appropriate (for a primary standard use PS, for primary reagent use PR).

7.3.2.4 Choose the appropriate Inventory Name. Be careful to watch the Lot # of the solution you are selecting. There may be several choices for your selection.

7.3.2.5 Lot and Vendor should automatically appear.

7.3.2.6 Fill in matrix (usually liquid), and the final volume/units found on the certificate. Fill in Opened and Received By. Fill in the Department and appropriate location.

7.3.2.7 Choose a component name, using abbreviated analyte names such as Am-241 versus Americium-241, H-3 versus Tritium.

7.3.2.8 Enter the calibrated activity that is found on the certificate, conventionally in pCi/g. Uncertainty should be in 2σ percentages, from the certificate. The calibration date is the reference date found on the certificate.

7.3.2.9 After all fields are completed, this form must be reviewed by someone else (who logs into LIMS to do an official review) before it can be used in order to create other

standards.

7.3.3 CREATING A STANDARD/REAGENT FROM A PRIMARY SOLUTION

7.3.3.1 Open RadChem Solutions Entry Form of the primary solution and push the button "Copy to New". This will open a new Solutions Form, which is now linked to the primary solution.

7.3.3.2 First change the solution ID by clicking on the underlined "Solution ID". A box will appear with the given, current ID. Fill in the "Change ID to" box with the new, Paragon-formatted ID.

7.3.3.3 Change the Solution Name from Primary Standard/Reagent to either Intermediate Standard/Reagent or Working Standard/Reagent, and select the appropriate "Type" (generally IS or IR; an Intermediate Standard/Reagent implies that other standards will be made from it).

7.3.3.4 Fill in the Preparation By, and if applicable, Verified and Validated By, and Expiration Date boxes. The reference date is set to today, but is a changeable date.

7.3.3.5 Choose the correct matrix.

7.3.3.6 IMPORTANT: Units must stay consistent throughout each form; if each level of the standard was prepared gravimetrically, the units must remain in grams until the final working dilution, which may then be density corrected. Therefore, if this standard is to be an intermediate standard (i.e., other standard dilutions will be made from this standard), do not fill in density. The 'final volume' field should be entered in from the standards logbook, depending on whether a standard was prepared gravimetrically (as is generally done) or volumetrically. If this standard is the final dilution (i.e., it was a dilution made directly from the original ampoule), enter in the determined density and the Final Volume with the appropriate units.

7.3.3.7 Choose a parent ID from the pick list. The Component Name should appear. Fill in the volume/units of how much of the parent was used. If two parents were used equally to create this standard, divide the final volume of parent used, in half. (i.e., if 10.0g of 615 and 616 were used to create

this standard, both 615 and 616 would be chosen as components, 5.0g each.)

7.3.3.8 This standard must be independently reviewed before it can be used in the preparation of future standards or on benchsheets.

7.3.3.9 Once this standard is created, it may be used to create other standards (i.e., be an intermediate standard). Follow Section 7.3.3. Again, final dilutions may be density corrected to volumetric units, since they are generally aliquotted at the bench volumetrically.

7.4 VERIFICATION OF STANDARDS AND CARRIERS

7.4.1 In the preparation and analysis of standard verifications, an in-house work order number is assigned, either manually or through LIMS, so that the verification data can be linked to the standard.

7.4.2 Standards and carriers will be prepared in triplicate for verification. In addition, standard verifications that employ a radioactive tracer will include an un-traced analysis to demonstrate that the standard is free of potentially interfering radionuclides.

7.4.3 Acceptance criteria will be handled on a case-by-case basis. The count result should, in general, match the expected value to within the limits of the total estimated error. As a default, agreement within 5% is an acceptable minimum tolerance for verification of standards. The 1-sigma counting uncertainty should be ½ of the acceptance criteria. For example, in instances where the acceptance criteria is 5%, the 1-sigma counting uncertainty, should be equal to or less than 2.5%. Stable carriers should be verified to within 10% of the expected value.

7.4.4 In addition, the verification data for radioactive standards should meet the criteria described below. Any standard that fails to meet any of these criteria may be rejected for use in certain work, but may be approved for other uses at the discretion of the Radiochemistry Manager.

7.4.4.1 For the triplicate analyses in a standard verification, a mean value (xav) and standard deviation (σ) must be calculated.

7.4.4.2 The value of 2σ must be less than or equal to 10% of xav.

7.4.5 If the verification results meet the acceptance criteria described above, the standard or carrier is considered to be acceptable for general use. If the verification results fail to meet any of the requirements in this Section, any usage limitations are noted on the verification summary.

Alternately, the standard or carrier may be prepared for reanalysis. In either case, the Radiochemistry Manager must then review and sign the bottom of the form. Completed forms are available through the Radiochemistry Department.

7.4.6 If reanalysis is required, the preparation analysts and Radiochemistry Manager must confer and decide how to proceed. Additional preparations, alternate preparations, or counting strategies may be considered. In this case, the involved personnel may not approve the verification form until the situation is resolved. Complete documentation is available through the Radiochemistry Department.

7.4.7 See Section 7.5 for the assignment of expiration dates.

7.4.8 A designee in the Instrument Lab will prepare a packet containing a copy of the completed and signed logbook page, all applicable traceability documents provided by the RSO, any applicable documentation of dilutions, a copy of the sheet showing calculation verification, the standards verification summary, instrument raw data, and instrument run log. This packet is forwarded to the Instrument Laboratory Supervisor for validation. Copies of this information are available through the Radiochemistry Department.

7.4.9 After verification of a standard is completed, working standards are given final approval in LIMS by the Radiochemistry Manager. Refer to Section 0. The Radiochemistry Manager will note completion of the verification in the Standards Preparation Logbook. This entry must be dated and initialed and a completed label must be attached to both the logbook and the standard bottle. Verification of carriers may be approved in LIMS by the Radiochemistry Manager, or their designee. The standard or carrier is now available for general use.

7.5 ASSIGNING EXPIRATION DATES

7.5.1 For radioactive standards, calculate an expiration date that is five half-lives, or one year after the verification analysis date, whichever is less.

Standards containing nuclides with relatively short half-lives (i.e., whose expiration dates would thus be shorter than 6 months), may be exempted from this restriction as long as useable standards may still be prepared from the activity remaining in the stock material. Approval of the Radiochemistry Manager must be obtained in these cases, as noted by his/her signature on the standard preparation documentation.

7.5.2 The expiration date for carriers will be 1 year from the verification analysis date.

7.5.3 The chemical stability of a material must be taken into account when assigning an expiration date for a standard. For example, iodine solution may not be chemically stable. Follow the manufacturer's guidance or consult with the Radiochemistry Manager to determine an expiration date in such cases.

7.5.4 Do not use a solution that shows visual or other signs of degradation. Floating particulate, color or clarity changes or unexplained vapors in the sample container are examples of possible indicators of degradation of a solution.

7.5.5 Standards and carriers that have passed their expiration date must be removed from service. Expired standards and carriers may be reused if they are re-verified as described above; a new expiration date may then be assigned. Stock, primary, and intermediate standards need not be re-verified during storage, or prior to subsequent dilutions, if the working standards being prepared are to be verified. The verification of a serial dilution or preparation of a parent standard is, in kind, considered to be verification of that material itself.

7.6 LABELING

7.6.1 Duplicate labels are prepared for the standard. The data entry for the label is reviewed by a designee prior to final release. One label is released to the applicable Prep Lab Supervisor to be placed on the verified standard container. The duplicate label is put into the Standards Preparation Logbook, with the entry corresponding to the standard ID.

7.6.2 Radioactive standard labels must include the following information:

- Standard ID number
- Name of standard or reagent
- Expiration date
- Activity concentration (include units)
- Standard Uncertainty (2-sigma), as given on the original radiostandard certificate, where applicable (include units)
- Activity reference date, where applicable
- Date of preparation
- Preparation analyst initials
- Chemical form, constituents
- Half-life

7.7 CONSIDERATIONS FOR SPECIFIC STANDARDS AND CARRIERS

Due to the wide variety of materials that could potentially fall under this SOP, the exact means of verifying standards and carriers must be handled on a case-by-case basis. Standards are verified against independent, NIST-traceable second source standards and/or instrument calibrations, which themselves have been generated using independent, NIST-traceable second sources. Difficult to obtain materials and very short-lived nuclides may occasionally require verification against a surrogate material that possesses similar decay properties as the material in question. Again, such situations must be addressed with the Radiochemistry Manager on a case-by-case basis.

7.7.1 AMERICIUM-241

7.7.1.1 Label four 220mL plastic specimen cups with the internal workorder ID numbers.

7.7.1.2 Using a calibrated pipette (SOP 321), transfer a volume of 243Am, equivalent to 20-80dpm, to three of the four cups. Add the same activity of the new 241Am standard to all four cups.

7.7.1.3 Place the cups on the steam bath and evaporate to dryness.

7.7.1.4 Continue with Am micro-precipitation as outlined in SOP 751.

7.7.2 AMERICIUM-243

The method for ^{243}Am is the same as ^{241}Am, however, three cups are traced with ^{241}Am and all four cups are spiked with the ^{243}Am solution to be verified.

7.7.3 BARIUM-133

7.7.3.1 For verification by gamma spectroscopy, the preferred technique is a direct comparison, in triplicate, of the standard to an independent second source. For this technique, the preparation of the standard into an established counting geometry is not necessary as long as the counting geometry for the two sources is identical. The volume and activity of the standard to be verified should be considered when choosing the container or geometry. Whenever possible, an effort should be made to avoid unnecessary dilutions of the standard.

7.7.3.2 If no second source is available, the standard must be prepared, in triplicate, in an established counting geometry for comparison to the current mixed-gamma efficiency

calibration for that geometry.

7.7.3.3 If there is insufficient standard volume to prepare triplicate samples for analysis, a single sample may be prepared, however, that sample must be analyzed on three separate gamma detectors.

7.7.3.4 If a second source is available:

- Label six containers with the internal work-order ID numbers.
- Add the appropriate amount of ^{133}Ba standard (target 1,000–5,000dpm) to three containers. Add a similar amount of activity of ^{133}Ba from a second source, to three different containers.
- Submit the samples and proper documentation to the Instrument Lab for gamma spectroscopy counting.

7.7.3.5 If a second source is NOT available:

- Label three containers with the internal work-order ID numbers.
- Add the appropriate amount of 133Ba standard (target 1,000–5,000dpm) to the three containers.
- Submit the samples and proper documentation to the Instrument Lab for gamma spectroscopy counting.

7.7.4 CARBON-14

7.7.4.1 Label nine 20mL liquid scintillation vials with the internal work-order ID numbers.

7.7.4.2 Add 5mL of DI water to each scintillation vial.

7.7.4.3 Determine the volume of 14C standard needed to deliver approximately 1,000dpm activity. Remove that volume of water from the scintillation vials that will be spiked with 14C.

7.7.4.4 Add the volume of the 14C standard to be verified, determined in the previous Step, to three of the vials. Add the same activity of a second, independent 14C standard to three different vials. If the diluent or the spiking volume is

different for the two standards, see the Technical Manager for further instructions.

7.7.4.5 Add 15mL of Ultima Gold LLTTM cocktail to each vial. Cap the vials tightly, mix thoroughly, and wipe clean with methanol and a lint-free laboratory wipe..

7.7.4.6 Submit the samples and proper documentation to the Instrument Lab for liquid scintillation counting.

7.7.5 CURIUM-244
The method for ^{244}Cm is the same as ^{241}Am, however, three cups are traced with ^{243}Am and all four cups are spiked with the ^{244}Cm solution to be verified.

7.7.6 IODINE-129
Refer to Section 7.7.4, using ^{129}I instead of ^{14}C.

7.7.7 IRON-55
Refer to Section 7.7.12, using ^{55}Fe instead of ^{241}Pu.

7.7.8 LEAD-210
Refer to Section 7.7.12, using ^{210}Pb instead of ^{241}Pu.

7.7.9 NICKEL-63
Refer to Section 7.7.12, using ^{63}Ni instead of ^{241}Pu.

7.7.10 NEPTUNIUM-237
The method for ^{237}Np is the same as ^{239}Pu, however, three cups are traced with ^{239}Pu and all four cups are spiked with the ^{237}Np solution to be verified.

7.7.11 PLUTONIUM-239

7.7.11.1 Label four 220mL plastic specimen cups with the internal workorder ID numbers.

7.7.11.2 Using a calibrated pipette, transfer a volume of 242Pu, equivalent to 20-80dpm, to three of the four cups. Add the same activity of the new 239Pu standard to all four cups.

7.7.11.3 Place the cups on the steam bath and take the solutions to dryness.

7.7.11.4 Continue with Pu micro-precipitation as outlined in SOP 777.

7.7.12 PLUTONIUM-241

7.7.12.1 Label nine 20mL glass liquid scintillation vials with the internal work-order ID numbers.

7.7.12.2 Add the appropriate amount of 241Pu standard (target 1200dpm) to three of the vials. Add the appropriate amount of 241Pu standard (target 1200dpm), of a second source, to three different vials. Note the matrix of the diluent, e.g. 5M HNO3. This will be used to prepare the three blank vials. If the diluent or the spiking volume is different for the two standards, see the Technical Manager for further instructions.

7.7.12.3 Add the same volume of unspiked diluent to the three blank vials.

7.7.12.4 Take all nine vials to dryness on a hotplate set to low temperature. Vials should be uncapped and taken just to dryness, not baked hard.

7.7.12.5 Remove vials from heat. Add 5mL 0.1M HNO3 to each vial.

7.7.12.6 Add 15mL Ultima Gold LLTTM cocktail.

7.7.12.7 Cap the vials tightly, mix thoroughly, and wipe clean with methanol and a lint-free laboratory wipe.

7.7.12.8 Submit the samples and proper documentation to the Instrument Lab for liquid scintillation counting.

7.7.13 PLUTONIUM-242

The method for ^{242}Pu is the same as ^{239}Pu, however, three cups are traced with ^{239}Pu and all four cups are spiked with the ^{242}Pu solution to be verified.

7.7.14 POLONIUM-209

7.7.14.1 Label four 220mL disposable cups with the internal work-order ID numbers.

7.7.14.2 Using a calibrated pipette (SOP 321), transfer a volume of 209Po, equivalent to 80-160dpm, to all four cups. Add the same activity of 210Po standard to three of the cups.

7.7.14.3 Place the sample cups on the steambath and take to complete dryness.

7.7.14.4 Re-dissolve the residue in 100mL of 1N HCl.

7.7.14.5 Add approximately 0.1g of ascorbic acid.

7.7.14.6 Electro-deposition is carried out per SOP 711.

7.7.15 POLONIUM-210
The method for ^{210}Po is the same as ^{209}Po, however, three cups are traced with ^{209}Po and all four cups are spiked with the ^{210}Po solution to be verified.

7.7.16 PROMETHIUM-147
Refer to Section 7.7.12, using ^{147}Pm instead of ^{241}Pu.

7.7.17 RADIUM-226
Refer to Section 7.7.3, using ^{226}Ra instead of ^{133}Ba. Also note that gamma analysis must be done by the 186 keV photopeak, NOT the emissions of the various progeny.

7.7.18 RADIUM-228
Refer to Section 7.7.3, using ^{228}Ra instead of ^{133}Ba.

7.7.19 STRONTIUM-89
Refer to Section 7.7.12, using ^{89}Sr instead of ^{241}Pu.

7.7.20 STRONTIUM-90
Refer to Section 7.7.12, using ^{90}Sr instead of ^{241}Pu.

7.7.21 TECHNICIUM-99

7.7.21.1 Label nine 20mL liquid scintillation vials with the internal work-order ID numbers.

7.7.21.2 Add 5mL of DI water to each scintillation vial.

7.7.21.3 Determine the volume of 99Tc standard needed to deliver approximately 1,000dpm activity. Remove that volume of water from the sample vials that will be spiked with 99Tc.

7.7.21.4 Add the volume of the 99Tc standard to be verified, determined in the previous Step, to three of the vials. Add the same activity of a second, independent 99Tc standard to three different vials. If the diluent or the spiking volume is different for the two standards, see the Technical Manager for further instructions.

7.7.21.5 Add 15mL of Ultima Gold ABTM cocktail to each vial. Cap the vials tightly, mix thoroughly, and wipe clean with

methanol and a lint-free laboratory wipe.

7.7.21.6 Submit the samples and proper documentation to the Instrument Lab for liquid scintillation counting.

7.7.22 THORIUM-229

7.7.22.1 Label four 220mL plastic specimen cups with the internal workorder ID numbers.

7.7.22.2 Transfer a volume of 230Th equivalent to 40-80dpm to three of the four cups. Spike a volume of the 229Th standard, at approximately half the 230Th activity into all four cups.

7.7.22.3 Take the cups to dryness on a steam bath and re-dissolve with 50mL 8N HNO3.

7.7.22.4 Load the solution onto a nitrate column and proceed with the Th separation and micro-precipitation as outlined in SOP 777.

7.7.23 THORIUM-230

The method for ^{230}Th is the same as ^{229}Th, however, three cups are traced with ^{229}Th and all four are spiked with ^{230}Th solution to be verified. Note that the ^{230}Th activity should, again, be approximately twice the ^{229}Th activity. This is to minimize the "tailing effect" of ^{229}Th that introduces a high bias to the ^{230}Th results.

7.7.24 TRITIUM (HYDROGEN-3)

Refer to Section 7.7.4, using ^{3}H instead of ^{14}C.

7.7.25 URANIUM-232

7.7.25.1 Label four 220mL plastic specimen cups with the internal workorder ID numbers.

7.7.25.2 Transfer a volume of 238U equivalent to 40-80dpm to three of the four cups. Add the same activity of 232U to all four cups.

7.7.25.3 Take the cups to dryness on a steam bath and re-dissolve with 50mL 9N HCl.

7.7.25.4 Load the solution onto a chloride column and proceed with the U separation and micro-precipitation as outlined in SOP 778. A chemical separation is necessary to remove the

ingrown 228Th progeny, which interferes with the 232U analytical region of interest (ROI).

7.7.26 URANIUM-238
The method for ^{238}U is the same as ^{232}U, however, three cups are traced with ^{232}U and all four cups are spiked with the ^{238}U solution to be verified.

7.7.27 STABLE CARRIERS (E.G., BA, FE, NI+CO, PB, SM, SR, Y)
Stable carriers are verified by ICP-AES in the metals Department. Prior to preparation, consult the metals Analyst to determine the appropriate dilution factor for the carrier solutions to be analyzed. Typically a 10,000-fold dilution will be acceptable, and is described below:

7.7.27.1 Label two sets of three 15mL ICP tubes with the internal workorder ID numbers or the carrier solution ID obtained from the reagent recipe logbook. One set will contain the intermediate dilution and the other will contain the final dilution.

7.7.27.2 Transfer 9.9mL DI water into each of the three intermediate tubes. Add 0.1mL of the carrier solution to be verified. Invert repeatedly and mix well.

7.7.27.3 Transfer 9.9mL ICP dilution solution into each of the three final tubes.

7.7.27.4 Remove 0.1mL of the intermediate dilution and add it to one of the final tubes containing 9.9mL of ICP diluent. Invert repeatedly and mix well.

7.7.27.5 Submit the final dilutions and proper documentation to the Metals Lab for analysis.

7.7.27.6 In addition to the normal LIMS entry, record all raw data and final results in the reagent recipe logbook.

8. QUALITY CONTROL

The successful routine analysis of batch Method Blanks and spiked Laboratory Control Samples serve as verification of the integrity of the standards and reagents used.

9. SAFETY, HAZARDS AND WASTE DISPOSAL

9.1 SAFETY AND HAZARDS

9.1.1 Read the component MSDSs prior to preparing standards or using any solvents or reagents.

9.1.2 Standards will be prepared using all reasonable precautions against the spread of contamination. The work area and all equipment will be surveyed at the end of the preparation.

9.1.3 Read the appropriate MSDSs before preparing standards or using any reagents.

9.1.4 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

9.1.5 Gloves, safety glasses, and a lab coat must be worn when working with any chemicals (e.g., standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

9.1.6 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

9.1.7 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

9.2 WASTE DISPOSAL

9.2.1 Remove expired standards from the storage area; submit to waste management personnel for disposal.

9.2.2 Non-halogenated solvent rinses are disposed of in the Non-Halogenated Organic Waste satellite collection vessel. Dichloromethane (Methylene Chloride) is disposed of in a separate Halogenated solvent waste stream.

9.2.3 All empty solvent bottles are disposed of appropriately. Please note that all labels and markings must be removed or defaced prior to disposal.

10. REFERENCES

10.1 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

10.2 Paragon SOP 711, “Preparation of Water and Soil Samples for the Analysis of Polonium-210”.

10.3 Paragon SOP 751, “Actinides – Americium / Curium Separation – Purification By TRU And TEVA Spec Column”.

10.4 Paragon SOP 765, “Separation and Analysis of Neptunium in Environmental Matrices”.

10.5 Paragon SOP 777, "Actinides – Thorium and Plutonium Sequential Separation by Anion Exchange".

10.6 Paragon SOP 778, "Actinides – Uranium, Plutonium And Americium/Curium (Partial) Sequential Separation By Ion Exchange".

DOCUMENT REVISION HISTORY

7/5/06: **SOP 300**: Completely restructured; storage considerations enhanced; discussion of Paragon's Standards & Solutions database augmented. Added 'RESPONSIBILITIES' and 'DOCUMENT REVISION HISTORY' Sections.

2/22/07: **SOP 798**: Rev5 expanded to include radioactive standards in the entire Radiochemistry Department, rather than just the Actinides Group. Verifications of carrier solutions, where required by the individual preparation SOPs, have also been included. The updated title of this SOP reflects these changes. Carrier solution verification was previously addressed in SOP 734 (now retired). Requirements for the preparation of carriers and other reagents is sufficiently addressed in SOP 300.

3/14/08: **Combined**: Incorporated IA061101 corrective action text into existing SOP 300r12 content; restructured. Added SOP 798r5 content (no changes except updating internal Section references). Updated existing SOP 300r12 Table content. Added Form 718.

Summary of Chemical Materials Requirements

Type	***Storage***	***Source***	***Expiration****
Concentrated Acids, Concentrated Bases	Ambient	Vendor	Shorter of vendor-supplied or 10 years from receipt
Solvents	Ambient	Vendor	Shorter of vendor-supplied or 5 years from receipt
Primary Reagents & Neat Chemicals	As required by method	Vendor	Shorter of vendor-supplied or 10 years from receipt

Type	***Storage***	***Source***	***Expiration****
Volatiles (includes all purgeable hydrocarbons, such as VOAs, Aromatics, GRO)	Freezer	Stock, Unopened	**Non-gases**: Vendor-supplied, if absent 1 year from receipt; **Gases**: **Vendor-supplied, if absent 1 year from receipt**
	As required by method	Stock, Opened	**Non-gases**: 3 months from date opened **Gases**: 1 week from date opened
	As required by method	Intermediate **	**Non-gases**: 1 month from preparation **Gases**: 1 week from preparation

* Replace sooner if contamination or degradation is evident.

** Date of expiration shall not exceed soonest of component materials.

Summary of Chemical Materials Requirements

Type	***Storage***	***Source***	***Expiration****
TOC	Refrigerate	Stock, Unopened or Opened Intermediate **	Shorter of vendor-supplied or 1 year 6 months from preparation

Type	***Storage***	***Source***	***Expiration****
Extractable Hydrocarbons (includes all GC and SVOC; pesticides, PCBs, Herbicides, PAHs, DRO)	Freezer	Stock, Unopened Opened Stock, Intermediate **	Shorter of vendor-supplied or 1 year from receipt Six months

Type	***Storage***	***Source***	***Expiration****
High Explosives	Freezer	Stock, Unopened or Opened Intermediate **	Shorter of vendor-supplied or 1 year from receipt 6 months (8332); 1 month if $\leq$1000ppm

* Replace sooner if contamination or degradation is evident.

Summary of Chemical Materials Requirements

Type	*Storage*	*Source*	*Expiration**
Metals by ICP or ICP/MS	Ambient	Stock, Unopened	**Shorter of vendor-supplied or 10 years from receipt**
		Stock, Opened	**Shorter of vendor-supplied or 5 years from receipt**; may be re-verified
		Intermediate **	**Shorter of vendor-supplied or 5 years from receipt**; may be re-verified
Mercury	Ambient	Stock, Unopened	**Shorter of vendor-supplied or 10 years from receipt**
		Stock, Opened	**Shorter of vendor-supplied or 5 years from receipt**; may be re-verified
		Intermediate **	**Shorter of vendor-supplied or 5 years from receipt**; may be re-verified
Nutrients, Anions and other Wet Chemistry tests	Refrigerate	Neat Stock (includes salts), Unopened or Opened	**Shorter of vendor-supplied or 5 years from receipt**; may be re-verified
		Stock Solutions, Unopened	**Shorter of vendor-supplied or 1 year from receipt**
		Intermediate **	**1 month from preparation**
Cyanide	Refrigerate	Stock, Unopened or Opened	**Shorter of vendor-supplied or 1 year from receipt**
		Intermediate **	6 months from preparation

* Replace sooner if contamination or degradation is evident.

Paragon Analytics

STANDARD VERIFICATION SUMMARY FORM

Code # _____ Standard Name _____ Date _____ Analyst _____

Aliquot for verification: _____

Work up: _____

_____

_____

_____

_____

_____

_____

_____

Expected activity and uncertainty: _____

_____

_____

_____

_____

_____

Results of Counting and counting uncertainty:

Average observed activity: _____ (units)

Standard deviation of observations: _____

Is the observed average activity within ± 5% of the expected value (PAI SOP 734)?	Yes ___	No ___
Were at least 3 replicates of the prepared standard analyzed (ICPT BOA, Attach. J, Sect. 2.9)?	Yes ___	No ___
Does the expected activity lie within the range of the average observed activity ± 2 standard deviations (ICPT BOA, Attach. J, Sect. 2.9)?	Yes ___	No ___
Is the value for 2 standard deviations used above less than or equal to 10% of the average observed activity (ICPT BOA, Attach. J, Sect. 2.9)?	Yes ___	No ___
Is the standard's expiration date set to one year from the verification date (PAI SOP 734 and ICPT BOA, Attach. J, Sect. 2.9)?	Yes ___	No ___

_____

_____

_____

_____

Reviewed by Radiochemistry Manager: _____ **Date:** _____

Form 718r4.frm (8/12/2003)

Acid Density Equivalents for Non-Diluted RAD Standards

	H2SO4	HCl	HNO3	CH3COOH	NH4OH
Density	1.84	1.19	1.42	1.049	0.90
18N	1.420	-	-	-	-
12N	1.277	1.190	1.315	1.034	0.920
10N	1.235	1.158	1.263	1.028	0.933
9N	1.210	1.143	1.235	1.025	0.940
8N	1.185	1.127	1.210	1.023	0.947
7N	1.160	1.110	1.185	1.020	0.953
6N	1.143	1.095	1.160	1.017	0.960
5N	1.118	1.080	1.130	1.014	0.967
4N	1.092	1.063	1.105	1.011	0.973
3N	1.070	1.048	1.080	1.008	0.980
2N	1.047	1.032	1.055	1.005	0.987
1N	1.024	1.016	1.026	1.003	0.993
0.5N	1.012	1.008	1.013	1.001	0.997
0.1N	1.002	1.002	1.003	1.000	0.999
0.05N	1.001	1.001	1.001	1.000	1.000
0.01N	1.000	1.000	1.000	1.000	1.000
Density g/cm3					

Dilution Matrix

Conc.	H2SO4 36N	HCl 12N	HNO3 16N	CH3COOH 17.5N	NH4OH 15N
18N	500	-	-	-	-
12N	330	1000	750	690	800
10N	280	830	625	570	670
9N	250	750	560	510	600
8N	220	670	500	460	530
7N	190	580	440	400	470
6N	170	500	380	340	400
5N	140	420	310	290	330
4N	110	330	250	230	270
3N	83	250	190	170	200
2N	56	170	130	110	130
1N	28	83	63	57	67
0.5N	14	42	31	29	33
0.1N	2.8	8.3	6.3	5.7	6.7
0.05N	1.4	4.2	3.1	2.9	3.3
0.01N	0.28	0.83	0.63	0.57	0.67
Volumes needed to make 1 liter.					

Must Discard 30 Days from _____ (date printed)

Date started & retired no longer required. 9/7/07 DAS

See red font, Section 4.4, for updated guidance pertaining to maintenance log entries. 1/29/08 DAS

See red font annotations regarding updated review policies. 3/30/09 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 303 REVISION 10

TITLE: CONTROL, FORMAT AND REVIEW OF LABORATORY LOGBOOKS

FORMS: 353

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9.10.06
QUALITY ASSURANCE MANAGER _____ DATE 9/7/06
LABORATORY MANAGER _____ DATE 9-10-06

HISTORY: Rev0, 2/3/92; Rev1, 7/30/92; Rev2, PCN #60, 12/20/93; Rev3, PCN #247, 8/01/94; Rev4, PCN #405, 2/28/95; Rev5, 7/15/99; Rev6, 10/08/01; Rev7, 4/07/03; Rev8, 9/15/03; Rev9, 6/5/04; Rev10, 9/11/06.

1. SCOPE AND APPLICATION

All analytical services performed by Paragon must be documented thoroughly in a legible, organized manner so that all information may be easily understood from laboratory records. The documentation must be available and defensible during casual inspection, internal and external audit, and legal testimony. Laboratory records must be retrievable, and kept in a manner that prevents loss, damage or deterioration (see also SOP 069).

This standard operating procedure (SOP) discusses the issuance, use and review of laboratory logbooks. Paragon uses both hardcover and custom (i.e., made in-house) laboratory logbooks (as well as electronic benchsheets which are utilized, protected, and archived in LIMS). Sample receipt and login functions are primarily addressed electronically, this SOP applies also to sample preparation and analysis, monitoring of support equipment (e.g., recording cooling unit and oven temperatures, balance calibration verifications, etc.), and instrument maintenance, where documented in laboratory logbooks. Chain-of-custody is documented electronically (see ~~SP~~ SOP 318). Preparation of standards and reagents is documented via use of Paragon's Standards and Reagents database (see SOP 300). Requirements pertaining to waste logs, Health & Safety, and training records are beyond the scope of this SOP.

2. SUMMARY

Use of laboratory logbooks helps to ensure that records are kept in a consistent, detailed, traceable and legally defensible manner. The user of the laboratory logbook must request the logbook from the QA Department. Key information pertaining to the laboratory logbook (e.g., title, unique laboratory identification number, etc.) is maintained by the QA Department in an electronic index. New logbooks are placed into service as needed; used logbooks are replaced and archived (electronically imaged) as needed.

All information pertinent to the task being conducted must be recorded, in a real time

manner, by the person performing the task, in the appropriate laboratory logbook (or electronic benchsheet). Any equipment used to perform analytical services (e.g., instruments, balances, pipettes, etc.) must be identified by their unique identifier.

Where the information maintained in an Operations' laboratory logbook has a direct effect on sample results (instrument run log, maintenance log, balance calibration verification logbook, etc.), that logbook's data must be reviewed ~~monthly~~ formally (see Section 4.7 for further details). Logbooks that do not contain original and official records (e.g., duplicate Radiochemistry sample transmittal logbooks -- official transmittal of prepared samples to Counting Room documented by LIMS benchsheets; out-going mail log, etc.) are exempted from ~~monthly~~ formal review. *Consult the Quality Assurance (QA) Manager for exemptions. Exempted Operations' logbooks must bear an annotation on the cover, dated and initialed by the QA Department, indicating that that particular laboratory logbook is exempt from monthly review.*

3. RESPONSIBILITIES

3.1 The QA Department is responsible for maintaining a current index of laboratory logbooks and for issuing controlled laboratory logbook numbers. The QA Department also maintains an on-going record of the printed names, signatures and initials of all personnel, to assist with ciphering logbook entries. The QA Department shall provide oversight as needed to ensure that archiving ~~monthly~~ and established logbook review processes are performed appropriately and in a timely manner.

3.2 It is the responsibility of the Department Manager to ensure that the laboratory logbook formats implemented sufficiently prompt all required information that needs to be recorded. The Department Manager is responsible for training laboratory staff in this procedure, and for monitoring satisfactory on-going performance.

Each Department shall perform and document a ~~monthly~~ formal review of the group's logbooks as applicable that addresses the accuracy, completeness and correctness of logbook entries and/or corrections. The review shall be documented by the entry of a second set of dated initials, that are independent from the dates and initials corresponding to the logbook entries themselves.

3.3 The Data Reporting Group is responsible for maintaining an organized system of scanned logbook images, and for processing logbooks submitted for scanning (archival) in a timely manner.

3.4 It is the responsibility of all personnel to maintain logbooks in accordance with this SOP, to guard against their damage or loss, and to submit them for archival, in a timely manner, when they are no longer in use.

4. PROCEDURES

4.1 ISSUING LOGBOOKS

4.1.1 Laboratory logbooks are controlled documents. The QA Department

issues laboratory logbooks via a sequential numbering system that is maintained via an electronic index. The following information is recorded in the electronic index for each logbook issued:

- laboratory logbook number
- title of laboratory logbook
- form reference or hardcover
- employee or group issued to
- date issued
- initials of issuer.

4.1.2 Identification as a Paragon Analytics logbook must be indicated on the front or inside cover of all laboratory logbooks. This identification must include Paragon's street address.

4.1.3 The following information must be marked on the outside front cover of the issued laboratory logbook:

- title
- group issued to
- assigned laboratory logbook number
- date issued
- ~~prompt for date started~~
- ~~prompt for date retired~~.

~~The user of the logbook must fill-in date started when the logbook is placed in service, and must fill-in date retired when the logbook is no longer to be used~~.

Where logbooks are dedicated to a specific piece of equipment, the unique identifier or serial number of the piece of equipment must also be indicated in the laboratory logbook.

4.1.4 End users and Departmental and QA staff may work with Paragon IS personnel to develop electronic benchsheets (for use in lieu of laboratory logbooks) where practicable.

4.2 PAGINATION

Numbering of logbooks pages is used to assure that the logbook is intact (i.e., that no pages have been removed or are missing).

4.2.1 All custom-made spiral bound logbooks are paginated in-house prior to issuance. The format of the pagination consists of a unique six-digit number, the first four of which indicates the assigned laboratory

logbook number, and the last two indicates page number (01 through 99, or less).

4.2.2 Hardcover logbooks are generally purchased with pre-numbered pages. Regardless, the binding of hardcover logbooks is such that intactness is inherently assured (i.e., page removal would be evident).

4.2.3 Some instrument run logs are printed out, annotated as needed, a copy is placed in the sample workorder folder, and the original is maintained in a designated three-ring binder. Pagination of the run log print out pages contained in the three-ring binder is not required as they are uniquely identified by their contents (e.g., contain unique sequence designations in the print out's header; depict unique batches as log entries).

A slip-sheet that depicts the information described in items 4.1.2 and 4.1.3 above, is placed as a cover to the three-ring binder. When the binder becomes full, the analyst clips the contents together, along with the slip-sheet cover, submits the contents to the Data Reporting Group for archival, and requests a new slip-sheet from the QA Department.

~~The contents of the three-ring binder are reviewed monthly in accordance with the procedures outlined in this SOP~~.

4.3 RECORDING ENTRIES IN LOGBOOKS

4.3.1 All logbook entries must be legible and must be recorded in indelible black or blue ink. Other colored ink may not be used as it may not photocopy well. Pencil may not be used as the original data must be recorded in an indelible manner (i.e., in a manner that cannot be easily altered).

4.3.2 All data and observations must be recorded directly, in a real time manner, by the person generating the data or making the observation. Use of "post-it" notes to record data for subsequent transcription into a laboratory logbook is prohibited.

4.3.3 Each person making entries in a laboratory logbook must review his/her work to ensure that all entries are clear, legible, and formatted well enough that a reviewer -- several years after the work is complete, working from a photocopy, and without the help of laboratory personnel -- can easily read and understand the entry.

4.3.4 Each entry (i.e., set of information recorded in the same time frame) must be dated and initialed by the person making the entry. If an entry requires more than one page, the preceding page number should be

referenced at the top of each following page.

Arrowing down is permissible as long as it is clear where the arrow stops. Arrowing down is not permissible if recording measured values (i.e., record gravimetric values as actual weights).

Use leading zeroes when recording values less than one (e.g., 0.0255g).

4.3.5 If multiple entries are made on the same page on various dates, then each entry must be dated and initialed separately.

4.3.6 Unused portions of a page or unused pages must be voided to prevent additional information being added at a later date. A large "Z" or "slash" can be used to void out a space or page (or group of errors). The mark used to void the space or page must be dated and initialed proximate to the mark.

4.3.7 Any information added to the logbook (e.g., run sequence logs, spectra) must be stapled or taped to a logbook page, and then signed and dated such that the signature/date is half on the attached sheet and half on the logbook page itself.

4.3.8 Benchsheets and other electronic records in LIMS are subject to restricted access controls to assure that entries (or corrections) are made only by appropriate authorized personnel.

4.4 MAINTENANCE LOG ENTRIES

Definition of Paragon's maintenance program, including requirements for documentation, are given in Section 8.0 of the LQAP.

Some data systems associated with instruments (e.g., ICP, **CVAA, LC/MS-MS**) can accommodate maintenance entries that appear as run log headers in lieu of using maintenance logbooks. Use of this type of electronic record is permissible.

Hardcover logbooks are assigned to each piece of major Paragon instrumentation. Where practicable, laboratory benchsheet logbooks may be modified to include maintenance attestations. The hardcover maintenance logbooks should be physically located in the laboratory in a convenient location proximate to the instrument. Routine maintenance, scheduled preventive maintenance and repairs are to be recorded.

At a minimum, each logbook entry must contain the following:

- **the date of the maintenance or repair;**
- **the reason for the maintenance or repair, including any modifications made to the instrument (e.g., preventive, replaced broken part, HPLC component switched-out);**
- **a full description of the maintenance or repair conducted;**
- **the name of the analyst or vendor who performed the maintenance or repair; and**
- **the initials of the analyst making the entry and date of entry.**

See SOP 317 for directives pertaining to tagging equipment out of service and placing repaired equipment back into service. Remember that the equipment must be demonstrated to be functioning within acceptable parameters before being placed back into service. **A reference that the equipment was verified and where this information can be found, should be noted in the maintenance log. Also, where applicable, the identity of the reference material used as an instrument check must also be recorded. Where applicable, a statement as to the calibration's expiration must also be made.**

4.5 ANCILLARY INFORMATION

Anomalies must be explained by annotation. For example, if the normal sequence of dates recorded in a laboratory logbook indicate a longer gap than usual, that gap must be explained by a comment indicating why the gap occurred (e.g., holiday, inadvertently missed reading, etc.) The annotation must be dated and initialed by the person making the entry.

Similarly, if a temperature excursion occurs, an explanation indicating why (e.g., refrigerator left open) and what corrective measures were taken, as applicable (e.g., ambient temperature higher, so adjusted temperature control colder) must be noted.

4.6 CORRECTING ERRORS

4.6.1 Information may not be obliterated in any manner. No correction devices or fluids (e.g., erasers, whiteout, labels) may be used. Information may not be cut out, pages must remain intact.

Errors must be corrected with a single line drawn completely through the erroneous entry, making it clear that the error is being crossed out but leaving it legible. The corrected entry must be initialed and dated by the person making the correction. If not evident, the reason for making the correction must be clearly stated.

4.6.2 It is acceptable to block or bracket a group of changes and initial and date those changes as a unit. However, it must be clear as to what group is being changed, the date the changes are made, and who made the changes.

A large "Z" or “slash” can also be used to void out a group of errors. The mark used to void the group of errors must be dated and initialed proximate to the mark, thus indicating the date the change was made and the person making the change. A comment may also be written to explain the reason that the entry was voided.

4.7 REVIEWING LOGBOOKS

All laboratory logbooks not cited as exempt from ~~monthly~~ **formal** review must be reviewed by a peer or Supervisor ~~on a monthly basis~~. ~~Custom~~ logbooks requiring ~~monthly~~ review contain a review prompt signature line on each page, hardcover logbooks contain a pre-printed signature line at the bottom of each page.

with direction to obtain a review signature at the time each page is completed.

4.7.1 The Department Manager is responsible for determining who may perform logbook reviews. It is Paragon’s policy that review/sign-off is performed by a knowledgeable, independent party. A technician or

Because the pages that comprise instrument run logs are copied as completed and included with the workorder/run documentation (reviewed subsequently), formal review of these logbook originals is not required.

analyst may not review his/her own work; however, in instances where multiple parties make entries onto a logbook page, it is permissible for one of the participants to function as the final review signature. Review by QA staff is also permissible.

4.7.2 The reviewer shall verify the following conditions:

- complete information for every entry; all information is legible
- all entries made in indelible black or blue ink
- all entries are initialed and dated
- no information obliterated; no correction devices or fluids used; corrections made properly (single line cross-out, date, initials)
- all pages intact
- supplemental information stapled or taped to logbook page and initialed and dated
- corrective actions recorded for non-compliant situations.

The QA Department issues monthly logbook review request attestations to each Department to assure that appropriate logbook review procedures are being followed.

The reviewer shall place his/her initials and date at the end of each page of entries reviewed to demonstrate that a review has been performed.

4.7.3 In instances where logbook entries are infrequently made (i.e., where a long duration of time is needed to complete a logbook page), the logbook shall ~~still~~ be reviewed monthly. The reviewer shall draw a line under the last entry made and place his/her initials and date at the end of the line to indicate an independent review.

4.8 ARCHIVING

Electronic records are subject to frequent backup and redundancies as explained in Paragon's IS and LIMS Policies and Procedures (posted to network for ready reference). A system for archiving (see SOP 069 for additional details) hardcopy laboratory logbooks by imaging (scanning) is in place. Transference of these records to electronic images preserves and protects them (via frequent backup and redundancies). The scanned images are accessible for reference lab-wide, hence completed logbooks should be turned in promptly to prevent loss or damage.

5. REFERENCES

Chapter 5 of the current NELAC standard
Client quality assurance guidances, as applicable

DOCUMENT REVISION HISTORY

9/11/06: Some content reorganized. Data Reporting Group identified as the lead for imaging (archival) of logbooks. Permissible use of electronic records for equipment data systems that can accommodate maintenance information was added; augmented other aspects of electronic records discussion. Attached Form.

Paragon Analytics

Attestation of Logbook Review

DATE: 9/6/06

FROM: Quality Assurance Department

RE: Logbook Review for month of **August, 2006**

DEPARTMENT MANAGER (or Designee):

_____ (Organic Extractions)
_____ (GC/MS SVOCs)
_____ (GC/MS VOAs)
_____ (Fuels/GC/HPLC)
_____ Steve Workman (Metals)
_____ Eric Lintner (WetChem)
_____ Charles Orchard (Sample Receiving)
_____ Rebecca Schwab (RAD Prep. Labs, Pre-Screening)
_____ Renee Gallegos (RAD Instrumentation)

_NA_ Project Management
_NA_ Reports Management
_NA_ Health & Safety
_NA_ Reporting Group
_NA_ Quality Assurance
_NA_ IS Department

This notice serves as a reminder to conduct your Group's monthly logbook review per SOP 303.

Don't forget instrument maintenance logs!

Your signature below attests that the monthly logbook review due, has been satisfactorily completed:

Printed Name	Signature	Date

THIS FORM MUST BE RETURNED TO THE QA DEPARTMENT BY 9/15/06.

Thank You!!

Form 353r5.doc (3/24/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 305 REVISION 10

TITLE: BALANCE CALIBRATION, VERIFICATION, AND UTILIZATION

FORMS: 301 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/15/07
QUALITY ASSURANCE MANAGER _____ DATE 1/12/07
LABORATORY MANAGER _____ DATE 1-12-07

HISTORY: Rev0, 1/24/92; Rev1, 12/20/93; Rev2, PCN #65, 1/6/94; Rev3, PCN #99, 1/20/94; Rev4, PCN #542, 10/18/95; Rev5, 5/9/97; Rev6, 1/10/00; Rev7, 4/17/02; Rev8, 9/22/03; Rev9, 7/20/05; Rev10, 1/12/07. re-released without revision 3/12/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) outlines the procedures to be followed for the daily use of laboratory balances (i.e., calibration verification and operation). The annual cleaning, calibration and certification of balances performed by a qualified vendor is also discussed.

2. SUMMARY

The calibration of all certified laboratory balances is to be verified daily before use, using annually verified laboratory weights, and per the calibration scheme prescribed in the balance's dedicated logbook (Form 301).

3. RESPONSIBILITIES

3.1 The Department Manager shall designate appropriately trained staff to conduct and record daily balance calibration verifications. The Department Manager or designee shall notify the QA Department of any new application the balance is used for, if the masses weighed for that application are not already bracketed by the balance's current verification scheme.

3.2 The Department Manager or designee shall notify the QA Department of any new balance acquisition so that certification can be arranged and a dedicated logbook issued before the balance is placed into service.

3.3 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review. Any anomalies or out-of-control events must be noted and corrective action taken and documented. It is the responsibility of the Technician to notify the QA Department of any balance that is malfunctioning or is not operational.

3.4 The QA Department is responsible for coordinating the annual balance servicing

and calibration certification performed by a qualified vendor. The QA Department shall also coordinate vendor servicing as needed when a balance malfunctions or is transported (by vehicle), thereby invalidating its certification.

3.5 The 3-point calibration verification scheme (Form 301) developed for each balance by the QA Department, brackets the balance's normal range of use and is based on the balance's intended use, capabilities, client quality control criteria, and other "good science" considerations. The QA Department shall evaluate the calibration schemes periodically to assure their appropriateness and adequacy.

3.6 The QA Department is responsible for coordinating the annual certification of Master weights, and performing the annual in-house verification of laboratory weights (SOP 901). The QA Department is responsible for the annual acquisition and change-out of static masters. Records of all balance certificates, servicing records, and an inventory of balances and their locations shall be maintained by the QA Department..

4. INTERFERENCES

4.1 The balance must be level and stable for proper operation.

4.2 Drafts can cause the balance to drift, yielding unstable readouts. Draft shields either integral to or external to the balance, must be used where needed.

4.3 The balance pan, and chamber, where applicable, and the weights used for verification must be clean or error may result. Use a Kimwipe™ or brush to clean the pan as needed. In the event of a spill, consult the operating manual (obtainable from the QA Department) if more thorough cleaning is required.

Use gloves, a Kimwipe™, or some other barrier (e.g., tweezers) when handling the weights. Do not handle the weights with bare hands. If the weights must be cleaned, use acetone or another suitable solvent and a Kimwipe™. Make sure the weights have air-dried completely before using them.

4.4 Use of static masters, to dissipate static charge and aid in drift control, is recommended for chambered analytical balances.

4.5 A balance's total capacity is usually incorporated in the model designation. For example, an AE104 balance has a total operational capacity of 104 grams. ***Know the limits of the balance being used. Never attempt to weigh anything whose mass exceeds the balance's capacity.***

5. APPARATUS AND MATERIALS

5.1 Balance with current certification (refer to balance's calibration sticker, good through one year from date of certification).

5.2 Verified laboratory weights (refer to verification sticker, good through one year from date of verification).

5.3 Dedicated balance calibration verification logbook.

6. PROCEDURE

6.1 GENERAL PROCEDURES

6.1.1 Note the considerations discussed in Section 4 Interferences; resolve any issues.

6.1.2 It is not necessary to turn the balance off after each use; the balance may be left on indefinitely. If the balance is not already on, power it on and allow it to warm up for a few moments before using it. Make sure all draft shields are tightly closed or in place, and zero the balance. Check the balance's readout to verify that the reading is stable.

6.1.3 Before using the balance to weigh any mass recorded for analytical use, check the dedicated balance logbook to determine if a daily balance calibration verification has been performed. If the balance's calibration has not yet been verified, perform the procedures outlined in Section 6.2 below. If the balance has been verified, tare the balance.

6.1.4 All objects to be weighed should be placed in the center of the balance pan. Allow the balance's readout to stabilize before recording the observed weight on the appropriate laboratory benchsheet. Where balances are interfaced with LIMS, the software monitors and requires the balance to stabilize before transmitting the mass information to LIMS. Allow the balance to completely return to zero between each weighing. Know the balance's limit! ***Never weigh anything whose mass exceeds the balance's total capacity!***

6.1.5 Remove the object. The balance may be left on when finished.

6.2 CALIBRATION VERIFICATION

The following procedures are to be carried out by qualified staff, near the beginning of the workshift, each day the balance is in use:

6.2.1 Verified laboratory weights are located strategically throughout the laboratory (e.g., Organics Extractions Lab, Organic Standards Lab, Actinides Water Lab). Obtain the appropriate weights/weight sets.

6.2.2 Use gloves, a Kimwipe™, or some other barrier (such as tweezers) when handling the weights.

6.2.3 Weigh each mass of the weight scheme (Form 301), and record the observed weight. Evaluate the recorded weight against the acceptance range depicted on Form 301.

If the observed weight does not fall within the acceptance range, check that the balance is level, stable, shielded from drafts, and that the balance pan and weights are clean. Reweigh.

If the observed weight still does not fall within the acceptance range, turn the balance off, wait a moment, then power the balance on again. Zero. Reweigh each weight per the 3-point verification scheme. If acceptance limits still are not met, notify the QA Department immediately so that appropriate corrective action may be taken.

6.2.4 Replace the weight(s) in the protective case and return them to their proper storage location.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

7.2 Safety glasses, a lab coat, and gloves must be worn at all times when working in the laboratory.

7.3 Food and drink are prohibited in all lab areas.

8. REFERENCES

None.

DOCUMENT REVISION HISTORY

1/12/07: Updated Section 3. Added “Where balances are interfaced with LIMS, the software monitors and requires the balance to stabilize before transmitting the mass information to LIMS.” to Step 6.1.4. Added DOCUMENT REVISION HISTORY.

EXAMPLE

BALANCE CALIBRATION VERIFICATION LOG FOR BALANCE #3
ACTINIDES LAB (SARTORIUS -- #10720694)

DATE / TIME	ANALYST'S INITIALS	NOMINAL VALUE of WEIGHT (g)	OBSERVED VALUE (g)	ACCEPTANCE RANGE (g)	COMMENTS
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	
	Use proper balance page and most current iteration of benchsheet.				
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	
		50.00		49.90 - 50.10	
		10.00		9.95 - 10.05	
		1.00		0.99 - 1.01	

Reviewed By / Date _____ **FORM 301r11.doc (9/26/04)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 306 REVISION 4

TITLE: **THE USE OF SIGNIFICANT FIGURES AND RULES FOR ROUNDING NUMBERS**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7/20/06
QUALITY ASSURANCE MANAGER _____ DATE 7/20/06
LABORATORY MANAGER _____ DATE 7-21-06

HISTORY: Rev0, 4/4/94 and 12/15/95; Rev1, 2/10/01; Rev2, 8/19/02; Rev3, 2/9/04; Rev4, 3/24/05 & 7/24/06.
re-released without revision 3/12/09 DAS

1. SCOPE AND APPLICATION

In order to report numerical results accurately and consistently, the laboratory must round numbers correctly and report the appropriate number of significant figures. This Standard Operating Procedure (SOP) describes the methods by which numerical values are rounded and the correct number of significant figures is reported.

2. SUMMARY

The rules presented below provide a consistent, systematic approach for rounding numbers and reporting the correct number of significant figures. These rules ensure that the "numbers reported are significant and that no significant numbers are lost in the calculations." (Reference 8.2)

3. RESPONSIBILITIES

3.1 It is the analyst's responsibility to understand and follow the procedures set forth in this SOP, to round numbers correctly, and to report the correct number of significant figures.

3.2 It is the Department Manager's responsibility to ensure that numbers have been rounded correctly and that the correct number of significant figures has been reported.

4. DEFINITIONS

4.1 Significant Figures: the number of leading non-zero digits in the reported value. Terminal zeros may or may not be significant (see Section 6.2 for details).

4.2 Experimental Observation: the measured quantity that is determined experimentally. It is the "raw" information that is recorded. The following are examples of such quantities - the height or area count from a chromatographic analysis; the measured volume of a pipette; the readout value from a balance or

spectrometer. Calculated values produced by a computer are not experimental observations.

5. ANALYTICAL MEASUREMENTS

5.1 Always record an experimental observation to the greatest number of significant figures possible. In general, it is not necessary to record more than 5 significant figures. Record all significant figures after the decimal place on the balance or other readout device. Rounding shall be performed ***after*** the final calculation.

5.2 Use the rules presented in Table 1 below to report the correct number of significant figures in the final result:

Table 1

SIGNIFICANT FIGURES TO BE REPORTED – DEFAULT REPORTING STANDARDS

Organics Sample Data:	Report 2 significant figures
Metals Sample Data:	Report 2 significant figures
General Chemistry Sample Data:	Report 2 significant figures
Radiochemistry Sample Data (use ANSI standard):	Report 2 significant figures for uncertainty, activity and MDC
Quality Control (QC) Data:	Report 3 significant figures for spikes; Report 2 significant figures for blanks; Report to the whole number units place for precision (%R) and accuracy (%RPD)

5.3 The only exception to the in-house rules presented in this SOP may be provided by a client's SOW or QAPjP.

6. RULES FOR ROUNDING NUMBERS AND REPORTING SIGNIFICANT FIGURES

6.1 ROUNDING

To round a numerical result to a certain place value, locate the digit in that place and the digit to its immediate right.

6.1.1 If the digit immediately following those to be retained is less than 5, drop the terminal digit(s) and do not change the digit in the rounding place.

Examples: 11.44 rounds to 11.4
0.480 rounds to 0.48
1233 rounds to 1230

6.1.2 If the digit following those to be retained is greater than 5, drop the terminal digit(s) and increase the digit in the rounding place by 1.

Examples: 11.46 rounds to 11.5
0.489 rounds to 0.49
1678 rounds to 1680

6.1.3 There are two different approaches to rounding if the digit following those to be retained is equal to 5:

- The simplest approach states that if the figure following those to be retained is equal to 5, increase the digit in the rounding place by 1. Most commercial applications (e.g., Excel, Access) follow this rule when rounding. Paragon's Laboratory Information Management System (LIMS) follows this convention.

- The second approach, for example, that required by the US EPA CLP SOW, states that: If the figure following those to be retained is equal to 5, and there are no figures other than zeroes beyond the 5, and the rounding place is even, drop the terminal digit(s) and do not change the digit in the rounding place.

Examples: 12.250000 rounds to 12.2
0.2445 rounds to 0.244
145 rounds to 140

If the figure following those to be retained is equal to 5, and there are no figures other than zeroes beyond the 5, and the rounding place is odd, drop the terminal digit(s) and increase the digit in the rounding place by 1.

Examples: 0.487500 rounds to 0.488
11.35 rounds to 11.4
135 rounds to 140

If the figure following those to be retained is equal to 5, and there are non-zero figures beyond the five, drop the terminal digit(s) and increase the digit in the rounding place by 1.

Examples: 0.48751 rounds to 0.488
11.352 rounds to 11.4

6.2 SIGNIFICANT FIGURES

The number zero may or may not be a significant figure. The "significance" of the number zero is case specific.

6.2.1 Final zeros after a decimal point are always significant figures, if the value of the number is greater than 1.

Example: To the nearest milligram, the number 9.8 is reported as 9.800 grams (four significant figures total).

6.2.2 Zeros before a decimal point with nonzero digits preceding them are significant. With no preceding nonzero digits, a zero before the decimal point is not significant.

Example: The zeros are significant in the number 100.8 (four significant figures total); the zero is not significant in the number 0.8 (one significant figure total).

6.2.3 If there are no nonzero digits preceding the decimal point, the zeros after the decimal point but preceding other nonzero digits are not significant. These zeros are intended as placeholders only and are written to indicate the position of the decimal point.

Example: The zeros are not significant in the number 0.00042 (two significant figures total).

6.2.4 One way to determine the significance of one or more zeros interspersed in a number is to write the number in exponential form. If the zeroes may be deleted when the number is expressed in exponential form, then the zeroes are not significant.

Example: 0.00042 may be written as $4.2 \bullet 10^{-4}$. The zeroes are not significant and may be deleted. This number has two significant figures.

Example: 100.01 may be written as $1.0001 \bullet 10^{2}$. The zeroes are significant and may not be deleted. This number has five significant figures.

6.2.5 Final zeros in a whole number may or may not be significant, depending upon the situation.

7. REPORTING DATA

7.1 Table 1 lists the number of significant figures to be reported for each kind of analysis. Use the rules for rounding and significant figures along with Table 1 to

report the correct number of significant figures. Reporting limits with less than (<) signs follow the rules listed in Table 1.

7.2 Values pertaining to QC raw data -- i.e., amount spiked, spike result, etc. -- shall be reported to three significant figures. The percent recovery shall be reported in whole numbers (to the units place) and the relative percent difference shall be reported in whole numbers (to the units place).

7.3 Paragon's LIMS does not display terminal zeroes.

8. REFERENCES

8.1 Washington Department of Ecology, Quality Assurance Manual - Manchester Laboratory, Appendix, "Rules for the Use of Significant Figures and for Rounding-Off."

8.2 Applied Statistics for Engineers, 2nd Edition, pp. 77-80.

8.3 Basic Mathematics for Trades and Technologies, 2nd Edition, p.88.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 317 REVISION 10

TITLE: REMOVING AND RETURNING EQUIPMENT FROM SERVICE

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/10/07
QUALITY ASSURANCE MANAGER _____ DATE 1/8/07
LABORATORY MANAGER _____ DATE 1-8-07

HISTORY: Rev0, 7/23/93; Rev1, PCN #37, 11/17/93; Rev2, PCN #239, 6/27/94; Rev3, PCN #547, 10/18/95; Rev4, 8/9/00; Rev5, 2/5/02; Rev6, 3/19/03; Rev7, 2/13/04 and 3/10/05 (updated format); Rev8, 6/8/05; Rev9, 9/7/06; Rev10, 1/8/07.

re-released without revision 3/12/09 DAS

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) details procedures for removing improperly or non-functioning equipment from use and gives guidelines for placing new or repaired equipment in service. This SOP applies to, but is not limited to, the following types of equipment: ovens, balances, cooling units, weights, thermometers, hoods, pipettors, and radiation survey equipment.

Corrective actions and documentation requirements for data generated using non-conforming equipment are prescribed in SOP 928 - Issuing and Tracking of Non-Conformance Reports.

2. SUMMARY

In order to ensure the generation of accurate and reproducible data, all analytical, reference and support equipment are maintained and operated in a controlled manner. When equipment is either not working at all, or is not working within specifications, the equipment is considered to be nonconforming and must be removed from service.

Equipment removed from service must be prominently tagged-out (see Example placard at end of SOP) and may be placed into service only after appropriate adjustments/repairs have been made and reliable performance within specifications has been demonstrated.

The parameters of performance for each equipment type are detailed in the associated operational SOP and/or the instrument's operator's manual.

3. RESPONSIBILITIES

3.1 Each equipment/instrument operator is responsible for the proper operation of the equipment and for inspecting the equipment for proper functioning prior to use. If the equipment/instrument is determined not to be in acceptable working order, the operator must tag-out the equipment per the requirements of this SOP and notify the Department Manager, and the Quality Assurance (QA) Manager, as applicable, in a timely manner. Excepting identified support equipment (records

for support equipment maintenance are retained by the QA Department, the equipment/instrument operator is also responsible for documenting the need for repair, and for maintaining repair records.

3.2 The Department Manager and QA Manager are responsible for coordinating and ensuring that appropriate corrective actions are taken, including the equipment's repair or replacement, and notification to clients of suspect data, as applicable. The Department Manager is responsible for ensuring that the repaired or replacement equipment is properly functioning before being placed into service.

4. PROCEDURE

4.1 Equipment is tested/inspected for proper functioning before use. Only properly functioning equipment that meets the calibration/performance criteria set forth in the unit's associated operational SOP can be used. If the equipment is not operational or does not function within the prescribed control parameters, it must be tagged-out as "Not In Service," and the Department Manager, and QA Manager, as applicable must be notified.

A "Not In Service" placard (see Example at end of SOP) must be prominently displayed on the nonconforming equipment. This equipment cannot be used until satisfactory repair has been completed and the unit demonstrates reliable performance. Appropriate corrective actions for potentially affected data shall be initiated by the Department Manager, or designee, per SOP 928.

4.2 As applicable, the Department and QA Mangers will coordinate the failed equipment's repair or replacement. Equipment found to be repeatedly out-of-service shall be removed from service entirely or shall be replaced.

4.3 Repaired or replaced equipment must demonstrate accurate and reliable performance before being placed into service. The "Not In Service" placard must remain in place while the unit is being repaired and during determination of reliable performance.

4.4 Notations documenting the equipment's failure, and detailing the equipment's repair order and status, shall be made in the associated equipment's logbook. Additional maintenance and repair records shall be maintained by the laboratory Department, as applicable.

5. REFERENCES

This SOP describes in-house procedures developed by Paragon. The requirements established herein are compliant with various quality assurance guidance documents, such as the most current versions of the National Environmental Laboratory Accreditation Conference (NELAC) Standard, the Department of Energy (DOE) Quality Systems for Analytical Services (QSAS) document, and the Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories.

DOCUMENT REVISION HISTORY

6/8/06: Minor clarifications made; 'References' Section enhanced; 'Document Revision History' added; example placard incorporated as part of SOP.

9/7/06: Header and history not updated 6/8/06, fixed (incremented), and published.

1/8/07: Minor format changes and text clarifications.

EXAMPLE PLACARD

NOT IN – SERVICE
DO NOT USE
REPAIR ORDERED _____

- QA Department -
(date)

NOTE: Be sure to include any other pertinent information on the placard as well.

Must Discard 30 Days from _____ (date printed)

Amended 9/11/08: SOP reference corrected p.1. Also, see Note added to Section 4.3 (i.e.,hardcopy benchsheet transaction of samples for direct count) DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 318 REVISION 6

TITLE: **CHAIN OF CUSTODY**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7/7/06
QUALITY ASSURANCE MANAGER _____ DATE 7/7/06
LABORATORY MANAGER _____ DATE 7/7/06

HISTORY: Rev1, 3/15/93; Rev2, 8/25/93; Rev3, PCN # 86, 1/18/94 and 10/18/95 (re-released w/o revision); Rev4, 4/23/02; Rev5, 2/13/04; Rev6, 7/5/06.

1. SCOPE AND APPLICATION

Chain-of-custody (COC) is a documented procedure used to demonstrate the flow of and responsibility for samples from field acquisition, receipt and analysis by the laboratory, to disposal or return to the client. COC is used to establish an intact and continuous record of the physical possession, storage and use of the sample, its fractioned aliquots, leachates, extracts, digestates, and remnants.

The USEPA defines custody of a sample as:

- in one's actual possession, *or*
- in one's view, after having been in one's physical possession, *or*
- in one's possession and then locked or sealed to prevent tampering, *or*
- kept in a secure area, restricted to authorized personnel only.

This standard operating procedure (SOP) describes Paragon's practices for barcoding and maintaining electronic COC through our Laboratory Information Management System (LIMS).

2. SUMMARY

A field COC is received with the samples. Paragon's Sample Custodian or designee uses the information on the field COC, as well as other laboratory information, to log the samples into LIMS (SOP 201~~1~~2. The sample receipt process is completed (SOP 202) and unique barcode labels are generated and applied to each sample container. Scanning of the barcoded samples is the means by which custody is transferred and tracked throughout the laboratory. Unique barcode labels are also generated and applied to all fractions, leachates, extracts and digestates derived from the samples.

Two types of paired events are performed and documented in LIMS to move samples, fractions, leachates, extracts and digestates throughout the laboratory. These paired events are: 'check out/check in' and 'relinquish/receive'. The sample (and like-wise fraction, leachate, extract and digestate) transactions are accomplished by scanning, using

the many hand-held scanners located throughout the laboratory, and on-screen data entry. The transaction events are traceable to the individual performing them because entry of the individual's unique LIMS username and password is required. Once initiated, the paired event must be completed before another custody event can be initiated.

Please note that Paragon's LIMS is proprietary and only limited detail is provided in this SOP. Access to LIMS and associated guidance materials is restricted to authorized personnel only.

3. RESPONSIBILITIES

3.1 All Sample Receiving, preparatory, analytical, and Waste Disposal staff are responsible for carrying out the procedures as described in this SOP, and for reporting problems encountered to the IS Department in a timely manner.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 IS Department staff are responsible for maintaining and augmenting LIMS as needed and for providing the necessary internal chain-of-custody (ICOC) training to laboratory staff.

4. PROCEDURE

4.1 Samples are received from the courier or directly from the client and logged in by Sample Receiving staff who enter information such as number of containers, sample matrix, etc. into LIMS for each workorder processed. Unique barcode labels are generated and applied to each sample container. The Sample Receiving staff maintains custody of the samples until they are 'relinquished' to the respective laboratory Groups who 'receive' them.

4.2 A list of storage and sample processing areas is maintained in LIMS. During the 'receive' event, the recipient has the opportunity to refine the sample's location to a shelf and bin designation if so desired. A 'search' utility exists in LIMS to assist with locating samples (or fractions, leachates, extracts and digestates thereof).

4.3 Laboratory personnel 'check out' samples as needed for preparation and/or analysis. The distinction between a 'check out/check in' event and a 'relinquish/receive' event is that sample containers that are expected to be returned to the sample location they were acquired from are 'checked out' then 'checked back in' when returned; whereas samples (or fractions, leachates,

extracts and digestates) that are not to be returned to the location acquired from are 'relinquished/received'. **

A "batch" barcode may be used to transfer the custody of entire sets of planchets, liquid scintillation vials, gamma containers, etc. from a laboratory preparatory Group to an analysis Group.

4.4 When samples are depleted upon preparation and/or analysis, their "depleted" status is designated as such in LIMS.

4.5 Sample remnants, including leachates, extracts and digestates, as well as unconsumed fractions such as counted planchets and gamma containers, are retained by Paragon for a period of 90 days (unless otherwise specified by the client). These sample remnants, unconsumed fractions, leachates, extracts and digestates may be transferred to designated sample archive areas for storage.

4.6 When a workorder is designated in LIMS for disposal, Paragon either returns the sample to the client according to contractual requirements, or proceeds with disposal in accordance with applicable local, State and Federal regulations. The Waste Compliance Officer coordinates and maintains records of final disposal.

5. REFERENCES

None.

DOCUMENT REVISION HISTORY

7/5/06: Complete re-write transitioning from hardcopy COC logs to barcoding and electronic chain-of custody. Added standard LIMS program specification reference to 'RESPONSIBILITIES' Section; added DOCUMENT REVISION HISTORY Section.

**** NOTE: For RUSH direct count work, the entire client sample(s) is `checked out' into the custody of Radiochemistry Prep. Lab personnel. However, a paper benchsheet (to accomplish the timeliness needed), is used to document the transfer of the sample(s) to the Instrument Lab for counting. The same benchsheet is then used to document the return of the sample(s) to the Prep. Lab for subsequent preparations. Note that for this RUSH counting, the sample(s) is not altered, it is merely counted `as is' (i.e., as received). After subsequent sample preparation(s) are completed, the remaining client sample, if not depleted, is `checked back in' via LIMS. The paper benchsheet used to accommodate the RUSH count work is included as part of the final data package report.**

Paper benchsheets are also used to transact non-RUSH filters from the Radiochemistry Prep. Lab to the Instrument Lab for direct gamma counting. The benchsheet is then used to document the return of the filters to the Prep. Lab for preparation for additional analytical testing. The benchsheet is included in the final data package report.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 319 REVISION 8

TITLE: **GENERATION AND MONITORING OF DEIONIZED (DI) WATER**

FORMS: **712 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3/1/07

QUALITY ASSURANCE MANAGER _____ DATE 3/1/07

LABORATORY MANAGER _____ DATE 3-1-07

HISTORY: Rev0, 3/19/93; Rev1, PCN #128, 2/4/94; Rev2, PCN # 507, 7/12/95; Rev3, 10/21/98; Rev4, 1/08/99; Rev5, 3/02/02; Rev6, 9/8/03; Rev7, 9/11/06; Rev8, 3/1/07.

re-released w/o revision 3/12/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the processes that Paragon uses during the monitoring and use of reagent water in the laboratory. The procedures described herein apply only to water that is purified and generated on-site, as part of Paragon's deionized (DI) water system, and does not apply to specialty grades of water (e.g., HPLC water) that are purchased from vendors.

Because water is such a 'universal solvent', it is susceptible to a host of extraneous materials (contaminants), such as: suspended particles (turbidity), ions (e.g., dissolved inorganics that constitute 'hard water'), dissolved organics (carbon-based materials that can particularly impact low-level HPLC analyses), bacteria (both live and cell debris), etc. The characteristics (purity) of the water (as reagent, diluent, laboratory control sample media, etc.) required, is contingent on the analytical method used and based on what properties could critically affect the measured outcome. This includes physical effects, such as turbidity, which may clog analytical columns, as well as interfere with photometric readings.

This SOP does not address the generation of reagent water used in volatile organic analyses (see SOP 511), nor does it address additional treatments that may be required by specific analytical methods (see appropriate method SOPs). Because the characteristics of water can change even as it sits in a sealed container (for extended periods), storage is a consideration, but is not addressed by this SOP (see applicable method SOP).

Laboratory staff must be aware that the meaning of the term 'reagent water' varies per application, and that not all 'reagent water' is the same thing.

2. SUMMARY

Water is highly susceptible to contamination. Considerations of 'purity' vary per application. Use of high purity water only is relevant to analytical processes, but not necessary or economically practical for initial stages of dishwashing (SOPs 334, 720).

Paragon operates several DI water systems to support the laboratory's needs. The quality of the DI water generated for general laboratory use is evaluated by measuring resistivity, which must be monitored and documented each business day. Veracity of the DI system monitoring sensors is verified monthly. Vendors are used to replenish and maintain the DI water systems.

3. RESPONSIBILITIES

3.1 Laboratory staff members are designated to perform the monitoring functions described in this SOP. It is their responsibility to conform to the requirements of this SOP, and to promptly notify the Paragon point-of-contact for vendor interface (currently Lance Steere), and the QA Manager, in the event of a failure of the purification system(s).

3.2 Department Managers are responsible for ensuring that staff are properly trained regarding concepts and procedures addressed by this SOP. The Department Managers must also assure that only reagent water as specified by each method is used for analytical procedures.

When Department Managers are informed of purification system problems or failures, their first responsibility is to determine the impact of the situation on the laboratory's analyses, and to take action to minimize the detrimental effects the situation may have on generated data. Temporary procedures that will alleviate any adverse effects must be implemented, and the general laboratory staff must be informed accordingly.

3.3 In the event that either routine maintenance or system failure require Paragon to contact the vendor, the Paragon point-of-contact is Lance Steere. All requests for equipment maintenance/service should be routed through him. Lance is responsible for maintaining the non-benchtop water purification system service records.

This individual is also responsible for conducting and documenting the monthly resistivity meter verification, and for properly maintaining the equipment necessary to conduct this testing.

3.4 The Quality Assurance Department is responsible for providing oversight of adherence to water purification system policies, and for providing monitoring logbooks as needed.

4. INTERFERENCES

For some of the water purification systems, prolonged disuse of the system can cause small amounts of organic and inorganic materials to be leached from the plumbing, thus compromising the quality of the water delivered. This disuse can cause resistivity readings to be lower than normal, or outside of acceptance limits. In cases where the DI system has not been used for some time (e.g., 4 days or more), it is good practice to open a DI faucet for approximately 30 seconds to briefly flush the DI lines of any accumulated dissolved material.

5. APPARATUS AND MATERIALS

Within the laboratory, there are two main DI water distribution systems available for glassware cleaning, bulk reagent preparation and general use. One system is located in the janitor's area and serves the radiochemistry side of the facility (ASTM Type II water generated). The other system is located adjacent to the metals laboratory area and serves the stable chemistry side of the facility (ASTM Type I water generated). These DI water systems are capable of continuously delivering water that meets the requirements specified for the ASTM water type, and are monitored and documented each business day to ensure that the water produced meets these criteria. Paragon also maintains a third treated water system that is used to support washing of laboratory glassware. Additionally, a benchtop Millipore Synergy 185^{TM} unit is available for laboratory use should further finishing be desired.

5.1 STABLE CHEMISTRY WATER PURIFICATION SYSTEM

5.1.1 Deionized Water Purification System (ASTM Type I)

Municipal (tap) water is passed serially through five tanks that contain ion exchange resins and organic adsorbents. These resins and adsorbents remove anions, cations and organic matter from the water. An in-line probe that monitors the water purity continually as it exits these tanks, is in place in the outflow of the fifth tank. This probe is connected to a meter whose display indicates the resistivity of the water passing over the electrode.

5.1.2 Millipore Purification System (ASTM Type I)

The DI water purified by the primary purification system is circulated through the Millipore system for further purification via high-quality ion exchange resins and carbon filters. This system generates ultra high-purity water to be used for critical applications. The Millipore system is equipped with an internal detector that indicates the resistivity of the water being produced.

5.2 RADIOCHEMISTRY WATER PURIFICATION SYSTEM (ASTM Type II)

Incoming municipal water is passed through a series of four ion exchange cylinders for initial purification. The water then enters a large fiberglass holding

tank. Water in this tank is pumped through two finishing resin cylinders, operating in parallel, and into a recirculating loop that continuously circulates water between the holding tank and the finishing cylinders. As deionized water is used in the laboratory areas, the initial incoming resin-washed tap water acts as the makeup volume for the holding tank.

System function and water quality is monitored at two points. The first monitoring point is a light (on vs off) located at the outflow of the fourth ion exchange cylinder, and the second monitoring point is the resistivity meter whose sensor is located at the outflow of the two parallel finishing scrubbers. Control systems also include a low level monitor in the holding tank, and sensors to control the flow of makeup water into the holding tank.

5.3 GLASSWARE WATER PURIFICATION SYSTEM

Tap water is passed through two tanks containing ion exchange resins and organic adsorbents, which remove anions, cations and organic matter from the water. The second tank is equipped with a resistivity detector that monitors the water purity continually as it exits this tank. This meter has a light that indicates, when lit, effective and correct operation of the purification system.

Water from this system is used only for the final rinsing of stable chemistry laboratory glassware, and not in the preparation of any reagents or standards used in the laboratory. Therefore, this water purification system is not routinely monitored. The system is, however, maintained by the vendor per the established maintenance schedule.

In concert with vendor requirements, an upgrade to this third system is under consideration. The upgrade will likely include installation of a carbon filter, followed by a particulate filter, before the resin tanks. This upgrade will prolong the service life of the resin tanks. With this configuration, ASTM Type II water will be able to be produced. Daily (each business day) monitoring of this system will likely be implemented once these system improvements are made. Staff notification and training will occur accordingly.

5.4 Conductivity probe, dedicated to resistivity meter verification.

NOTE: This dedicated probe must **never** be used for any other purpose than monitoring purification system water quality. Use of this probe for any other purpose, my ruin the probe's viability for the monitoring application.

6. REAGENTS

Not Applicable

7. PROCEDURE

7.1 DEFINITIONS

7.1.1 **DI water** is defined as municipal tap water that has been treated by passing it through a particulate filter, activated carbon unit, cation exchange resin, anion exchange resin, mixed bed resin, and a final "polishing" cartridge. This water contains no detectable heavy metals or inorganic compounds of interest, and is free of organic compounds of analytical interest above Paragon's routine analyte reporting limits (RLs). Additionally, a benchtop Millipore Synergy 185™ unit is available for laboratory use should further finishing be desired.

7.1.2 **ASTM D1193-91 Standard Specification for Reagent Water.** This specification covers requirements for water suitable for use in methods of chemical analysis and physical testing. Four grades are specified:

Property	Type I	Type II	Type III	Type IV
Conductivity (uS/cm at 25° C)	0.056	1.0	0.25	5.0, max
Resistivity (megohm-cm at 25° C)	18.0	1.0	4.0	0.2, min
pH at 25° C	NA	NA	NA	5.0 to 8.0
Total Organic Carbon (µg/L)	50	50	200	no limit
Sodium (µg/L)	1	5	10	50, max
Chlorides (µg/L)	1	5	10	50, max
Total silica (µg/L)	3	3	500	no limit

Type I water is typically used for analytical procedures. Type II water is routinely used to wash and rinse glassware.

7.2 MONITORING THE STABLE CHEMISTRY AND MILLIPORE SYSTEMS

7.2.1 These systems are monitored each business day. Designated laboratory staff record the resistivity readings shown in the display window of the system's meter in the DI water quality logbook (Form 712).

7.2.2 The acceptance criterion for both systems is resistivity ≥18 Meg ohm-cm (18 M Ω-cm).

7.2.3 Note that for the Millipore system, it may take a few minutes for the meter reading to stabilize if the unit has not been used for several hours.

7.2.4 If the resistivity meter of the primary purification system displays a value lower than the acceptance criterion, the laboratory staff should first attempt to flush the system to rid it of materials leached from the

piping. This can be done by opening a DI faucet in the laboratory for approximately 30 seconds. This will cause any accumulated residue to be flushed out of the system, and allow freshly purified water to come in contact with the resistivity probe. If this flushing procedure is effective in raising the resistivity of the system to required levels, no further action is necessary, except to record that day's reading in the water quality monitoring logbook.

7.2.5 In the event that the DI system cannot meet acceptance requirements, the laboratory staff must follow the procedures specified in Section 7.6.

7.2.6 Conductivity is inverse to resistivity. A monthly conductivity check is performed at a delivery tap of each DI system. A dedicated conductivity probe with a meter is used to take a reading at this tap under flow conditions. This reading must be $\leq$0.06 µmho (i.e., reciprocal to ≥18 M Ω-cm), for ASTM Type I specifications. This monthly check is conducted to ensure that the probe from which daily readings are taken is accurate. Documentation that this check was performed is recorded in the system's water quality monitoring logbook.

7.3 MONITORING THE RADIOCHEMISTRY WATER SYSTEM

7.3.1 The DI water purification system is monitored daily by designated staff who record the operational light's status and resistivity reading shown on the display window of the meter, in the DI water quality logbook (Form 712).

7.3.2 The acceptance criterion for this system is resistivity ≥1.0 Mega ohm-cm (1.0 M Ω-cm). Typically, this system produces a resistivity reading of about 17.5 M Ω-cm. If the reading falls below 5 M Ω-cm, notify Lance Steere so that the vendor can be contacted for maintenance to be performed before a system failure occurs.

7.3.3 The monitoring light on the outflow of the first four purification tanks is examined daily to ensure that it is on, thus ensuring that these initial purification tanks are performing properly. If this light is not on, this is an indication that the purification capacity of these tanks has been exhausted, and that they need to be replaced. Replacement is done to prevent rapid saturation of the "finishing" tanks that perform the final purification of the water. **It is not necessary to shut off the DI system if the monitoring light is not on.** However, a visit from the service vendor for this system should be scheduled as soon as possible (coordinate through Lance Steere).

7.3.4 In the event that the DI system cannot meet acceptance requirements,

the laboratory staff must follow the procedures specified in Section 7.6.

7.3.5 A monthly conductivity check is conducted at the outflow of the system under flow conditions. The acceptance criteria for this system check is that the inverse of the conductivity reading must agree to within ±0.01 µmho of the current resistivity value recorded in the daily log. For example, given a typical log reading of 17.5 M Ω-cm (i.e., 0.057µmho), the conductivity should read between 0.04–0.07µmho. **Note that per ASTM conductivity requirements, the conductivity reading for this system must always be <1.00 µmho.**

7.4 MONITORING THE GLASSWARE WATER SYSTEM

Because water from this system is only used for rinsing glassware, and not used to prepare reagents or standards for use in the laboratory, this organic water purification system is not routinely monitored. This system is serviced once or twice a year by the vendor, at Paragon's request. See also Section 5 of this SOP regarding potential upgrades under consideration for this system.

7.5 All water purification systems, except for the Millipore system which is maintained by Paragon staff, are maintained, under contract, currently by United States Filter Corporation. A vendor service representatives performs any required maintenance, repairs, or replacements to the systems. Documentation (service records) are managed by Lance Steere.

7.6 CORRECTIVE MEASURES

7.6.1 Immediately upon discovering that the water purification system cannot meet the acceptance criterion, the person discovering this situation must notify their Department Manager, Lance Steere, and the QA Manager, so that appropriate corrective actions can be effected.

7.6.2 If the situation cannot be corrected immediately, the purification system must be turned off to prevent it from delivering inadequately purified water to the laboratory areas. All systems discussed in this SOP have inlet water valves that prevent the inflow of municipal tap water into the purification tanks. These valves should be turned off. For the radiochemistry system, the delivery pump at the foot of the holding tank should also be turned off.

A tag must be placed over the closed valve (or pump switch) that indicates that the unit should remain off until maintenance is performed (refer to SOP 317).

7.6.3 All laboratory groups that use the affected purification system should be immediately notified of the failure, and be cautioned against using

the system for any purpose. Taps should be tagged out (SOP 317) until successful system repairs have been achieved.

7.6.4 The vendor point-of-contact (Lance Steere) will contact the service agency so that maintenance and repair can be performed.

7.6.5 The service agency will be responsible for correcting the problem, and ensuring that the systems are properly flushed after their activities are completed. Only the vendor point-of-contact (Lance Steere) can inform the laboratory staff that the purification system is fully operational, and that laboratory staff can remove the tag-out placards and resume use of the delivered reagent water.

7.6.6 Department Managers must determine the impact of the situation on the laboratory's analyses, and take action to minimize the detrimental effects the situation may have on data that has been generated. As necessary, these Managers will implement temporary procedures that will alleviate any adverse effects.

8. QUALITY CONTROL

Quality control measures are addressed with PROCEDURES above.

9. DEVIATIONS FROM METHOD

Not Applicable.

10. SAFETY, HAZARDS AND WASTE DISPOSAL

Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents), or within a laboratory area.

11. REFERENCES

"Standard Specification for Reagent Water", D 1193-91, American Society for Testing and Materials (ASTM), Volume 11.01.

DOCUMENT REVISION HISTORY

9/11/06: Content restructured. Conceptual information (theory) added. ASTM criteria Table added. DOCUMENT REVISION HISTORY added. Form attached.

3/1/07: Republished to put into a better publication cycle. Minor format and content corrections. Discussed potential improvements to be made to the third water treatment system (Section 5), and added a stronger warning regarding dedication of the monitoring probe.

SOP 319 *Paragon Analytics*

DI Water Quality Check Log

DATE	TIME	INITIALS	**Inorganics DI System** (ASTM Type I) ***Reading must be ≥ 18 MΩ-cm***		
			Light On? Y / N	Resistivity (MΩ-cm)	COMMENTS

DATE	TIME	INITIALS	**Milli-Q System** (ASTM Type I) ***Reading must be > 18 MΩ-cm***	
			Resistivity (MΩ-cm)	COMMENTS

* Logbook entries are reviewed monthly with conductivity check performed. See monthly conductivity check notations above, as applicable.

Notify Management *immediately* if acceptance criterion is not met! Form 712r4a.doc (10/17/2003)

SOP 319

Paragon Analytics

DI Water Quality Check Log

DATE	TIME	INITIALS	**RadChem DI System** (ASTM Type II) ***Reading must be ≥ 1.0 M Ω-cm***		
			Light On? Y / N	Resistivity (M Ω-cm)	COMMENTS

DATE	TIME	INITIALS	**RadChem DI System** (ASTM Type II) ***Reading must be ≥ 1.0 M Ω-cm***		
			Light On? Y / N	Resistivity (M Ω-cm)	COMMENTS

* Logbook entries are reviewed monthly with conductivity check performed. See monthly conductivity check notations above, as applicable. Form 712r4b.doc (10/17/2003)

Notify Management *immediately* if problems are noted; notify Management if reading falls below 5.0 M Ω-cm.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 320 REVISION 8

TITLE: MONITORING AND RECORDING OVEN TEMPERATURES

FORMS: 312 (varied per application, use current iterations)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/27/07
QUALITY ASSURANCE MANAGER _____ DATE 2/27/07
LABORATORY MANAGER _____ Lance Steere for KDC DATE 2/27/07

HISTORY: Rev0, 12/5/92; Rev1, PCN #82, 1/12/93; Rev2, PCN #526, 9/5/95; Rev3, 11/4/99; Rev4, 4/17/02; Rev5, 10/3/03; Rev6, 7/20/05; Rev7, 7/24/06; Rev8, 2/27/07.
re-released w/o revision 3/12/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes procedures for the operation and monitoring of laboratory ovens within specified limits. Procedures to follow in the event of oven malfunction, or other impairment such as catastrophic loss of power, and requirements for placing new or repaired ovens in service are also provided.

2. SUMMARY

Paragon uses laboratory ovens for a variety of applications -- in the course of sample preparation (e.g., ashing), analytical testing (e.g., TDS, percent moisture determinations) or to dry or condition glassware or reagents. Proper use and operation of each laboratory oven is the responsibility of the laboratory Department utilizing that oven. The Quality Assurance (QA) Department assists with facilitating repair when needed, record keeping, and in establishing and overseeing the temperature acceptance limits assigned to each oven.

Oven thermometers are managed by the QA Department. With the exception of the muffle furnaces, each oven is assigned a liquid-in-glass or digital thermometer (verified annually against a NIST-traceable master; SOP 923). Unless otherwise excepted, oven temperatures are read each business day from the dedicated thermometer and the temperature is recorded in a laboratory logbook (Form 312).

3. RESPONSIBILITIES

3.1 Each laboratory is responsible for maintaining operation of the ovens located in that laboratory area within acceptable limits. The Department Manager shall designate and train staff to read and record the oven temperatures each business day (unless oven is otherwise excepted). The Department Manager or designee is also responsible for coordinating oven repair or replacement as needed with the QA Department, and for reviewing temperature record logbooks per SOP 303.

3.2 It is the responsibility of the staff assigned to perform these duties to complete these tasks as described in this SOP, including all documentation required for review.

Laboratory staff are also responsible for ensuring that the thermometer(s) are functioning properly and that the correct thermometer is indicated in the laboratory logbook. Laboratory staff shall make minor adjustments to oven settings as needed (must be recorded in logbook) and are responsible for reporting malfunctions of thermometers or ovens to the Department Supervisor and the Quality Assurance Department.

3.3 The QA Department is responsible for managing thermometers, providing temperature record logbooks, and, in conjunction with Department Managers, assigning oven temperature acceptance limits (contingent upon oven's application). Oven repair or replacement is coordinated between the Department and QA Managers. The QA Department is also responsible for maintaining records of all laboratory oven identifications, the identities of the dedicated thermometer assigned to each oven, and oven repair records.

3.4 It is the responsibility of all personnel who are involved with this process to note any anomalies or out-of-control events. Corrective action must be taken and documented for any discrepancies noted.

4. PROCEDURES

4.1 Ovens and thermometers are uniquely identified (managed by the QA Department). Each business day and near to the beginning of the workshift, temperature readings are obtained from dedicated thermometers that have been verified in-house annually against a certified Master.

Exceptions: Wet Chemistry Department OV#12 is only used intermittently; muffle furnaces are used only intermittently and are not monitored with laboratory thermometers.

The oven thermometers are immersed in containers filled with sand or vermiculite to prevent fluctuations due to drafts when the oven's door is opened. The readings are recorded in laboratory logbooks (Form 312).

4.2 The QA Department issues dedicated logbooks that indicate the oven's acceptance limits. The acceptable temperature range varies with the oven's use (e.g., analytical testing, drying glassware, etc.). The established limits are set to address the requirements of analytical methods, where applicable.

As needed, laboratory staff shall perform minor temperature setting adjustments and shall document these adjustments in the oven's temperature record logbook.

4.3 The Department Supervisor and QA Department must be notified immediately if a significant excursion occurs, so that appropriate corrective actions may be taken. An excursion is deemed significant if the current temperature reading is significantly outside the unit's acceptable range, or if two or more sequential readings exceed the acceptance limits. **An oven cannot be used for analytical testing if it cannot maintain its temperature within specified limits.**

4.4 If an oven is taken out of service, it must be properly tagged-out (SOP 317). All corrective actions taken must be documented or referenced in the oven's temperature record logbook. Where the oven is used for analytical testing, potential impact to client data must be assessed. Repair or replacement of the oven will be coordinated between the Department and QA Managers. Additionally, refer to the Paragon Emergency & Contingency Plan (ECP) for further information regarding actions to be taken in cases of extended power outages or other catastrophic failures.

4.5 Before a new or repaired oven can be placed into service, evidence that the oven can maintain a stable and appropriate temperature must be documented. This is accomplished by recording acceptable oven temperatures for several readings over a span of time before the oven is used (allow the thermometer to come to a stable temperature before beginning the readings). Be aware that the oven may require additional temperature setting adjustment after samples or glassware have been loaded.

5. SAFETY, HAZARDS AND WASTE DISPOSAL

5.1 SAFETY AND HAZARDS

5.1.1 Use tongs, asbestos gloves, or other barrier when removing items from ovens.

5.1.2 Safety glasses, a lab coat, and gloves must be worn at all times when working in the laboratory.

5.1.3 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

5.2 WASTE DISPOSAL

Place damaged or broken **spirit-filled** thermometers in containers that can be sealed to safely contain the pieces and contents. Give container to Waste Disposal personnel for proper discard. **NOTE:** Broken **mercury-filled** thermometers can *only* be handled for cleanup and disposal by the laboratory Health & Safety Manager. *Under no circumstances are other laboratory personnel to handle or dispose of these mercury-containing materials.*

6. REFERENCES

Test Methods for Evaluating Solid Waste Physical/Chemical Methods SW-846, Third Edition, Final Update III, Chapter 1, Volume IA.

Paragon Emergency & Contingency Plan (ECP), current revision.

DOCUMENT REVISION HISTORY

7/24/06: Augmented RESPONSIBILITIES. Included references to other SOPs where applicable. Enhanced adjustment and failure directives. Added DOCUMENT REVISION HISTORY.

2/27/07: Re-published to put on a better publication cycle. Digital thermometer allowance provided for in SUMMARY and Step 4.1. Minor format corrections.

Paragon Analytics

Temperature Logbook

Acceptance Ranges: **OV#9** (%Moisture Determinations) -- 100 -110°C
OV#11 (Glassware Drying) -- 130 - 150°C

Notify QA Department immediately if temperature exceeds acceptable range!

DATE	TIME	OV #9 Therm: HB-2367 Temp. (°C)	OV #11 Therm: #3187 Temp. (°C)	INITIALS	COMMENTS

Reviewed by/date: _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 321 REVISION 5

TITLE: CALIBRATION VERIFICATION OF PIPETTES AND PIPETTORS

FORM: 311 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9-11-06

QUALITY ASSURANCE MANAGER _____ DATE 9/8/06

LABORATORY MANAGER _____ DATE 9-11-06

HISTORY: NEW, 10/14/93; Rev1, PCN #251, 8/4/94 & 10/18/95 (re-released without revision; Rev2, 1/8/99; Rev3, 4/29/02; Rev4, 5/1/02; Rev5, 9/11/06.

re-released w/o revision 3/12/09 DAS

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the practices performed by laboratory personnel to verify the calibration of mechanical pipettes and pipettors. This SOP does not apply to volumetric glassware (i.e., transfer) pipettes.

2.0 SUMMARY

Mechanical pipettes (i.e., Eppendorf, Oxford, etc.) are hand-held devices that assist in drawing up and delivering specific volumes of liquid (µL to several mL amounts) in a manner that can be repeated rapidly and with accuracy. Mechanical pipettes may be fixed volume or adjustable, with tips (i.e., dispensing ends) integral to the device or disposable. Pipettors are devices with delivery spouts and a 'feeding tube' that resides in the liquid, that are used to dispense larger amounts of liquid (e.g., reagents) repeatedly and rapidly, when fitted onto a container of liquid, and set to deliver a specified volume. Mechanical pipettes are typically used to measure critical volumes of sample or reagent (e.g., used to prepare standards, perform laboratory quality control sample spikes, etc.) and, therefore, must be uniquely identified (for traceability purposes) and verified before each use (of a particular volume setting), whereas the accuracy requirements for pipettor dispensers (e.g., solvent delivery in the Organics Extractions Lab, preservative addition when preparing bottle kits, etc.) are typically not critical, these devices need not be uniquely identified, and may be checked periodically (monthly).

Mechanical pipette verification is performed gravimetrically, by weighing a dispensed aliquot of deionized water and evaluating the resultant mass against specified tolerance limits. Pipettor dispensers are verified volumetrically, by dispensing a volume of liquid into a graduated cylinder and comparing the amount delivered to the nominal volume setting of the pipettor. Only devices that perform within limits can be used in the laboratory. Those devices that do not meet criteria must be segregated and clearly marked 'DO NOT USE' (refer also to SOP 317) until they can be repaired and verified successfully. Verification checks are recorded in laboratory logbooks (Form 311).

Each laboratory area is responsible for maintaining its own pipettes and pipettors.

3.0 RESPONSIBILITIES

3.1 Each chemist shall perform the tasks described herein, strictly as prescribed by this SOP. Each chemist must notify their Supervisor of malfunctioning devices promptly.

3.2 Department Managers are responsible for ensuring that staff are properly trained regarding concepts and procedures addressed by this SOP. The Department Managers must determine the type of pipette or pipettor suitable for each task, and assure that only the correct type of device is used for each application.

Department Managers are responsible for overseeing the maintenance of all pipettes and pipettors, for ordering new/replacement devices that are suitable to their Department's applications, and for ensuring that each mechanical pipette is uniquely identified.

3.3 The Quality Assurance Department is responsible for providing oversight of adherence to pipette/pipettor policies, and for providing logbooks as needed.

4.0 INTERFERENCES

4.1 The analytical balance must be level and stable for proper operation.

4.2 Drafts can cause the balance to drift, yielding unstable readouts. Draft shields either integral to or external to the balance, must be used where needed.

4.3 The balance pan and chamber (where applicable), must be clean or error may result. Use a Kimwipe™ or brush to clean the pan as needed.

5.0 MATERIALS AND APPARATUS

5.1 pipettes and pipettors, disposable tips, as applicable

5.2 analytical balance, 0.0001g resolution

5.3 graduated cylinder of appropriate volume

6.0 REAGENTS

Deionized (DI) water, obtainable from the laboratory's deionized water system.

7.0 PROCEDURE

7.1 The tolerance guide for pipette verification is given on page 2 of Form 311 (attached). A tolerance of ±1.0% has been established for all mechanical pipettes.

7.2 Mechanical pipettes must be verified before each use of a specified volume setting, pipettor dispensers should be verified periodically (monthly).

7.3 To verify **mechanical pipettes**:

7.3.1 Make sure the analytical balance is turned on, and that the balance's calibration has been verified per SOP 305. Tare out a container of suitable size to receive the volume to be dispensed by the pipette.

7.3.2 Perform any needed maintenance on the pipette, attach a suitable tip (if applicable), and adjust the setting (if applicable).

7.3.3 Draw up and dispense the volume measured by the pipette into the container tared on the analytical balance.

NOTE: Pipettes set to deliver <2uL may require multiple aliquots to be dispensed so that a sizeable enough mass can be successfully weighed by the analytical balance.

7.3.4 Compare the mass delivered to the tolerance guide. If acceptable, record the results in the logbook (Form 311). If not acceptable, repeat maintenance and test again. If still not acceptable, segregate the device, clearly marking it 'DO NOT USE', and inform your Supervisor.

7.4 To verify **pipettors**:

7.4.1 Obtain a graduated cylinder of suitable size.

7.4.2 Perform any needed maintenance on the pipettor, set adjustment to deliver the desired volume.

7.4.3 Draw up and dispense one volume into the graduated cylinder, read the volume delivered. If the result is acceptable, record the results in the logbook (Form 311). If not acceptable, repeat maintenance, readjust setting, and test again. If still not acceptable, clearly mark the device 'DO NOT USE', and inform your Supervisor.

7.5 New pipettes must have an ID number marked before being placed into service.

8.0 QUALITY CONTROL

Quality control measures are addressed with PROCEDURES above.

9.0 DEVIATIONS FROM METHOD

Not Applicable.

10.0 SAFETY, HAZARDS AND WASTE DISPOSAL

Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents), or within a laboratory area.

11.0 REFERENCES

Current NELAC Standard
Client quality assurance guidance documents, as applicable.

DOCUMENT REVISION HISTORY

9/11/06: Updated format. Resolved tolerance conflict between text and Form. Added DOCUMENT REVISION HISTORY. Attached Form.

Paragon Analytics

PIPETTE CALIBRATION VERIFICATION LOG

Balance ID_____

Date	Analyst	Pipet ID Number	Nominal Volume (mL)	Observed Wt. (g)	Pipet Setting	Comment

PIPETTE TOLERANCE: ± 1.0 % (regardless of volume dispensed)

Reviewed by _____ Date: _____

Paragon Analytics

PIPETTE TOLERANCE GUIDE

Nominal Dispensed Volume (mL)	Associated Weight Tolerance (g)
0.025	0.0248 - 0.0252
0.050	0.0495 - 0.0505
0.075	0.0742 - 0.0758
0.100	0.0990 - 0.1010
0.200	0.1980 - 0.2020
0.250	0.2475 - 0.2525
0.300	0.2970 - 0.3030
0.400	0.3960 - 0.4040
0.500	0.4950 - 0.5050
0.600	0.5940 - 0.6060
0.700	0.6930 - 0.7070
0.750	0.7425 - 0.7575
0.800	0.7920 - 0.8080
0.900	0.8910 - 0.9090
1.000	0.9900 - 1.0100
1.250	1.2375 - 1.2625
1.500	1.4850 - 1.5150
1.750	1.7325 - 1.7675
2.000	1.9800 - 2.0200
2.250	2.2275 - 2.2725
2.500	2.4750 - 2.5250
2.750	2.7225 - 2.7775
3.000	2.9700 - 3.0300
3.250	3.2175 - 3.2825
3.500	3.4650 - 3.5350
3.750	3.7125 - 3.7875
4.000	3.9600 - 4.0400
4.250	4.2075 - 4.2925
4.500	4.4550 - 4.5450
4.750	4.7025 - 4.7975
5.000	4.9500 - 5.0500
6.000	5.9400 - 6.0600
6.500	6.4350 - 6.5650
8.000	7.9200 - 8.0800
10.000	9.9000 - 10.1000

Must Discard 30 Days from _____ (date printed)

Amended 3/26/09 by DAS to include Cooling Unit List Operator's Aid (facilitates weekend/holiday temperature monitoring/documentation).

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 326 REVISION 7

TITLE: **MONITORING AND RECORDING REFRIGERATOR AND FREEZER TEMPERATURES**

FORMS: **347 (customized per Department; use current revision)**

APPROVED BY:

TECHNICAL MANAGER Deb Echerd DATE 2/27/07

QUALITY ASSURANCE MANAGER Deb Echerd DATE 2/27/07

LABORATORY MANAGER Lance Steere for KDC DATE 2/27/07

HISTORY: Rev0, PCN #206, 1/12/94; Rev1, PCN #386, 2/20/95; Rev2, PCN #527, 9/6/95; Rev3, 11/4/99; Rev4, 4/17/02; Rev5, 10/3/03; Rev6, 7/20/05; Rev7, 7/24/06 and 2/27/07. re-released w/o revision 3/12/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes procedures for the operation and monitoring of laboratory cooling units (i.e., refrigerators and freezers) within specified limits. Procedures to follow in the event of unit malfunctions, or other impairment such as catastrophic loss of power, and requirements for placing new or repaired cooling units into service are also provided.

2. SUMMARY

Paragon uses refrigerators and freezers to store samples, extracts and standards (segregated in dedicated units) per analytical method requirements. The proper operation of each cooling unit is to be verified each day the unit is in use. Temperature is monitored using dedicated electronic min/max thermometers that are verified in-house annually (SOP 923). These thermometers provide for continuous cooling unit monitoring (7 days/week, 24 hrs/daily). The observed temperatures are recorded in laboratory logbooks (Form 347). The min/max memory of the thermometers is reset each time a reading is taken.

Laboratory refrigerated storage areas are maintained at just above freezing to 6°C (centered at 4±2°C). Laboratory freezer units are maintained at 0°C and lower (centered at -15±5°C). These limits address the sample and standard storage requirements specified in analytical methods. However, certain sample or container types may require different storage temperature ranges to be assigned to specifically designated cooling units.

3. RESPONSIBILITIES

3.1 Each laboratory is responsible for maintaining operation of the cooling units located in that laboratory area within acceptable limits. The Department Manager is responsible for designating and training personnel to monitor the operation and

record the temperatures of all cooling units in that particular laboratory area. The Department Manager or designee is also responsible for coordinating repair or replacement as needed with the QA Department, and for reviewing temperature record logbooks per SOP 303.

3.2 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review. Any anomalies or out-of-control events must be noted and corrective action taken and documented.

Laboratory staff are also responsible for ensuring that the thermometer(s) are functioning properly (as needed, replacement batteries can be obtained from the QA Department) and that the correct thermometer is indicated in the laboratory logbook. Laboratory staff shall make minor adjustments to unit settings as needed (must be recorded in logbook) and are responsible for reporting malfunctions of thermometers or units to the Department and Quality Assurance Managers.

3.3 The QA Department is responsible for managing thermometers, providing temperature record logbooks, and, in conjunction with Department Managers, assigning cooling unit temperature acceptance limits (contingent upon units's application and other client criteria, as applicable). Unit repair or replacement is coordinated between the Department and QA Managers. The QA Department is also responsible for maintaining records of all laboratory cooling unit identifications, the identities of the dedicated thermometer assigned to each unit, and repair records.

4. PROCEDURE

4.1 Cooling units and thermometers are uniquely identified (managed by the QA Department). Each business day and near to the beginning of the workshift, temperature readings are obtained from electronic thermometers that have been verified in-house annually against a certified Master. The electronic thermometer probes are immersed in containers of liquid to prevent fluctuations due to drafts when the unit's door is opened. The current, minimum and maximum readings are recorded in laboratory logbooks (Form 347). The min/max memory of the electronic thermometers are reset each time a temperature reading is taken.

4.2 The QA Department issues dedicated logbooks that indicate the unit's acceptance limits (typically just above freezing to 6°C -- centered at 4±2°C for refrigerators; and 0°C and lower -- centered at -15±5°C for freezers). The established limits are set to address the requirements of analytical methods, where applicable, and other client quality assurance guidance documents.

4.3 As needed, laboratory staff shall apply minor temperature setting adjustments to the cooling units and shall document these adjustments in the cooling unit's

temperature record logbook. As needed, laboratory staff shall replace the batteries of the electronic thermometer. Electronic thermometers that are rendered unusable are to be immediately removed from service. Notify the QA Department so that the unusable thermometer can be disposed and a suitable replacement thermometer provided.

4.4 The Department and QA Managers must be notified immediately if a significant excursion occurs so that appropriate corrective actions may be taken. An excursion is deemed significant if the current temperature reading is significantly outside the unit's acceptable range, or if two or more sequential readings exceed the acceptance limits. Appropriate corrective actions may include NCR initiation (SOP 928) and/or temporary transfer of the cooling unit's contents to another suitable location. Where applicable, potential impact to client data must be assessed.

4.5 If a cooling unit is taken out of service, it must be properly tagged-out (SOP 317). All corrective actions taken must be documented or referenced in the unit's temperature record logbook. Repair or replacement of the unit will be coordinated between the QA Department and the laboratory staff. Additionally, refer to the Paragon Emergency & Contingency Plan (ECP) for further information regarding actions to be taken in cases of extended power outages or other catastrophic failure.

4.6 Before a new or repaired cooling unit can be placed into service, evidence that the unit can maintain a stable and appropriate temperature must be documented. This is accomplished by recording acceptable temperatures for several readings over a span of time before the unit is placed into service (be sure to allow the thermometer's probe to come to a stable temperature before beginning the readings). Be aware that the unit may require additional temperature setting adjustment after samples, extracts or standards have been added.

5. SAFETY, HAZARDS AND WASTE DISPOSAL

5.1 SAFETY AND HAZARDS

5.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

5.1.2 Safety glasses, a lab coat, and gloves must be worn at all times when working in the laboratory

5.2 WASTE DISPOSAL

5.2.1 Unusable electronic thermometers may be disposed in the sanitary trash.

5.2.2 Inoperable cooling units must be disposed in accordance with local and

other regulatory requirements.

6. REFERENCES

Test Methods for Evaluating Solid Waste Physical/Chemical Methods SW-846, Third Edition, Final Update III, Chapter 1, Volume IA.

Paragon Emergency & Contingency Plan (ECP), current revision.

DOCUMENT REVISION HISTORY

7/24/06: Augmented RESPONSIBILITIES and WASTE DISPOSAL. Enhanced adjustment and failure directives. Added DOCUMENT REVISION HISTORY.

2/27/07: Re-published to put on a better publication cycle.

Paragon Analytics

Temperature Logbook - QA Department must be notified immediately if any temperature exceeds limits!

Acceptance Ranges: *0°C and lower (centered at -15±5°C) **Freezers*** just above freezing to 6°C (centered at 4±2°C) **Refrigerators**

Use the min/max button to toggle through display; record Current, Max and Min OUT temps.
Then hold min/max button for 3 seconds to reset memory.

Units are °C **Reviewed by/date:** _____

		RU #8A (refrigerator) Therm: #41503693			RU #8B (freezer) Therm: #41549925			RU #9 (freezer) Therm: #41549922			RU #10 (refrigerator) Therm: #22022003						
DATE	TIME	Current	Min.	Max.	Current	Min.	Max.	Current	Min.	Max.	Current	Min.	Max.	Current	Min.	Max.	INITIALS

Comments:

Form 347r4H.xls (6/9/05)

List of Cooling Units in Service

LOCATION	UNIT	COMMENTS
Sample Control (stand alone)	RU #25	
Sample Control (walk-in cooler)	RU #19	
Sample Control (walk-in cooler)	RU #20	
Wet Chem (freezer portion NIS!!)	RU #28	
TOC Room - (Freezer portion NIS!!)	RU #37	
Organic Extractions	RU #34	Not Applicable - Only being used for desiccator storage (not temperature storage)
Organic Extractions	RU #07	Not Applicable - Only being used for desiccator storage (not temperature storage)
Organic Extractions	RU #32	Not Applicable - Only being used for desiccator storage (not temperature storage)
Organic Extractions (Bottom of RU #23)	RU #16	
Organic Extractions (refrigerator portion NIS!!)	RU #01	
Organic Extractions (Top of RU #16)	RU #23	
Organic Extractions (walk-in cooler)	RU #03	
Organics Hallway - Refrigerator	RU #42	
Organic Standards Prep. (refrig. portion NIS!!)	RU #17	
Organics Standards Prep. - Refrigerator	RU #41	
Fuels/HPLC - (Bottom of RU #08B)	RU #08A	
Fuels/HPLC - (Bottom of RU #13)	RU #14	
Fuels/HPLC - (Bottom of RU #9) - Refrigerator	RU #10	
Fuels/HPLC - (Top of RU #08A)	RU #08B	
Fuels/HPLC - (Top of RU #10) - Refrigerator	RU #09	
GC/MS-SVOCs (Bottom RU #36)	RU #35	
GC/MS-SVOCs (Top of RU #35)	RU #36	
GC/MS-SVOCs Storage (Stand alone)	RU #33	
GC/MS-SVOCs Storage (Stand alone)	RU #04	
Metals (walk-in cooler)	RU #18	
GC/MS-VOAs - Refrigerator	RU #39	
GC/MS-VOAs - Refrigerator	RU #40	
GC/MS-VOAs (freezer portion NIS!!)	RU #26	
GC/MS-VOAs (stand alone)	RU #29	
GC/MS-VOAs (stand alone) - Freezer	RU #38	

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 329 REVISION 6

TITLE: **METHOD DEMONSTRATION PROCEDURES: INSTRUMENT DETECTION LIMIT (IDL) AND METHOD DETECTION LIMIT (MDL) STUDIES; DEMONSTRATION OF CAPABILITY (DOC)**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/31/07

QUALITY ASSURANCE MANAGER _____ DATE 8/31/07

LABORATORY MANAGER _____ DATE 8/31/07

HISTORY: NEW, PCN #520, 8/10/95; Rev1, 7/15/99; Rev2, 11/12/99; Rev3, 8/25/02; Rev4, 4/3/04; Rev5, 9/11/06; Rev6, 8/28/07.

1. SCOPE, APPLICATION AND SUMMARY

This standard operating procedure (SOP) specifies the requirements for performance and documentation of IDL and MDL studies, and demonstrations of capability (both method and analyst).

IDLs and MDLs are stable chemistry concepts. IDLs pertain to metals analysis methods, and establish instrument performance capabilities. MDLs apply to both inorganic and organic procedures (see 5.2.1 for exceptions), and establish the capabilities of the method (i.e., preparatory and analysis techniques).

Note that the sample-specific radiochemistry concept of minimum detectable concentration (MDC) is not addressed by this SOP (refer to SOP 708).

Also not addressed by this SOP are analyte Reporting Limits (RLs), which are values equal to or above the MDL, that the laboratory establishes for each analyte of a stable chemistry method, that *represent the lowest concentration of an analyte that can reliably (i.e., within specified limits of precision and accuracy) be achieved and reported, under routine operating conditions*. (RLs are also corrected for sample aliquot size, and moisture content, as applicable).

Refer to LQAP Chapter 14-Glossary, for definitions of terms used in this SOP. Refer to 40 CFR 136 Appendix B, for further information on conducting MDL studies.

2. RESPONSIBILITIES

2.1 Each Department Manager is responsible for ensuring that all studies and demonstrations are conducted and documented as needed. The Department Manager shall ensure that all staff are properly trained regarding concepts and procedures addressed by this SOP. All work performed under this SOP must be reviewed by the Department Manager, or his or her qualified designee. The

Department Manager is responsible for submitting all documentation to designated parties for management and retention.

2.2 Where creation of a workorder is necessary to accomplish the work (i.e., MDL studies, DOCs) and to report through LIMS, the workorder shall be created by Data Reporting Group staff, the Department Manager, or other designated individual.

2.3 Data Reporting Group staff are responsible for managing the IDL and MDL data in LIMS.

2.4 The Quality Assurance Manager (QAM) is responsible for retaining and managing DOC (and other training records) as described in the LQAP. The QAM shall provide oversight of the effectiveness and conformance to IDL, MDL and DOC processes.

2.5 Laboratory staff are responsible for performing the tasks described in this SOP as prescribed, and for completing all documentation required for review.

3. INTERFERENCES

Varies with type of analyses performed. Refer to applicable preparation and determinative SOPs.

4. APPARATUS, MATERIALS, REAGENTS

Varies with type of analyses performed. Refer to applicable preparation and determinative SOPs.

5. PROCEDURE

5.1 IDL STUDIES

5.1.1 IDL studies are to be performed for each analyte per instrument.

5.1.2 IDL studies must be completed quarterly as defined by the method, including whenever there is a significant change in instrument components or reagents.

5.1.3 The manner in which IDL studies are to be performed is described in US EPA CLP SOW ILMO4.0 (see References section of this SOP).

5.1.4 IDL studies must include the following information:

- Analyst who performed IDL study
- Instrument identifier
- Spike Level
- Measured concentration of seven replicates
- Standard Deviation
- Mean

- Determined IDL
- Concentration Units
- Date(s) the study was analyzed
- Analysis Method Number
- Raw data
- Supervisor or senior analyst review signature

5.1.5 Per CLP requirements, all IDLs must meet the Contract Required Detection Limit (CRDL), as specified in the US EPA CLP SOW (ILMO4.0).

Generally, the analyte IDL must be < the analyte MDL.

Other client-specified guidance may apply. Refer to applicable LIMS program specification.

5.2 MDL STUDIES

5.2.1 MDL studies are to be performed for each analyte per matrix, per preparatory and determinative method combination, and instrument (analytical column).

An MDL study must be performed for each PCB analyzed (i.e., Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260).

MDL studies are <u>not</u> performed for any parameter for which spiking solutions are not available or relevant (e.g., pH, ignitability).

5.2.2 MDL studies must be completed annually, or as otherwise defined by the method (i.e., ion chromatography and flow injection analyzer methods stipulate every six months). An MDL study must also be performed as a component of method validation, or whenever the basic chemistry of a procedure changes.

5.2.3 MDL studies shall be performed according to 40 CFR Part 136 Appendix B.

In summary, a minimum of seven, but typically eight, replicates are spiked with the same concentration of the analytes of interest, such that the spike concentration is between 1 and 10 times the calculated MDL. These replicates are processed using the same procedures used for field samples. The MDL is defined to be equal to the standard deviation (σ) of the values times the appropriate student t value (t, 99% confidence interval).

5.2.4 An MDL check sample shall be run with each MDL study (immediately following). The concentration of this check sample is

about half the concentration spiked for the MDL study, and approximately twice the calculated MDL. Performance criteria is that the MDL check is acceptable if it yields a confident positive detection (i.e., all analytes in the check sample can be identified by method-specified criteria).

If MDL check sample results do not support the determined MDL, appropriate corrective actions must be taken (e.g., repeat MDL check sample analysis, repeat MDL study, raise MDL).

5.2.5 All MDL studies must include the following information:

- Analyst(s) who performed extraction and analysis
- Instrument and column identifier
- Spike Level
- Recovery of replicates
- Standard Deviation
- Mean
- Student t factor (99% confidence interval)
- Calculated MDL value
- Reporting limit currently in use, (typically lowest)
- Units
- Dates(s) of analysis
- Date(s) of digestion or extraction (if applicable)
- Raw Data (including copy of digestion or extraction log)
- Method Number (for digestion, extraction, and analysis)
- MDL check standard verification (~2-5x calculated MDL value)
- Reviewer's signature and date

5.2.6 All MDL studies must be submitted to the Data Reporting Group for LIMS processing. After the data are incorporated into the LIMS MDL application and the application is run, summary reports are provided to the Department Manager for review.

5.2.7 The Department Manager shall review the study information:

- compare spike value to calculated MDL
- if calculated MDL is > spike concentration, repeat study at a higher spike concentration.
- If spike concentration is > 10x times calculated MDL, repeat study at a lower spike concentration

After review and sign-off, the Department Manager forwards the MDL information to the QA Department for review and approval.

5.2.8 Paragon's MDL application allows for the Dixon Outlier test to be applied. If any datapoints are excluded as outliers, all datapoints for that analytical run must be excluded (specific analytes within an analytical run cannot be selected for exclusion ***except*** in the case where one or two datapoints represent a separate injection that was made).

5.2.9 The MDL should be 2 to10 times lower than the RL. In the case of methods that include many target compounds (e.g., SW8260 and SW8270), Paragon will accept sporadic marginal failures for this relationship.

It should be noted that MDL studies are performed on interference-free matrix. Hence, the calculated MDL may not be achievable in environmental matrices, and adjustment of the MDL (and/or RL), based on practical performance experience, may be required. Additionally, client-specified criteria may apply (consult applicable LIMS program specifications). The QAM in conjunction with the Department Manager, will establish MDL and RL values based on these considerations.

5.2.10 Once the MDL study receives final approval from the QAM, the information is submitted to the Data Reporting Group for scanning and retention.

5.3 DEMONSTRATIONS OF CAPABILITY

5.3.1 Method DOCs are to be performed for each analyte per matrix, per preparatory and determinative method combination, and instrument (analytical column). Method DOCs must be performed each time a method is modified. Unless otherwise defined by the method, the successful analysis of a PT sample can serve as a method DOC.

5.3.2 Chemist DOCs are to be performed for each analyte per matrix and preparatory and determinative method combination. A chemist must demonstrate a successful initial demonstration of capability (IDOC) ***before*** that chemist is permitted to prepare or analyze client samples.

The IDOC is generally accomplished by the chemist preparing and/or analyzing four replicates of laboratory media (i.e., DI water or Ottawa sand), spiked with the same concentrations of analytes of interest. An average and standard deviation is calculated for the results for each analyte. If the results meet established control criteria, then the DOC is accepted, and the chemist is permitted to process client samples.

Each chemist must also perform a successful continuing DOC (CDOC) annually. This requirement can be fulfilled by compiling results from

four acceptable LCS analyses, or by the successful participation in IDL, MDL or PT studies.

DOC summary and raw data are submitted to the QA Department for review/approval, and retention as a training record.

5.3.3 All DOC studies must include the following information:

- Analyst who performed the DOC
- Instrument identifier
- Spike level
- Concentration of four replicates (as applicable)
- Acceptable recovery (per established acceptance criteria)
- Average and standard deviation of recoveries
- Units
- Date(s) of analysis
- Date(s) of extraction (if applicable)
- Extraction Technician's Name (as applicable)
- Analysis and Extraction Method Number

6. QUALITY CONTROL

See 40 CFR 136 Appendix B for further details pertaining to how MDL studies are conducted and evaluated. See also applicable determinative methods.

7. DEVIATIONS FROM METHOD

None.

8. SAFETY, HAZARDS AND WASTE DISPOSAL

Refer to applicable preparatory and determinative SOPs.

9. REFERENCES

9.1 "Definition and Procedure for the Determination of the Method Detection Limit", Revision 1.11, 40 CFR, Part 136, Appendix B, page 505-507.

9.2 EPA 600 Series Methods, Section 8 of each method, 40 CFR Part 136, Appendix A.

9.3 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Method 8000B, Revision 2, December 1996, Section 8.

9.4 USEPA CLP SOW for Inorganics Analysis, ILMO4.0.

DOCUMENT REVISION HISTORY

9/11/06: Rearranged sequence and reformatted. Updated RESPONSIBILITIES. Introduced preparatory and determinative method combination concept. Included directives for outliers. Included statements regarding method DOCs, augmented discussions of IDOCs and CDOCs. Augmented QC limit discussion. Incorporated Data Reporting

Group involvement and imaging for record retention. Added MDL check sample analysis and performance criteria. Added DOCUMENT REVISION HISTORY.

8/28/07: Removed QC limit discussion (just doesn't belong here, addressed in LQAP); edited RESPONSIBILITIES accordingly. Moved some technical information from RESPONSIBILITIES to PROCEDURE. Added 'whenever there is a significant change in instrument components or reagents' to the requirements of when an IDL study needs to be performed (5.1.2). Expanded IDL criteria (5.1.5). Some general re-structuring/re-formatting. Refined role of Data Reporting Group (rather than IS Department) throughout. Augmented discussion of when an MDL study is to be performed (5.2.2). Expanded/revamped MDL check standard discussion (5.2.4). Added discussion re: adjustments to MDLs or RLs (5.2.9). Restructured DOC section.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 334 REVISION 7

TITLE: **LABORATORY GLASSWARE CLEANING AND MAINTENANCE PROCEDURES**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3.6.08

QUALITY ASSURANCE MANAGER _____ DATE 3/6/08

LABORATORY MANAGER _____ DATE 3-6-08

HISTORY: **As SOP 334:** Rev0, 1/29/98; Rev1, 7/15/99; Rev2, 2/17/00; Rev3, 11/13/01; Rev4, 4/07/03; Rev5, 2/13/04 and 3/10/05; Rev6, 2/27/07; **As SOP 720:** Rev0, 2/10/93; Rev1, PCN #146, 3/2/94; Rev2, 6/13/97; Rev3, 3/24/00; Rev4, 4/26/02; Rev5, 3/28/03; Rev6, 4/22/04 & 2/9/05 & 9/11/06 & 2/27/07 (no revisions). **Combined**, Rev7, 3/4/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps to be followed for cleaning glassware used in the various laboratory Departments. General measures used to identify levels of radioactivity for the segregation of glassware used by the Radiochemistry Department, are also outlined.

2. SUMMARY

Interferents/contaminants cause difficulty in the interpretation of analytical results. To prevent cross-contamination, suitable disposable glassware and plasticware is used for laboratory processes wherever technically practical and economically feasible. If glassware, particularly specialty glassware, must be reused, then stringent cleaning protocols are followed in order to minimize the potential for cross-contamination. Additionally, for radiochemical applications, glassware is segregated according to levels of radioactivity processed.

Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, or any other glassware that comes in contact with an extract or digestate that will be evaporated to a smaller volume. The process of concentrating the extract or digestate may cause contaminants to be concentrated as well, thus potentially distorting analytical results.

Radiochemical glassware is dedicated to the analysis of either low-level, routine or elevated levels of radioactivity. Glassware is disposed of, or re-assigned for use with higher level radioactive samples, when necessary.

3. RESPONSIBILITIES

It is the responsibility of the technician to perform these procedures according to this

SOP. Consult your Supervisor should any questions or problems arise.

4. INTERFERENCES

4.1 Glassware used for the analysis of elevated levels of radioactivity is not to be re-used for routine level determinations. Such glassware is either to be disposed of, or permanently marked to allow immediate identification as high-level glassware.

4.2 Glassware labeled as "LL" is dedicated exclusively for use in the determination of ultra-low levels of radioactivity (i.e., levels of less than one-half routinely detectable levels), or for ambient or environmental level monitoring where the absence of analyte at routine levels is expected. This glassware may be re-assigned for routine or elevated levels as long as the "LL" label is permanently removed and the glassware is re-labeled for use at the appropriate level.

4.3 Only clean, rinsed glassware shall be hung on the pegboards. Inversion of clean glassware prevents re-contamination of glassware prior to use.

5. APPARATUS AND MATERIALS

5.1 Assorted brushes

5.2 Dishwasher

5.3 Drying Racks or fresh bench paper

5.4 Drying oven

5.5 Kiln

5.6 Aluminum foil, heavy-duty, clean

6. REAGENTS

Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

6.1 Tap water

6.2 Detergent: Alconox™ or Alcojet™ commercial detergent or equivalent; a suitable domestic (i.e., grocery store) detergent may also be used. Particularly for stable chemistry applications, use of phosphate-free detergents is desirable.

6.3 Deionized (DI) water, obtainable from the laboratory's deionized water system.

6.4 2N HCl / 2N HNO_3 Solution (used to rinse Metals Department glassware): Make by adding 3.3L concentrated HCl and 2.5L HNO_3 (***use Trace Metals grade HNO_3 only***) to 14L DI water. Store in a stoppered container. *Shelf Life = Until degradation is evident* TLV HCL = 5ppm; TLV HNO_3 = 2ppm (TWA); irritant, corrosive.

6.5 Aqua Regia (used in the Radiochemistry Department): Make fresh for each use. Only make as much as needed, or, preferably, mix directly in the vessel to be

cleaned or to be used for cleaning. **CAUTION: Never keep aqua regia in a tightly closed container.** Carefully mix 12N HCl and 16N HNO_3 in an approximate ratio of 3:1. *The mixture is highly reactive and will evolve gas,* ***mix and use in a fume hood****.* TLV HCL = 5ppm; TLV HNO_3 = 2ppm (TWA); irritant, corrosive.

6.6 RadiacWash™ or equivalent

6.7 **Solvents** (stable chemistry applications) - **Only pesticide residue grade or chromatography grade solvents shall be used**:

6.6.1 Acetone

6.6.2 Methylene Chloride

6.6.3 Methanol, purge & trap grade (volatiles) or pesticide residue grade (organic extractions)

6.6.4 Isopropanol, chromatography grade

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Not applicable.

8. STABLE CHEMISTRY PROCEDURES

8.1 The following Sections detail procedures to be used in cleaning the types of glassware specified. In general, however, the basic stable chemistry (Organics and Inorganics Departments) cleaning steps include:

- Remove surface residue immediately after use.
- Soak in hot water to loosen and float most particulate material. Soap may be used to facilitate the removal of oily residues.
- Rinse with tap water to remove soap residue.
- Soak or rinse with acid (metals only).
- Thoroughly rinse with DI water.
- Rinse with alcohol, i.e., isopropanol or methanol, (organic analyses only), to flush any traces of organic materials and to remove the water. **This step is used only if the glassware will *not* be dried in a kiln.**

  NOTE: Although rinsing with alcohol is a means of removing trace levels of organic materials, SW-846 3rd Edition, Chapter, 4 Section 4.1.4 does allow the use of a high temperature bake-out (>300°C) as an alternative.

- Air dry or dry in an oven or kiln.

Even after glassware has been rigorously cleaned and stored, it is good laboratory practice to rinse the glassware with small aliquots of the extraction/digestion solvent that will be used in the analysis, just before the glassware is used.

8.2 VOLATILE ORGANICS ANALYSIS (VOAS) GLASSWARE

8.2.1 Rinse with tap water.

8.2.2 Scrub all surfaces with a brush in warm soapy water.

8.2.3 Rinse with hot tap water.

8.2.4 Place glassware in a drying oven (110-150 ºC), and dry overnight. Store glassware in drying oven until use.

8.2.5 SYRINGES: After use, flush by drawing and expelling several volumes of clean methanol.

8.3 SEMIVOLATILE ORGANICS (SVOCs) VOLUMETRIC GLASSWARE

NOTE: Never place volumetric glassware in the kiln!

8.3.1 Use solvent (medium polarity) to remove any external labels or writing on the outside of the glass.

8.3.2 Rinse glassware with tap water.

8.3.3 Scrub all glassware surfaces with a brush in warm soapy water.

8.3.4 Rinse with hot tap water.

8.3.5 Rinse 4 times with DI water.

8.3.6 Rinse with alcohol.

8.3.7 Wrap opening of glassware with clean aluminum foil.

8.3.8 Dry in 110-150 °C oven for 1/2 hour (minimum).

8.3.9 After cooling, store glassware promptly to avoid contamination.

8.4 SEMIVOLATILE ORGANICS NON-VOLUMETRIC GLASSWARE

8.4.1 Follow Steps 8.3.1.through 8.3.5 above.

Concentrating Tubes: **Never place more than one layer in the sink at one time.** Always use a brush when washing; check the brush to ensure that no metal is exposed that can scratch the glassware, thereby allowing sites where contamination can collect. Check the ends of the concentration tubes for residue.

8.4.2 DO NOT rinse glassware with solvent before placing in kiln.

8.4.3 Wrap glassware with clean aluminum foil:

- Rip squares of foil in advance.
- Cover all open ends of glassware.
- Cover all ground glassware joints (rough to the touch).
- Cover funnels, stirring rods, Snyder columns, GPC tubes, and thimbles completely.
- Glass Stoppers. wrap as many as possible (same size) in one piece of foil.
- Set Soxhlets aside. These are the first items to be placed in the kiln (upright).

8.4.4 Dry glassware in a kiln set at approximately 450 °C for a minimum of three hours.

8.4.5 After cooling, store glassware promptly to avoid contamination.

8.5 METALS GLASSWARE

8.5.1 Follow Steps 8.4.1.through 8.4.4 above.

8.5.2 Rinse glassware with 2N HCl / 2N HNO_3 acid solution, allowing the acid to drain into the sink. Alternatively, immerse and store glassware in a covered acid bath.

8.5.3 Rinse with DI water.

8.5.4 Invert glassware and air dry.

8.5.5 Return glassware to storage cabinet; glassware is ready to use.

8.6 WETCHEM GLASSWARE

8.6.1 Use a solvent to remove any external labels or writing on the outside of the glass.

NOTE: If oily residue is present inside the glassware, rinse with methylene chloride, then wipe with a KimWipe®; repeat until glassware is free from oily residue.

8.6.2 Rinse 4 times with DI water.

8.6.3 Invert glassware and air dry.

8.6.4 Return glassware to storage cabinet; glassware is ready to use.

9. RADIOCHEMISTRY PROCEDURES

9.1 SEGREGATION OF REUSABLE GLASSWARE

Reusable glassware is segregated according to working levels (broadly defined below). Method blank experience may be used to indicate the need for more or less restrictive levels than these listed here:

- ROUTINE GLASSWARE
  Glassware designated for routine use need not be specifically marked. Routine levels are defined as expected levels approximately one-half to five hundred times routinely detected levels for target analytes. This glassware is generally available for use in the laboratory and need not be physically segregated.

- ELEVATED ACTIVITY GLASSWARE
  Glassware designated for use with elevated samples is permanently marked "H". This glassware is physically segregated from other glassware for purposes of storage, processing and cleaning. Elevated levels are defined as expected levels greater than approximately five hundred times routinely detected levels for target analytes. Glassware used for elevated activities may be preferentially disposed of if levels exceed 10,000 times routinely analyzed levels.

- ULTRA-LOW LEVEL GLASSWARE
  Glassware designated for use with ultra-low level samples is marked "LL". This glassware is physically segregated from other glassware for purposes of storage, processing and cleaning. Ultra-low levels are defined as requested detectable and/or expected levels less than approximately one-half routine minimum detectable levels for target analytes, or samples for environmental, drinking water or ambient monitoring work where no or extremely low analyte or minimum detectable levels are expected. Glassware used for Ultra-low level activities may be re-designated for routine or elevated levels if potential for contamination at those levels is suspected.

9.2 RADIOCHEMISTRY CLEANING PROCEDURE FOR SMALL GLASSWARE

9.2.1 For very small glassware, see Step 9.2.4, otherwise, rinse the glassware with copious amounts of hot tap water at the sink. Transfer the dishes into the sinks, fill the sink with hot water. Add ~25mL of RadiacWash™ per manufacturer's instructions. Soak glassware for at least 2 hours.

9.2.2 Rinse the glassware with hot tap water.

9.2.3 Load the glassware into the dishwasher so that the items will not break during washing. Wash the glassware with detergent (6.2).

NOTE: To save energy, use the short cycle on the automatic dishwasher. Do not use the drying cycle, as glassware must be DI rinsed before drying.

9.2.4 **Acid washing** is done only when the prep. method to be used requires it; otherwise, skip to Step 9.2.5.

9.2.4.1 Place the very small glassware in a 4L glass beaker (or in a larger container that needs to be acid washed). In a fume hood, add aqua regia to produce significant fumes. Cover with a watch glass. Allow the very small glassware to sit for a minimum of 4 hours or preferably overnight.

9.2.4.2 In the fume hood, carefully decant the aqua regia into a waste beaker containing a small amount of water. Rinse the small glassware collectively with DI water, decant the rinse water into the waste beaker. Discard the waste beaker's contents down the laboratory drain (which discharges into Paragon's wastewater system), with large amounts of cold water.

9.2.5 Continue by rinsing each piece of cleaned glassware with liberal quantities of DI water at the sink.

9.2.6 Allow the glassware to dry on clean bench paper or on a clean drying rack.

9.3 RADIOCHEMISTRY DISHWASHING PREPARATION FOR LARGE GLASSWARE

9.3.1 Rinse the glassware with copious amount of hot water at the sink.

9.3.2 Fill glassware with hot water and ~5-10mL RadiacWash™. Soak for a minimum of 2 hours.

9.3.3 Rinse the glassware with hot tap water.

9.3.4 Load the glassware in the dishwasher so that the items will not break during washing. Wash with detergent (6.2).

NOTE: To save energy, use the short cycle on the automatic dishwasher. Do not use the drying cycle, as glassware must be DI rinsed before drying.

9.3.5 **Acid washing** is done only when the prep. method to be used requires it; otherwise, skip to Step 9.3.6. If acid washing cannot be done immediately, rinse the washed glassware with DI water and hang on the drying rack until acid washing can be done.

9.3.5.1 Place the glassware inside a fume hood. Add 10-30mL aqua

regia to each vessel. Cover and leave for 4 hours or preferably overnight so that the aqua regia fumes will clean the sides of the vessel.

9.3.5.2 In the fume hood, carefully decant the aqua regia into a waste beaker containing a small amount of water. Rinse the glassware with DI water and decant the rinse into the waste beaker.

9.3.5.3 Discard the waste beaker's contents down the laboratory drain (which discharges into Paragon's wastewater system), with large amounts of cold water.

9.3.6 Remove glassware from the hood and rinse with liberal quantities of DI water at the sink.

9.3.7 Allow the glassware to dry on clean bench paper or a clean drying rack.

10. QUALITY CONTROL

Not applicable

11. DEVIATIONS FROM METHOD

This method was developed in-house; there are no deviations from a promulgated method.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before using any reagents.

12.1.2 Gloves, safety glasses and lab coats must be worn when working with any chemicals (e.g., standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

12.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

12.1.4 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: the compound name, NFPA Health, Flammability and Reactivity ratings, and date.

12.1.5 Use extreme care when working with aqua regia. Work only in a fume hood that has adequate ventilation and personnel safety features. Never inhale or allow skin or clothing to be exposed to aqua regia fumes.

12.1.6 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

12.1.7 Wearing Kevlar® gloves is recommended when handling glassware prone to breakage. This material minimizes the risks of lacerations in the event of glassware breakage.

12.1.8 Wearing insulated gloves is required when removing glassware from the kiln.

12.2 WASTE DISPOSAL

12.2.1 Wastes that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity), such as hydrochloric and nitric acid waste, are disposed of by discharging into the Paragon wastewater treatment facility.

12.2.2 All empty solvent bottles are to be disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

13. REFERENCES

13.1 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 4, December 1996.

DOCUMENT REVISION HISTORY

2/27/07: (SOP 334) Tie-in with SOP 720 Radiochemistry glassware cleaning, added to SCOPE AND APPLICATION. Under PROCEDURES (5.6), WetChem glassware is not acid-rinsed; corrected in text and in Operator's Aide. Excerpted Operator's Aide Section created, postings replaced. Added DOCUMENT REVISION HISTORY Section.

3/4/08: Combined current iterations of SOP 334r6 and 720r6. Revamped acid washing for Radiochemistry sections.

GLASSWARE CLEANING – STABLE CHEMISTRY

Basic cleaning steps:
(Surface residue should be removed immediately after use)

- Use solvent to remove labels and markings
- Rinse with tap water
- Soak in hot water
- Use soap to remove oily residues (scrub only glassware that is not excepted)
- Rinse thoroughly with tap water
- Soak or rinse with acid (metals glassware only)
- Thoroughly rinse with DI water
- Rinse with alcohol, isopropanol or methanol, (only non-kilned organics glassware)
- Dry by appropriate means (air, oven, kiln -- note restrictions)

VOAs glassware:

Perform first five steps above, use a hot tap water rinse. Oven-dry.

SVOCs glassware (volumetric, **un-kilned**):

Perform first five steps above, use a hot tap water rinse.
Rinse 4 times with DI water, then alcohol.
Wrap opening of glassware with clean aluminum foil, oven-dry.

SVOCs glassware (**kilned**):

Observe special handling for concentrating tubes.
Perform first five steps above, use a hot tap water rinse.
Rinse 4 times with DI water
Wrap appropriately with aluminum foil, kiln.

Metals glassware:

Perform first five steps above, use a hot tap water rinse.
Rinse or bathe using 2N HCl / 2N HNO_3 acid solution.
Rinse thoroughly with DI water.
Invert glassware and air-dry.

WetChem glassware:

Use solvent to remove labels and markings.
(methylene chloride may be used to remove oily residues)
Rinse 4 times with DI water.
Invert glassware and air-dry.

GLASSWARE CLEANING – RADIOCHEMISTRY

Keep glassware segregated! Dispose of or re-label for use as necessary.

Follow acid washing procedure for small glassware.

Basic cleaning steps:

- Use solvent to remove labels and markings
- Rinse with hot tap water
- Soak in hot tap water, to which RadiacWash^{TM} is added
- Rinse with hot tap water
- Wash in dishwasher (short cycle, do not use drying cycle)
- Rinse thoroughly with tap water
- Acid wash as necessary
- Thoroughly rinse with DI water
- Air dry

Must Discard 30 Days from _____ (date printed)

Amended 12/30/07 - Section 5.2 'Allow sample to warm to room temperature before subsampling.' removed. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 336 REVISION 0

TITLE: **REPRESENTATIVE LABORATORY SUBSAMPLING**

FORMS: **302, 631** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 12-28-07

QUALITY ASSURANCE MANAGER _____ DATE 12/28/07

LABORATORY MANAGER _____ DATE 12-28-07

HISTORY: **Formerly SOP 721:** Rev1, 4/26/93; Rev2, PCN #35, 11/17/93; Rev3, PCN #80, 1/12/94; Rev4, PCN #276, 9/29/94; Rev5, PCN #471, 5/3/95; Rev6, 10/7/99; Rev7, 11/1/00; Rev8, 6/15/01; Rev9, 8/20/01; Rev10, 3/19/03; Rev11, 4/22/04; Rev12, 11/29/04; Rev13, 9/8/06; Rev14, 8/24/07. **As SOP 336**: Rev0, 12/27/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the physical procedures used to prepare environmental samples prior to chemical preparation and analysis. These physical preparations are crucial to ensuring that subsamples (aliquots), and their subsequent test results, are representative of the client sample as a whole.

2. SUMMARY

Subsamples must be representative to avoid bias in the analytical result. Incorrect analytical results could lead to making wrong environmental decisions that could impact environmental preservation or human health. Correct subsampling allows for the results to be duplicated (i.e., minimizes variability and the associated uncertainty of the resultant test value). Incorrect subsampling can be a significant source of error in the whole measurement process.

The specific subsampling techniques to employ vary with matrix and constituents of interest. This document is not intended to be stand-alone guidance; the procedures described herein must be used in close conjunction with established preparation SOPs.

Section 4 of this SOP addresses general representative laboratory subsampling concepts, and is applicable labwide. Stable chemistry, organic and inorganic, representative subsampling considerations are highlighted in Section 5. SOP Section 6 addresses additional representative subsampling concepts that are particularly applicable to radiochemical procedures.

3. RESPONSIBILITIES

3.1 Departmental Supervisory staff or designees are responsible for providing adequate training and oversight of proper subsampling technique.

3.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review, including completion of Sample Condition Form 631, as dictated by Departmental policy. Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification (text directives) and associated project analyte nicknames (electronic controls) are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. Criteria defined in the applicable program specification supercede Paragon's standard criteria. All personnel are responsible for consulting the applicable LIMS program specification prior to initiating handling of project samples or data.

3.4 Internal chain-of-custody procedures (SOP 318) must be observed.

3.5 It is the responsibility of all personnel who process/analyze samples or data, to note and document all anomalous conditions (generally recorded on a Quality Assurance Summary Sheet, QASS, Form 302), and any occurrences that may impact data quality (a Non-Conformance Report, NCR, must be initiated in LIMS). Supervisory, QA and Project Management staff must be notified in a timely manner, as applicable, so that proper corrective actions may be directed and taken.

4. GENERAL CONCEPTS

4.1 Good subsampling technique is especially critical where only small portions of sample are aliquotted for testing.

4.2 Always work using clean surfaces.

4.3 Work as quickly as possible to minimize potential degradation or loss of constituents.

4.4 Unlike evenly dispersed liquids, soil and sediment samples are not homogeneous. Therefore, special steps must be taken to obtain aliquots that are 'representative' of the source material. For example, sticks, leaves, rocks, etc. that are not characteristic of the overall sample must be excluded from the subsample. **Do not take one "grab" sample**, instead, select several small, 'random' increments. Then, thoroughly mix these increments to achieve homogeneity. A disposable tongue depressor can generally be used to acquire/mix solid matrix subsamples.

4.5 Discard excess quantity taken from the original sample container, do not return unused homogenized subsample to original sample container.

4.6 After acquiring sufficient mass (use laboratory balance with calibration verified per SOP 305), record aliquot weight on appropriate datasheet.

4.7 Do not adjust for moisture unless directed by SOP or project requirements.

5. STABLE CHEMISTRY PROCEDURES

5.1 Apply general concepts discussed above.

~~5.2 Allow samples to come to room temperature before subsampling.~~ 12/30/07 DAS

5.3 **Organics**: Unless otherwise directed by LIMS program specification, decant and discard any water layer on top of a sediment sample when preparing for Soxhlet extraction.

For volatile (VOAs, BTEX, etc.) analyses, and for inorganics, gently mix/blend contents of sample container, obtain portions for subsample while in the process of mixing/blending. **Note that the subsample obtained for % Moisture analysis (SOP 642) must be acquired in the same manner as the subsample for constituent analysis.**

For volatile (VOAs, BTEX, etc.) samples that are tightly packed, carefully scrape off a thin top layer of sample before proceeding with subsampling (due to the nature of volatile compounds, this top layer may not be representative of sample constituents due to potential analyte loss).

5.4 **Inorganics**: Use only non-metal scooping devices.

Subsample particles that are larger than the others can be gently mashed.

6. RADIOCHEMICAL SUBSAMPLING PROCEDURES

6.1 GENERAL CONSIDERATIONS

6.1.1 This SOP serves as the starting point for nearly all radiochemical analyses, and is referenced by the SOPs relating to the analysis of individual nuclides or other radiochemical tests. After this pretreatment has been performed, the remainder of the analysis is performed according to the individual preparation SOPs

6.1.2 For radiochemical preparations, any abnormal conditions encountered during storage/receipt and preparation of the samples must be documented on a Quality Assurance Summary Sheet (QASS). A copy of the QASS must accompany the benchsheet. A copy of the sample preparation logbook is also attached to the benchsheet for all analyses that use the dried, and milled sample fraction.

6.1.3 Water samples having visible sediment will generally be filtered through a qualitative paper filter prior to chemical separation.

6.1.4 If a particular analysis requires no preparations, then a subsample is taken before any other preparations are started. The general sequence of soil preparations starts with removing an appropriate representative aliquot followed in turn by drying, sieving and milling. The preparation steps used on a soil depend on the analyses requested for that sample. The requirements for each analysis are described in the individual SOPs. When more than one analysis is requested for a sample, it is possible that a sub sample will be aliquoted at various points in the preparations.

6.1.5 Soil samples are routinely milled in a half-pint ball mill. By specific request, the samples may, instead, be milled with a Spex #8500 shatter box miller. Solid samples that have been milled in the half-pint ball mill are stored in the same clean, labeled containers. The containers are not reusable. A logbook is maintained to document the sample information such as sample ID, date, balance number, oven number, milled sample weight, batch ID (page#) for preparation.

6.1.6 It is important that soil samples for tritium analysis be handled at a minimum so as to preserve their original moisture content. If a separate container is not provided for tritium analysis, coordinate with the tritium analyst and arrange to complete tritium analysis before preparing the sample for other analyses.

6.1.7 Paragon typically reports solid sample results on a dry weight basis. The basis on which water sample results are reported depends on whether the samples require filtration. For moisture content determinations, refer to SOP 642. If the sample volume is very limited, the sample aliquot used for moisture content analysis may subsequently be used for milling.

6.1.8 Before beginning any actual preparations, the LIMS program specs must be reviewed to determine whether project instructions indicate non-routine analytical requirements or special handling due to Health and Safety concerns or sample activity levels (e.g., retaining the "+" fraction of a solid matrix, removing organic and metallic debris). This may influence the quantity of sample needing to be processed through each stage of the preparation sequences. The sample preparation logbook is filled out with the work order numbers.

For each soil sample, determine the total weight of material required to be prepared at each of the stages, (i.e., no-prep, #4 sieve, mill, etc.). Refer to Table 1 for a summary of the amount of material and type of preparation required for various analyses. If unsure of the type or

quantity of required soil preparation, consult the Department Manager or the Project Manager.

6.2 APPARATUS AND MATERIALS

6.2.1 drying oven, set at 105+5°C

6.2.2 sieves, #4 (4.75mm) and others, as specified by the client, and associated collection pan

6.2.3 mortar and pestle (M/P), 150mL, 1L, 4L sizes

6.2.4 Red Devil 5400 shaker or Spex #8500 shatter box miller, or equivalents

6.2.5 Scotch BriteTM scrubbing sponge, or equivalent

6.2.6 SOS™, Brillo™ or equivalent steel wool cleaning pads

6.2.7 gamma spec containers (16oz LERMER JARS) and Ra containers (#2 steel cans)

6.2.8 half-pint steel paint cans

6.2.9 tongue depressors, spatulas or scupulas

6.2.10 Snap-cap vials, 60mL, plastic

6.2.11 balance, top loading, readable to 0.1g

6.2.12 weighing dishes and pans, aluminum

6.2.13 steel ball bearings, 1/2”

6.2.14 rubber mallet

6.2.15 qualitative fluted filter paper, VWR #313 or equivalent

6.2.16 Quartz sand, reagent grade

6.3 DOCUMENT CLIENT SAMPLE ID, LABEL CONTAINERS

6.3.1 Sign-out the samples (scan barcodes to record transaction in LIMS) from Sample Storage. Return samples promptly to Sample Storage once aliquots have been obtained (sign samples back in by scanning barcodes to record transaction in LIMS).

6.3.2 Label the necessary drying pans and dishes with the Paragon work order number.

6.3.3 Assemble and label the required number of secondary containers for each sample (refer to Table 1). More than one container may be needed for each type of preparation if the amount required for the total number of analyses will exceed the capacity of the listed container. Label the containers with the Paragon sample number, type of preparation, date and your initials. If more than one container is

needed for a given type of preparation, also serialize the containers (e.g., 1 of 3, 2 of 3, etc.).

6.3.4 The secondary container may be a LERMER JAR if the only analysis requested on a soil sample is gamma spectrometry.

6.4 NO-PREP SOIL SAMPLEs

6.4.1 Soil sample analyses such as tritium, C-14, and I-129 are performed on an "As Received" basis due to the potential volatility of the analyte. These samples should not be dried or milled prior to analysis, and can be taken directly from the original container with minimum handling. Percent moisture results are used to subsequently convert from 'wet weight' to final reporting dry weight results.

6.4.2 Using a minimal amount of handling, stir and blend the sample with a new tongue depressor before taking an aliquot. Document non-homogeneous, non-stirrable or problematic samples on a Quality Assurance Summary Sheet (QASS, Form 302).

6.5 DRYING

6.5.1 Use labeled aluminum pans and weighing dishes to dry the samples. Add up the total weights required for all preps needing sieving or milling. Weigh out roughly double this amount of sample into the drying trays.

6.5.2 The amount needed for drying will depend on the moisture content of the sample. Extra sample must be dried to account for the weight loss expected. Drier soils may require less and wet soils may require more than double the needed dry weight mass. If the percent moisture has already been determined in prescreening, use this value to estimate the amount required for drying. Consult the Department Manager for directions especially for wet soils and sludges, or if unsure of how to estimate the required amount.

6.5.3 If the sample amount required for gamma fraction (#4 sieving) will use up most or the entire sample, notify the Department Manager. The γ analysis may have to be completed before releasing the sample for the remainder of the soil preparations.

6.5.4 If the weight needed for drying exceeds the total received amount of sample, dry the entire sample immediately. Inform the Project Manager of the insufficient sample size.

6.5.5 Dry the samples in a drying oven set at 105$\pm$5°C. Samples should be dried for a minimum of 16 hours or to a constant weight (+/-2%). Wet

samples may require drying overnight until a constant weight (+/-2%) is obtained.

6.5.6 Examine each container as it is removed from the oven. Return to the oven any that still contain moisture until sample is thoroughly dry. This can be determined by weighing the sample every hour until constant weight (+/-2%) is achieved (overnight is generally more convenient).

6.6 NUMBER 4 SIEVING

NOTE: If the client requires the inclusion of rocks and large material with the final sample aliquot, consult the Department Manager for further instruction.

6.6.1 If the sample will pass a #4 sieve without further processing, proceed to Step 6.6.3.

6.6.2 If the sample requires size reduction before it can pass the #4 sieves, use a mortar and pestle to break up the sample.

6.6.3 Sieve the material, using a #4 sieve, into a clean sieve collection pan. Return the unsievable material to an appropriately labeled soil waste container, if the sample remaining is in excess of what is needed for all analyses. (If the unsievable material must be retained, place it in a new appropriately sized container labeled with the sample identification and the words “dry, unsievable material”.)

6.6.4 Remove the amount of #4 sieved material required to the labeled, tared, secondary container(s) from Section 6.3. If only γ analysis was requested, or if the γ analysis must be completed first due to limited sample size, the sieved material may be weighed into a 16oz LERMER JAR. Document the net weight on the secondary container as well as the sample preparation logbook.

6.6.5 The remaining sample continues through additional preparation in the following Steps. If no further preparation is required, the unused portion may be disposed of in an appropriately labeled soil waste container.

6.6.6 Thoroughly wash and dry the sieve after each use to avoid potential cross-contamination of the samples. First remove any gross sample remaining on the sieve, then wash in Radiacwash™ solution. A nylon brush may be used if necessary. Rinse the sieve with DI water and air dry completely before use.

6.7 MILLING

Milling is accomplished through the use of the Red Devil 5400 paint can shaker (or equivalent). The Spex #8500 shatter box is only used when requested by the client or in special cases where needed to address particular matrices

6.7.1 HALF-PINT SHAKER

6.7.1.1 Transfer the entire dried sample, up to 30g, from the small weighing dish into the labeled half-pint steel can.

6.7.1.2 The maximum mass in the paint can should not exceed 30g. If larger quantity of the same sample needs to be milled, multiple cans should be used. Add 5 clean and dry, half-inch, steel ball bearings into the can. Cover the can with the lid and tighten it using the rubber mallet. The ball bearings stay in the cans and they are not reusable.

6.7.1.3 The paint shaker is equipped with two clamping jaws that can hold up to four cans each. The cans are secured between the jaws by turning the clamp handle clockwise. Care should be taken when tightening the clamp handle because excess pressure may damage the can or the clamping assembly.

6.7.1.4 Turn the timer knob to 15 minutes and the paint shaker will begin shaking. The clamping assembly will move quickly in a vertical and horizontal motion so caution should be taken when working near the shaker. The operator and anyone else in the room should wear hearing protection.

6.7.1.5 Once the shaker stops, loosen the clamps and remove the cans from the clamping jaws. Check the approximate weight of the milled sample by taring a common “empty can with 5 steel ball bearings” as a weight for all the empty cans used to mill samples. Document the milled weight in the sample preparation logbook. Here the exact weight of the milled sample is not required; therefore, a standard can with 5 ball bearings is used as a common empty weight.

6.7.2 SPEX #8500 SHATTER BOX

6.7.2.1 Used only by specific client request or the Department Manager’s instructions.

NOTE: The shatter box may only be operated in an operating fume hood. The pre-screening data, if available, should be reviewed prior to starting.

When feasible, the samples should be ground in order of increasing activity to minimize the potential for sample cross-contamination.

6.7.2.2 Load the dry sample aliquot into the outer ring of the puck portion of the shatter box, ensuring the sample does not protrude above the neoprene 0-ring. The capacity of the mill is up to 100mL of material with a particle size smaller than 1/4" on a side.

6.7.2.3 Place the cover over the puck making sure a tight seal is made with the neoprene O-ring and the lid, and place the puck on shatter box. Bring the damping lever down and tighten the hand knob firmly. To prevent loosening of the knob insert the locking pin in the hole ahead of the knob.

6.7.2.4 Set the timer for one (1) minute by turning the timer switch past five minutes first and then turn it back to the one (1) minute position. Allow the unit to come to a complete stop after one (1) minute.

6.7.2.5 Remove the clamping lever. Remove the puck from the shatter box. Remove the cover and inner puck and ring.

6.7.2.6 Transfer the milled soil to the tared, labeled secondary container from Section 6.3. Use a spatula or small scoop. Document the weight on the container. Place any unused milled material into an appropriately labeled soil waste container.

6.7.2.7 Replace the inner puck and ring, and then cover.

6.7.2.8 Transfer to a sink filled with water and RadiacwashTM detergent and completely submerse the puck. Disassemble under the water.

6.7.2.9 Using a Scotch Brite™ sponge or equivalent, scrub the components of the puck assembly to remove any gross material. Drain the sink and re-fill with fresh RadiacwashTM solution. Thoroughly scrub each component with a new steel wool pad. DO NOT USE ABRASIVE PADS ON THE RUBBER O-RING.

6.7.2.10 Rinse the puck assembly with deionized water and dry immediately with hot air dryer as the puck rusts easily when exposed to water for any length of time. Proceed to the next

sample.

6.7.2.11 It has been demonstrated that a five-minute timed grind using the shatter box achieves a nominal 200-mesh particle size (See Reference 12.1). A five minute timed grind may be used to meet this requirement, if the client requests a mesh size reduction as low as 200 mesh.

6.8 HOMOGENIZATION OF PREPARED SAMPLE ALIQUOTS

When multiple grinds are needed to meet a client's prep requirements, the individual fractions may be combined into a one quart steel can, with five 1/2" steel ball bearings, and shaken as described in Section 6.7 for five minutes. This will adequately homogenize up to 500 grams of ground sample material.

6.9 STORAGE OF PREPARED SAMPLE ALIQUOTS

6.9.1 Verify that all containers are labeled properly. Wipe off the exteriors of all containers before taking them to the Sample Storage unit.

6.9.2 Following procedures given in SOP 318 and the LIMS User Manual, create the proper designations for the prepared sample aliquots in LIMS (appropriate fraction identities must be created for the milled samples and gamma containers). Scan the barcodes to sign the prepared samples into the Sample Storage area, the Sample Custodian will take the responsibility distributing them to the appropriate location.

6.9.3 The preparation analyst is responsible for logging out the prepared samples and gamma containers on behalf of the Actinides Preparation Lab and Gamma Counting Lab.

6.10 EQUIPMENT CLEANING

6.10.1 Sieves, mortar/pestle, blender parts, mixing pans, hand trowels, spatulas and scoops are thoroughly washed with regular water first to remove all gross dirt. Then they are soaked in the sink filled with hot water w/approximately 20oz/gal Radiacwash™.

6.10.2 Mortar/Pestle may be scrubbed with a clean Scotch Brite pad (or equivalent). Do not use cleansing powders (e.g., Ajax, Comet, etc.) on m/p unless authorized to do so by the Department Manager.

6.11 PROCEDURE FOR WATER SAMPLES

Water samples with visible sediment will be filtered through a VWR #313 qualitative fluted filter paper or equivalent before proceeding with other preparation procedures. This practice does not apply to tritium analyses, in which the presence of sediment is not believed to be a significant interferent. In cases

where EPA drinking water methodologies are required, the sample is to be analyzed in total to estimate the actual dose to the consumer.

6.12 CALCULATIONS

6.12.1 Estimated tare weights needed in this SOP may be obtained by weighing another dry, empty container of identical kind

6.12.2 Intermediate prep weights may be obtained by zeroing the balance to include the clean, dry, empty container.

7. QUALITY CONTROL

7.1 Quality control procedures for the drying ovens and top loading balances are covered in SOPs 320 and 305, respectively.

7.2 Reagent grade quartz sand is milled for every batch of samples when the shatter-box mill is used. These serve as equipment blanks to verify that no cross contamination between samples has occurred in the grinding process. The milled sand blank is labeled with an in-house number and documented in the sample preparation logbook. The milled sand blanks are stored with the client samples. When a ground fraction of the client samples are analyzed, the equipment blank will also be analyzed. Detectable quantities of man-made radionuclides will be reported to the client as a Non-Conformance Report (NCR) and the original sample will be re-ground and re-analyzed. Analysis of naturally occurring uranium and thorium isotopes will be evaluated against previously measured quantities occurring in the sand material.

8. SAFETY, HAZARDS AND WASTE DISPOSAL

8.1 SAFETY AND HAZARDS

8.1.1 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or potentially contaminated materials or equipment.

8.1.2 Any chemicals with a Threshold Limit Value (TLV) of less than 50PPM shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

8.1.3 Loose hair and clothing must be restrained while working with or near machinery.

8.1.4 Perform any operation that produces noticeable dust in a working fume hood (especially sieving and milling).

8.1.5 Wipe down all working areas with damp paper towels whenever dust accumulation is evident, even between each sample handling if necessary. Cross-contamination of samples with dust can thus be

avoided. Wipe down all working areas at the end of the day (or shift), even if dust accumulation seems minimal or unnoticeable.

8.1.6 Hearing protection must be worn during milling.

8.2 WASTE DISPOSAL

8.2.1 Materials contaminated with dust residues such as paper towels must be surveyed prior to disposal in trash. Materials with no readings above background may be disposed of in the sanitary trash. This should include most environmental level soils.

8.2.2 Special disposal instructions may be imposed for certain samples with higher activity levels, as identified by the Radiation Safety Officer (RSO) through the prescreening process.

9. REFERENCES

9.1 Grinding study data is located in Paragon radiochemistry controlled logbook #2129, pages 22-28.

9.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Final Updates I, IIA, IIB, and III, Revision 1, December 1996.

9.3 Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, EPA/600/R-03/027, November 2003.

9.4 Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual, NUREG-1576, July 2004.

9.5 "Gy Sampling Theory in Environmental Studies", Journal of CHEMOMETRICS, 16: 321-328, 2002.

9.6 "Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities", ASTM D6323.

10. APPENDICES

Various client-specific Appendices (Confidential) have been developed as needed. This additional information is proceduralized as SOP addendums, but is only performed on an as-needed basis (i.e., when referenced in the applicable LIMS program specification).
Applied Appendices: A, B

DOCUMENT REVISION HISTORY

9/8/06: **SOP 721:** LIMS program specification language augmented. Clerical changes made. DOCUMENT REVISION HISTORY added. Form attached.

8/24/07: **SOP 721:** Added Appendices.

12/27/07: **SOP 336:** Updated/consolidated and re-issued as labwide SOP. Added Form 631.

TABLE 1

ANALYSIS *	PREPARATION TYPE	MINIMUM AMOUNT (in grams)	SECONDARY CONTAINERS
Percent Moisture	No-prep	10 (SOP 642)	60mL plastic vial/half-pint paint can
Tritium	No-prep	200	16oz jar, wide mouth
Gamma Spec	#4 Sieve	150-550	16oz jar, wide mouth
Gross A/B	Mill	20	half-pint paint can/60mL plastic vial
Ra 226/228	No-prep (% moist. required)	varies	Ra Geo-17 aluminum can
Ra	Mill	20	half-pint paint can/60mL plastic vial
Actinides	Mill	20	half-pint paint can/60mL plastic vial
Sr	Mill	20	half-pint paint can/60mL plastic vial
C-14	No-prep	NA	NA
Po-210	Mill	20	half-pint paint can/60mL plastic vial
Other total dissolution	Mill	20	half-pint paint can/60mL plastic vial
Pb-210	Mill	20	half-pint paint can/60mL plastic vial
Fe-55	Mill	20	half-pint paint can/60mL plastic vial
I-129	No-prep	NA	NA
Tc-99	Mill	20	half-pint paint can/60mL plastic vial

* *For analyses not listed, consult the appropriate SOP or the prep Department Supervisor for instructions.*

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Paragon Analytics

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE ~~721~~ 336

APPENDIX A: SUBSAMPLING PROTOCOL FOR ENVIRONMENTAL SOILS AND INDUSTRIAL FILL SAMPLES FOR MWH (FMC POCATELLO, IDAHO)

HISTORY: Rev0, 5/30/07.

1. OVERVIEW

This protocol describes the proposed procedures for sub-sampling environmental soils samples and industrial fill samples from the FMC site, for MWH.

Sub-sampling of environmental soils will be performed on the entire dried sample, up to 1 kg, using a standard riffle splitter to partition the aliquot for gamma analyses and approximately 30 – 50 g. for metals, fluorides and other radionuclides prior to grinding. The equipment will then be cleaned prior to use for the next sample by wet wiping the splitting mechanism with a lint-free lab wipe, followed by a dry wipe.
Due to the nature of the slag matrix, good homogeneity in a single grab sample is reasonably expected. Also, the extreme hardness of the sample matrix is expected to cause the potential metallic contamination in the grinding of large aliquots for analysis as well as significant time. Consequently, entire fill samples, up to 1 kg. will be dried and sieved, using a standard #10 sieve (1.5 mm mesh size) and the sieved material will be mixed by hand and aliquotted directly for analyses. In the event that sieving does not produce enough fine material for analysis, a 100-200 g. portion of the sample will be ground in a Roalox ceramic jar mill until sufficient material is obtained for analysis. After sub-sampling, digestion and analysis will proceed per the individual preparation SOPs for the requested analyses.

2. INTERFERENCES

Fill samples that require grinding in a jar mill may acquire trace amounts of alumina (Al_2O_3) from the Roalox mill jars during the grinding process. While the possibility of this potential contaminant should be noted to the client, aluminum is not an analyte of interest for this project and should be of no consequence to the data quality.

3. APPARATUS AND MATERIALS

3.1 forced air drying oven, set at 25±5°C
3.2 balance, top loading, readable to 0.1g
3.3 sieves, #10 (1.50 mm) and associated collection pans
3.4 mortar and pestle, ceramic
3.5 Riffle Splitter, Gilson SP-3 or equivalent, with collection pans
3.6 Roalox mill jar, with o-ring and lid
3.7 ½" Burundum grinding cylinders
3.8 weighing dishes and pans, aluminum

4. PROCEDURE

NOTE: Any abnormal conditions encountered during storage/receipt and preparation of the samples must be documented on a Quality Assurance Summary Sheet (QASS) and a copy of the sheet must accompany the benchsheet. A copy of the sample preparation logbook is also attached to the benchsheet for all analyses that use the dried, and milled sample fraction.

4.1 ENVIRONMENTAL SOILS

4.1.1 Sign-out the samples (scan barcodes to record transaction in LIMS) from Sample Storage. Return samples promptly to Sample Storage once aliquots have been obtained (sign samples back in by scanning barcodes to record transaction in LIMS).

4.1.2 Label the necessary drying pans and dishes with the Paragon work order number.

4.1.3 Assemble and label the required number of secondary containers for each sample. More than one container may be needed for each type of preparation if the amount required for the total number of analyses will exceed the capacity of the container. Label the containers with the Paragon sample number, type of preparation, date and your initials. If more than one container is needed for a given type of preparation, also serialize the containers (e.g., 1 of 3, 2 of 3, etc.).

4.1.4 Use labeled aluminum pans and weighing dishes to dry the entire sample. If the entire sample mass exceeds approximately 1 kg, a maximum of 1 kg. may be dried.

4.1.5 Either air-dry the samples in ambient conditions, or use a forced-air drying oven, set at 25±5°C. Samples should be dried for a minimum of 16 hours or to a constant weight (+/-2%). Wet samples may require drying overnight until a constant weight (+/-2%) is obtained.

4.1.6 Examine each container as it is removed from the oven. Return to the oven any that still contain moisture until sample is thoroughly dry. This can be determined by weighing the sample every hour until constant weight (+/-2%) is achieved (overnight is generally more convenient).

4.1.7 After drying, thoroughly mix the sample and load the entire dried sample into a riffle splitter, making sure that the catch pans are in place and the door is in the closed position. The sample may be manually crushed with a ceramic mortal and pestle (to break up dirt clods, etc.), if necessary, to allow passage through the riffle splitter.

4.1.8 Open the splitter door to divide the sample into the two pans. One pan will be randomly assigned for "accumulated residuals" and the other will contain the "analytical fraction".

4.1.9 Place two additional empty pans under the splitter and, repeating step 4.1.7, load the contents of the remaining "analytical fraction" pan for further splitting. With each successive split of the sample, the residual fraction may be added to the pan designated for accumulating residuals. When sufficient residuals have been accumulated, the contents of this pan may be used, as necessary, for gamma analyses.

4.1.10 Continue this process until a representative aliquot of 30 – 50 grams is deposited into each of the two catch pans. Take the contents of one pan as the analytical fraction.

4.1.11 Aliquots for metals, fluoride, and mercury analysis may be taken, by fractional shoveling, directly from the analytical fraction. The 336 remainder may be ground, per SOP ~~721,~~ as required for radiochemistry analyses. Note that analytical fractions for gamma spectroscopy are not ground prior to analysis, but are taken from the "accumulated residuals".

4.1.12 After placing the remaining material in an appropriately labeled container, to be retained for future use, the drying pans may be wet cleaned in Radiacwash and water, then rinsed and dried for later use.

4.1.13 The riffle splitter mechanism, including the body, hopper, riffle fingers, and door will be hand wiped with a lint-free laboratory wipe (large Kimwipe), moistened with DI water, then wiped again with a dry wipe to prepare the mechanism for the next sample.

4.2 FILL SAMPLES

4.2.1 Dry the sample material, as described in sections 4.1.1 through 4.1.6, above.

4.2.2 If necessary, split the dried sample by alternate shoveling, dedicating one fraction for gamma analysis and one fraction for further sample preparation..

4.2.3 Sieve the appropriate dried material, using a #10 sieve, into a clean, tared sieve collection pan. Return the remaining (>#10-sized) material to an appropriately labeled container, to be retained for future use.

4.2.4 Weigh the mass of sieved material, to determine whether additional material is needed. If no additional sieved material is needed, clean the sieve, per SOP ~~721~~, in preparation for the next sample, and proceed to

section 4.2.9.

4.2.5 If additional sieved material is needed, aliquot by fractional shoveling 100 – 200 grams of material and load into an appropriately sized Roalox mill jar. Add approximately ten individual ½" Burundum grinding cylinders, then close and seal the lid.

4.2.6 Rotate on a jar roller at approximately 40-50 rpm, overnight.

4.2.7 Transfer the contents of the jar to a #10 sieve and proceed from step 4.2.1, adding the retrieved sieved material to the previously collected, sieved material. Repeat this process, as necessary to acquire sufficient material for the requested analyses

4.2.8 After use, the Burnundum grinding media will be disposed in the appropriate waste stream. All other equipment, including the jar, lid, o-ring, etc. will be cleaned with Radiacwash (20oz/gal solution), rinsed in DI water, and thoroughly dried prior to re-use.

4.2.9 After sieving, the sample may be split by fractional shoveling for various analyses. Sample fractions for metals, fluoride and mercury analysis will be aliquotted directly from the sieved material. Sample fractions for radiochemistry analyses (non-gamma) will be ground and homogenized, per SOP ~~721~~. 336

5. SAFETY, HAZARDS AND WASTE DISPOSAL

5.1 SAFETY AND HAZARDS

5.1.1 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or potentially contaminated sample materials or equipment.

5.1.2 Loose hair and clothing must be restrained while working with or near machinery.

5.1.3 Perform any operation that produces noticeable dust in a working fume hood (especially sieving and milling).

5.1.4 Wipe down all working areas with damp paper towels whenever dust accumulation is evident, even between each sample handling if necessary. Cross-contamination of samples with dust can thus be avoided. Wipe down all working areas at the end of the day (or shift), even if dust accumulation seems minimal or unnoticeable.

5.2 WASTE DISPOSAL

5.2.1 Materials contaminated with dust residues such as paper towels must be surveyed prior to disposal in trash. Materials with no readings

above background may be disposed of in the sanitary trash. This should include most environmental level soils.

5.2.2 Special disposal instructions may be imposed for certain samples with higher activity levels, as identified by the Radiation Safety Officer (RSO) through the prescreening process.

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE ~~721~~ 336

APPENDIX B: CONING AND QUARTERING (NFS SAMPLES)

HISTORY: Rev0, 8/14/07.

PROCEDURE

1. Place two sheets of 8 x 16 copy paper (Sheets A and B) onto a tray, where A is slightly overlapping B.
2. *Slowly* pour the entire sample from the bottle onto the middle of paper A, so that a cone shape forms. The slow pouring allows natural particle distribution to occur.
3. Lightly flatten the sample with a clean spatula until it is circular in shape, with an approximate depth of ~1/2 inch.
4. Using a clean putty knife, quarter the sample evenly (by approximation), then slightly separate each quarter.
5. Move two **opposite** quarters onto Paper B.
6. Carefully move Paper B to another tray and set aside. This is considered the residual sample.
7. Lift both sides of Paper A to form a U-shape. Pour the remaining sample back into the original sample container.
8. Place Paper A back onto the tray. Place another paper (Paper C) onto the tray. Paper A should slightly overlap Paper C.
9. Repeat Steps 2-4.
10. Move two **opposite** quarters onto Paper C.
11. For the contents remaining on Paper A, repeat Steps 2-5 (placing residuals on a clean piece of paper) until a sample of ~30-50g is achieved. This sample can then be placed in the puck grinder to be ground for alpha-spec and Pu-241 analysis.
12. Use Paper C contents as the gamma fraction. If the amount of sample is still too much for a geometry 11 gamma, the sample may be coned and quartered again by following Steps 1-5, until an ideal volume is reached. If the volume of sample is too small for a geometry 11, the residuals from this Step and from paper B may be coned and quartered until an appropriate amount is achieved.
13. Place all remaining sample back into the original sample container for reserve.

Must Discard 30 Days from _____ (date printed)

Amended 12/30/07 - Section 5.2 'Allow sample to warm to room temperature before subsampling.' removed. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 336 REVISION 0

TITLE: **REPRESENTATIVE LABORATORY SUBSAMPLING**

FORMS: **302, 631** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 12-28-07

QUALITY ASSURANCE MANAGER _____ DATE 12/28/07

LABORATORY MANAGER _____ DATE 12-28-07

HISTORY: **Formerly SOP 721:** Rev1, 4/26/93; Rev2, PCN #35, 11/17/93; Rev3, PCN #80, 1/12/94; Rev4, PCN #276, 9/29/94; Rev5, PCN #471, 5/3/95; Rev6, 10/7/99; Rev7, 11/1/00; Rev8, 6/15/01; Rev9, 8/20/01; Rev10, 3/19/03; Rev11, 4/22/04; Rev12, 11/29/04; Rev13, 9/8/06; Rev14, 8/24/07. **As SOP 336**: Rev0, 12/27/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the physical procedures used to prepare environmental samples prior to chemical preparation and analysis. These physical preparations are crucial to ensuring that subsamples (aliquots), and their subsequent test results, are representative of the client sample as a whole.

2. SUMMARY

Subsamples must be representative to avoid bias in the analytical result. Incorrect analytical results could lead to making wrong environmental decisions that could impact environmental preservation or human health. Correct subsampling allows for the results to be duplicated (i.e., minimizes variability and the associated uncertainty of the resultant test value). Incorrect subsampling can be a significant source of error in the whole measurement process.

The specific subsampling techniques to employ vary with matrix and constituents of interest. This document is not intended to be stand-alone guidance; the procedures described herein must be used in close conjunction with established preparation SOPs.

Section 4 of this SOP addresses general representative laboratory subsampling concepts, and is applicable labwide. Stable chemistry, organic and inorganic, representative subsampling considerations are highlighted in Section 5. SOP Section 6 addresses additional representative subsampling concepts that are particularly applicable to radiochemical procedures.

3. RESPONSIBILITIES

3.1 Departmental Supervisory staff or designees are responsible for providing adequate training and oversight of proper subsampling technique.

3.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review, including completion of Sample Condition Form 631, as dictated by Departmental policy. Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification (text directives) and associated project analyte nicknames (electronic controls) are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. Criteria defined in the applicable program specification supercede Paragon's standard criteria. All personnel are responsible for consulting the applicable LIMS program specification prior to initiating handling of project samples or data.

3.4 Internal chain-of-custody procedures (SOP 318) must be observed.

3.5 It is the responsibility of all personnel who process/analyze samples or data, to note and document all anomalous conditions (generally recorded on a Quality Assurance Summary Sheet, QASS, Form 302), and any occurrences that may impact data quality (a Non-Conformance Report, NCR, must be initiated in LIMS). Supervisory, QA and Project Management staff must be notified in a timely manner, as applicable, so that proper corrective actions may be directed and taken.

4. GENERAL CONCEPTS

4.1 Good subsampling technique is especially critical where only small portions of sample are aliquotted for testing.

4.2 Always work using clean surfaces.

4.3 Work as quickly as possible to minimize potential degradation or loss of constituents.

4.4 Unlike evenly dispersed liquids, soil and sediment samples are not homogeneous. Therefore, special steps must be taken to obtain aliquots that are 'representative' of the source material. For example, sticks, leaves, rocks, etc. that are not characteristic of the overall sample must be excluded from the subsample. **Do not take one "grab" sample**, instead, select several small, 'random' increments. Then, thoroughly mix these increments to achieve homogeneity. A disposable tongue depressor can generally be used to acquire/mix solid matrix subsamples.

4.5 Discard excess quantity taken from the original sample container, do not return unused homogenized subsample to original sample container.

4.6 After acquiring sufficient mass (use laboratory balance with calibration verified per SOP 305), record aliquot weight on appropriate datasheet.

4.7 Do not adjust for moisture unless directed by SOP or project requirements.

5. STABLE CHEMISTRY PROCEDURES

5.1 Apply general concepts discussed above.

~~5.2 Allow samples to come to room temperature before subsampling.~~ 12/30/07 DAS

5.3 **Organics**: Unless otherwise directed by LIMS program specification, decant and discard any water layer on top of a sediment sample when preparing for Soxhlet extraction.

For volatile (VOAs, BTEX, etc.) analyses, and for inorganics, gently mix/blend contents of sample container, obtain portions for subsample while in the process of mixing/blending. **Note that the subsample obtained for % Moisture analysis (SOP 642) must be acquired in the same manner as the subsample for constituent analysis.**

For volatile (VOAs, BTEX, etc.) samples that are tightly packed, carefully scrape off a thin top layer of sample before proceeding with subsampling (due to the nature of volatile compounds, this top layer may not be representative of sample constituents due to potential analyte loss).

5.4 **Inorganics**: Use only non-metal scooping devices.

Subsample particles that are larger than the others can be gently mashed.

6. RADIOCHEMICAL SUBSAMPLING PROCEDURES

6.1 GENERAL CONSIDERATIONS

6.1.1 This SOP serves as the starting point for nearly all radiochemical analyses, and is referenced by the SOPs relating to the analysis of individual nuclides or other radiochemical tests. After this pretreatment has been performed, the remainder of the analysis is performed according to the individual preparation SOPs

6.1.2 For radiochemical preparations, any abnormal conditions encountered during storage/receipt and preparation of the samples must be documented on a Quality Assurance Summary Sheet (QASS). A copy of the QASS must accompany the benchsheet. A copy of the sample preparation logbook is also attached to the benchsheet for all analyses that use the dried, and milled sample fraction.

6.1.3 Water samples having visible sediment will generally be filtered through a qualitative paper filter prior to chemical separation.

6.1.4 If a particular analysis requires no preparations, then a subsample is taken before any other preparations are started. The general sequence of soil preparations starts with removing an appropriate representative aliquot followed in turn by drying, sieving and milling. The preparation steps used on a soil depend on the analyses requested for that sample. The requirements for each analysis are described in the individual SOPs. When more than one analysis is requested for a sample, it is possible that a sub sample will be aliquoted at various points in the preparations.

6.1.5 Soil samples are routinely milled in a half-pint ball mill. By specific request, the samples may, instead, be milled with a Spex #8500 shatter box miller. Solid samples that have been milled in the half-pint ball mill are stored in the same clean, labeled containers. The containers are not reusable. A logbook is maintained to document the sample information such as sample ID, date, balance number, oven number, milled sample weight, batch ID (page#) for preparation.

6.1.6 It is important that soil samples for tritium analysis be handled at a minimum so as to preserve their original moisture content. If a separate container is not provided for tritium analysis, coordinate with the tritium analyst and arrange to complete tritium analysis before preparing the sample for other analyses.

6.1.7 Paragon typically reports solid sample results on a dry weight basis. The basis on which water sample results are reported depends on whether the samples require filtration. For moisture content determinations, refer to SOP 642. If the sample volume is very limited, the sample aliquot used for moisture content analysis may subsequently be used for milling.

6.1.8 Before beginning any actual preparations, the LIMS program specs must be reviewed to determine whether project instructions indicate non-routine analytical requirements or special handling due to Health and Safety concerns or sample activity levels (e.g., retaining the "+" fraction of a solid matrix, removing organic and metallic debris). This may influence the quantity of sample needing to be processed through each stage of the preparation sequences. The sample preparation logbook is filled out with the work order numbers.

For each soil sample, determine the total weight of material required to be prepared at each of the stages, (i.e., no-prep, #4 sieve, mill, etc.). Refer to Table 1 for a summary of the amount of material and type of preparation required for various analyses. If unsure of the type or

quantity of required soil preparation, consult the Department Manager or the Project Manager.

6.2 APPARATUS AND MATERIALS

6.2.1 drying oven, set at 105+5°C

6.2.2 sieves, #4 (4.75mm) and others, as specified by the client, and associated collection pan

6.2.3 mortar and pestle (M/P), 150mL, 1L, 4L sizes

6.2.4 Red Devil 5400 shaker or Spex #8500 shatter box miller, or equivalents

6.2.5 Scotch BriteTM scrubbing sponge, or equivalent

6.2.6 SOS™, Brillo™ or equivalent steel wool cleaning pads

6.2.7 gamma spec containers (16oz LERMER JARS) and Ra containers (#2 steel cans)

6.2.8 half-pint steel paint cans

6.2.9 tongue depressors, spatulas or scupulas

6.2.10 Snap-cap vials, 60mL, plastic

6.2.11 balance, top loading, readable to 0.1g

6.2.12 weighing dishes and pans, aluminum

6.2.13 steel ball bearings, 1/2”

6.2.14 rubber mallet

6.2.15 qualitative fluted filter paper, VWR #313 or equivalent

6.2.16 Quartz sand, reagent grade

6.3 DOCUMENT CLIENT SAMPLE ID, LABEL CONTAINERS

6.3.1 Sign-out the samples (scan barcodes to record transaction in LIMS) from Sample Storage. Return samples promptly to Sample Storage once aliquots have been obtained (sign samples back in by scanning barcodes to record transaction in LIMS).

6.3.2 Label the necessary drying pans and dishes with the Paragon work order number.

6.3.3 Assemble and label the required number of secondary containers for each sample (refer to Table 1). More than one container may be needed for each type of preparation if the amount required for the total number of analyses will exceed the capacity of the listed container. Label the containers with the Paragon sample number, type of preparation, date and your initials. If more than one container is

needed for a given type of preparation, also serialize the containers (e.g., 1 of 3, 2 of 3, etc.).

6.3.4 The secondary container may be a LERMER JAR if the only analysis requested on a soil sample is gamma spectrometry.

6.4 NO-PREP SOIL SAMPLEs

6.4.1 Soil sample analyses such as tritium, C-14, and I-129 are performed on an "As Received" basis due to the potential volatility of the analyte. These samples should not be dried or milled prior to analysis, and can be taken directly from the original container with minimum handling. Percent moisture results are used to subsequently convert from 'wet weight' to final reporting dry weight results.

6.4.2 Using a minimal amount of handling, stir and blend the sample with a new tongue depressor before taking an aliquot. Document non-homogeneous, non-stirrable or problematic samples on a Quality Assurance Summary Sheet (QASS, Form 302).

6.5 DRYING

6.5.1 Use labeled aluminum pans and weighing dishes to dry the samples. Add up the total weights required for all preps needing sieving or milling. Weigh out roughly double this amount of sample into the drying trays.

6.5.2 The amount needed for drying will depend on the moisture content of the sample. Extra sample must be dried to account for the weight loss expected. Drier soils may require less and wet soils may require more than double the needed dry weight mass. If the percent moisture has already been determined in prescreening, use this value to estimate the amount required for drying. Consult the Department Manager for directions especially for wet soils and sludges, or if unsure of how to estimate the required amount.

6.5.3 If the sample amount required for gamma fraction (#4 sieving) will use up most or the entire sample, notify the Department Manager. The γ analysis may have to be completed before releasing the sample for the remainder of the soil preparations.

6.5.4 If the weight needed for drying exceeds the total received amount of sample, dry the entire sample immediately. Inform the Project Manager of the insufficient sample size.

6.5.5 Dry the samples in a drying oven set at 105$\pm$5°C. Samples should be dried for a minimum of 16 hours or to a constant weight (+/-2%). Wet

samples may require drying overnight until a constant weight (+/-2%) is obtained.

6.5.6 Examine each container as it is removed from the oven. Return to the oven any that still contain moisture until sample is thoroughly dry. This can be determined by weighing the sample every hour until constant weight (+/-2%) is achieved (overnight is generally more convenient).

6.6 NUMBER 4 SIEVING

NOTE: If the client requires the inclusion of rocks and large material with the final sample aliquot, consult the Department Manager for further instruction.

6.6.1 If the sample will pass a #4 sieve without further processing, proceed to Step 6.6.3.

6.6.2 If the sample requires size reduction before it can pass the #4 sieves, use a mortar and pestle to break up the sample.

6.6.3 Sieve the material, using a #4 sieve, into a clean sieve collection pan. Return the unsievable material to an appropriately labeled soil waste container, if the sample remaining is in excess of what is needed for all analyses. (If the unsievable material must be retained, place it in a new appropriately sized container labeled with the sample identification and the words “dry, unsievable material”.)

6.6.4 Remove the amount of #4 sieved material required to the labeled, tared, secondary container(s) from Section 6.3. If only γ analysis was requested, or if the γ analysis must be completed first due to limited sample size, the sieved material may be weighed into a 16oz LERMER JAR. Document the net weight on the secondary container as well as the sample preparation logbook.

6.6.5 The remaining sample continues through additional preparation in the following Steps. If no further preparation is required, the unused portion may be disposed of in an appropriately labeled soil waste container.

6.6.6 Thoroughly wash and dry the sieve after each use to avoid potential cross-contamination of the samples. First remove any gross sample remaining on the sieve, then wash in Radiacwash™ solution. A nylon brush may be used if necessary. Rinse the sieve with DI water and air dry completely before use.

6.7 MILLING

Milling is accomplished through the use of the Red Devil 5400 paint can shaker (or equivalent). The Spex #8500 shatter box is only used when requested by the client or in special cases where needed to address particular matrices

6.7.1 HALF-PINT SHAKER

6.7.1.1 Transfer the entire dried sample, up to 30g, from the small weighing dish into the labeled half-pint steel can.

6.7.1.2 The maximum mass in the paint can should not exceed 30g. If larger quantity of the same sample needs to be milled, multiple cans should be used. Add 5 clean and dry, half-inch, steel ball bearings into the can. Cover the can with the lid and tighten it using the rubber mallet. The ball bearings stay in the cans and they are not reusable.

6.7.1.3 The paint shaker is equipped with two clamping jaws that can hold up to four cans each. The cans are secured between the jaws by turning the clamp handle clockwise. Care should be taken when tightening the clamp handle because excess pressure may damage the can or the clamping assembly.

6.7.1.4 Turn the timer knob to 15 minutes and the paint shaker will begin shaking. The clamping assembly will move quickly in a vertical and horizontal motion so caution should be taken when working near the shaker. The operator and anyone else in the room should wear hearing protection.

6.7.1.5 Once the shaker stops, loosen the clamps and remove the cans from the clamping jaws. Check the approximate weight of the milled sample by taring a common “empty can with 5 steel ball bearings” as a weight for all the empty cans used to mill samples. Document the milled weight in the sample preparation logbook. Here the exact weight of the milled sample is not required; therefore, a standard can with 5 ball bearings is used as a common empty weight.

6.7.2 SPEX #8500 SHATTER BOX

6.7.2.1 Used only by specific client request or the Department Manager’s instructions.

NOTE: The shatter box may only be operated in an operating fume hood. The pre-screening data, if available, should be reviewed prior to starting.

When feasible, the samples should be ground in order of increasing activity to minimize the potential for sample cross-contamination.

6.7.2.2 Load the dry sample aliquot into the outer ring of the puck portion of the shatter box, ensuring the sample does not protrude above the neoprene 0-ring. The capacity of the mill is up to 100mL of material with a particle size smaller than 1/4" on a side.

6.7.2.3 Place the cover over the puck making sure a tight seal is made with the neoprene O-ring and the lid, and place the puck on shatter box. Bring the damping lever down and tighten the hand knob firmly. To prevent loosening of the knob insert the locking pin in the hole ahead of the knob.

6.7.2.4 Set the timer for one (1) minute by turning the timer switch past five minutes first and then turn it back to the one (1) minute position. Allow the unit to come to a complete stop after one (1) minute.

6.7.2.5 Remove the clamping lever. Remove the puck from the shatter box. Remove the cover and inner puck and ring.

6.7.2.6 Transfer the milled soil to the tared, labeled secondary container from Section 6.3. Use a spatula or small scoop. Document the weight on the container. Place any unused milled material into an appropriately labeled soil waste container.

6.7.2.7 Replace the inner puck and ring, and then cover.

6.7.2.8 Transfer to a sink filled with water and RadiacwashTM detergent and completely submerse the puck. Disassemble under the water.

6.7.2.9 Using a Scotch Brite™ sponge or equivalent, scrub the components of the puck assembly to remove any gross material. Drain the sink and re-fill with fresh RadiacwashTM solution. Thoroughly scrub each component with a new steel wool pad. DO NOT USE ABRASIVE PADS ON THE RUBBER O-RING.

6.7.2.10 Rinse the puck assembly with deionized water and dry immediately with hot air dryer as the puck rusts easily when exposed to water for any length of time. Proceed to the next

sample.

6.7.2.11 It has been demonstrated that a five-minute timed grind using the shatter box achieves a nominal 200-mesh particle size (See Reference 12.1). A five minute timed grind may be used to meet this requirement, if the client requests a mesh size reduction as low as 200 mesh.

6.8 HOMOGENIZATION OF PREPARED SAMPLE ALIQUOTS

When multiple grinds are needed to meet a client's prep requirements, the individual fractions may be combined into a one quart steel can, with five 1/2" steel ball bearings, and shaken as described in Section 6.7 for five minutes. This will adequately homogenize up to 500 grams of ground sample material.

6.9 STORAGE OF PREPARED SAMPLE ALIQUOTS

6.9.1 Verify that all containers are labeled properly. Wipe off the exteriors of all containers before taking them to the Sample Storage unit.

6.9.2 Following procedures given in SOP 318 and the LIMS User Manual, create the proper designations for the prepared sample aliquots in LIMS (appropriate fraction identities must be created for the milled samples and gamma containers). Scan the barcodes to sign the prepared samples into the Sample Storage area, the Sample Custodian will take the responsibility distributing them to the appropriate location.

6.9.3 The preparation analyst is responsible for logging out the prepared samples and gamma containers on behalf of the Actinides Preparation Lab and Gamma Counting Lab.

6.10 EQUIPMENT CLEANING

6.10.1 Sieves, mortar/pestle, blender parts, mixing pans, hand trowels, spatulas and scoops are thoroughly washed with regular water first to remove all gross dirt. Then they are soaked in the sink filled with hot water w/approximately 20oz/gal Radiacwash™.

6.10.2 Mortar/Pestle may be scrubbed with a clean Scotch Brite pad (or equivalent). Do not use cleansing powders (e.g., Ajax, Comet, etc.) on m/p unless authorized to do so by the Department Manager.

6.11 PROCEDURE FOR WATER SAMPLES

Water samples with visible sediment will be filtered through a VWR #313 qualitative fluted filter paper or equivalent before proceeding with other preparation procedures. This practice does not apply to tritium analyses, in which the presence of sediment is not believed to be a significant interferent. In cases

where EPA drinking water methodologies are required, the sample is to be analyzed in total to estimate the actual dose to the consumer.

6.12 CALCULATIONS

6.12.1 Estimated tare weights needed in this SOP may be obtained by weighing another dry, empty container of identical kind

6.12.2 Intermediate prep weights may be obtained by zeroing the balance to include the clean, dry, empty container.

7. QUALITY CONTROL

7.1 Quality control procedures for the drying ovens and top loading balances are covered in SOPs 320 and 305, respectively.

7.2 Reagent grade quartz sand is milled for every batch of samples when the shatter-box mill is used. These serve as equipment blanks to verify that no cross contamination between samples has occurred in the grinding process. The milled sand blank is labeled with an in-house number and documented in the sample preparation logbook. The milled sand blanks are stored with the client samples. When a ground fraction of the client samples are analyzed, the equipment blank will also be analyzed. Detectable quantities of man-made radionuclides will be reported to the client as a Non-Conformance Report (NCR) and the original sample will be re-ground and re-analyzed. Analysis of naturally occurring uranium and thorium isotopes will be evaluated against previously measured quantities occurring in the sand material.

8. SAFETY, HAZARDS AND WASTE DISPOSAL

8.1 SAFETY AND HAZARDS

8.1.1 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or potentially contaminated materials or equipment.

8.1.2 Any chemicals with a Threshold Limit Value (TLV) of less than 50PPM shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

8.1.3 Loose hair and clothing must be restrained while working with or near machinery.

8.1.4 Perform any operation that produces noticeable dust in a working fume hood (especially sieving and milling).

8.1.5 Wipe down all working areas with damp paper towels whenever dust accumulation is evident, even between each sample handling if necessary. Cross-contamination of samples with dust can thus be

avoided. Wipe down all working areas at the end of the day (or shift), even if dust accumulation seems minimal or unnoticeable.

8.1.6 Hearing protection must be worn during milling.

8.2 WASTE DISPOSAL

8.2.1 Materials contaminated with dust residues such as paper towels must be surveyed prior to disposal in trash. Materials with no readings above background may be disposed of in the sanitary trash. This should include most environmental level soils.

8.2.2 Special disposal instructions may be imposed for certain samples with higher activity levels, as identified by the Radiation Safety Officer (RSO) through the prescreening process.

9. REFERENCES

9.1 Grinding study data is located in Paragon radiochemistry controlled logbook #2129, pages 22-28.

9.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Final Updates I, IIA, IIB, and III, Revision 1, December 1996.

9.3 Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, EPA/600/R-03/027, November 2003.

9.4 Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual, NUREG-1576, July 2004.

9.5 "Gy Sampling Theory in Environmental Studies", Journal of CHEMOMETRICS, 16: 321-328, 2002.

9.6 "Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities", ASTM D6323.

10. APPENDICES

Various client-specific Appendices (Confidential) have been developed as needed. This additional information is proceduralized as SOP addendums, but is only performed on an as-needed basis (i.e., when referenced in the applicable LIMS program specification).
Applied Appendices: A, B

DOCUMENT REVISION HISTORY

9/8/06: **SOP 721:** LIMS program specification language augmented. Clerical changes made. DOCUMENT REVISION HISTORY added. Form attached.

8/24/07: **SOP 721:** Added Appendices.

12/27/07: **SOP 336:** Updated/consolidated and re-issued as labwide SOP. Added Form 631.

TABLE 1

ANALYSIS *	PREPARATION TYPE	MINIMUM AMOUNT (in grams)	SECONDARY CONTAINERS
Percent Moisture	No-prep	10 (SOP 642)	60mL plastic vial/half-pint paint can
Tritium	No-prep	200	16oz jar, wide mouth
Gamma Spec	#4 Sieve	150-550	16oz jar, wide mouth
Gross A/B	Mill	20	half-pint paint can/60mL plastic vial
Ra 226/228	No-prep (% moist. required)	varies	Ra Geo-17 aluminum can
Ra	Mill	20	half-pint paint can/60mL plastic vial
Actinides	Mill	20	half-pint paint can/60mL plastic vial
Sr	Mill	20	half-pint paint can/60mL plastic vial
C-14	No-prep	NA	NA
Po-210	Mill	20	half-pint paint can/60mL plastic vial
Other total dissolution	Mill	20	half-pint paint can/60mL plastic vial
Pb-210	Mill	20	half-pint paint can/60mL plastic vial
Fe-55	Mill	20	half-pint paint can/60mL plastic vial
I-129	No-prep	NA	NA
Tc-99	Mill	20	half-pint paint can/60mL plastic vial

* *For analyses not listed, consult the appropriate SOP or the prep Department Supervisor for instructions.*

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Paragon Analytics

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

STANDARD OPERATING PROCEDURE 402 REVISION 13

TITLE: DETERMINATION OF ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY - METHODS SW8081A OR B, AND EPA 608

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 4.7.09

QUALITY ASSURANCE MANAGER _____ DATE 4/7/09

LABORATORY MANAGER _____ DATE 4-7-09

HISTORY: New, Rev0, 8/4/92; re-released without revision (updated format), 4/13/94; Rev1, PCN #482, 5/25/95; Rev3, 3/26/96; Rev4, 6/10/96; Rev5, 1/29/99; Rev6, 11/10/01; Rev7, 8/29/02; Rev8, 2/12/03; Rev9, 3/14/03; Rev10, 4/16/04; Rev11, 11/22/04; Rev12, 7/5/06; Rev13, 3/19/09.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references – SW8081A or B, and EPA 608, are used to determine the concentration of certain organochlorine pesticides in liquid (SW8081 and EPA 608) and solid matrices (SW8081). The following compounds typically comprise ALS Laboratory Group - Fort Collins (ALSLG-FC)'s target analyte list:

aldrin	4,4'-DDD	endrin
alpha(α)-BHC	4,4'-DDE	endrin aldehyde
beta(β)-BHC	4,4'-DDT	endrin ketone
gamma(γ)-BHC (lindane)	dieldrin	heptachlor
delta(δ)-BHC	endosulfan I	heptachlor epoxide
alpha(α)-chlordane	endosulfan II	methoxychlor
gamma (γ) chlordane	endosulfan sulfate	toxaphene
technical chlordane		

Other compounds may be analyzed if successful demonstration of capability (DOC) and method detection limit (MDL) studies are performed.

2. SUMMARY

Samples are extracted and the extracts concentrated and solvent exchanged using appropriate ALSLG-FC SOPs (i.e., 625 [Soxhlet]; 626 [Separatory Funnel]; 607 [Kuderna-Danish Reduction]; and 637 [Concentration and Solvent Exchange]). The extracts are injected into a gas chromatograph (GC) containing a sample splitter and two columns of varying selectivity (i.e., dissimilar elution and retention time properties). The target analytes are separated in the columns and detected by two electron capture detectors (ECDs). This chromatography system allows tentative identification by one column and confirmation by the other column to be performed simultaneously. Quantitation is performed using the best column response yielded for each analyte. The Analyst considers performance data such as separation of interferences, calibration performance and matrix

spike results in selecting the primary quantitation column for each analyte detected and reported. The particular value that is selected for reporting is often marked (designated) in the raw data (e.g., quantitation report, run log). If results from both columns are comparable, the highest result is reported.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 ALSLG-FC 's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALSLG-FC's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Interference from phthalate esters can be minimized by using plastic-free solvent containers and scrupulously cleaned glassware (SOP 334) that has been kiln-baked or solvent-rinsed prior to use. Use of low phthalate gloves, such as nitrile, may also important. These practices are important both in the field and in the laboratory.

4.2 Method SW3620B Florisil cleanup may be used to remove polar interferences from sample extracts (SOP 648).

4.3 Elemental sulfur (particularly in sediment samples) may interfere with early-eluting pesticides. Method SW3660B sulfur cleanup may be performed (SOP 634).

NOTE: The recovery of endrin aldehyde can be drastically reduced when using the TBA procedure in Method SW3660B. For this reason, only the copper powder technique will be used.

4.4 Dilution is performed if high molecular weight organic interferences are present. Alternatively these may be removed using Method SW3640A GPC cleanup (SOP 641).

4.5 The presence of Aroclors in the sample may interfere with the recognition and quantitation of single components, such as 4,4'-DDT, or multi-component pesticides such as technical chlordane and toxaphene. Interpretive examples are provided in Appendix I of this SOP. If multi-component interference is observed, the interference is discussed in the data package narrative. Consult the LIMS program specification and ensure that the Project Manager is informed if interferences are present.

4.6 Particular caution is used in identifying the presence of interferences. It should be noted that methoxychlor may also be susceptible to interference.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH (GC), AUTOSAMPLER AND DETECTORS - Hewlett Packard (HP) 5890 Series II GC equipped with HP 7673A autosampler and electron capture detectors (ECDs) or equivalents

5.2 CHROMATOGRAPHIC DATA ACQUISITION AND PROCESSING SYSTEM - Hewlett Packard ChemStation (Enviroquant™) or equivalent

5.3 COLUMNS -

RTx-CLPesticides or equivalent (30m, 0.25 or 0.32mm ID, 0.5µm film), RTx-CLPesticides II or equivalent (30m, 0.25 or 0.32mm ID, 0.25µm film), guard column

Restek Pesticide Column:	RTX-CLPesticides	#11123	(0.25mm)
Restek Pesticide Column:	RTX-CLPesticides2	#11323	(0.25mm)
Restek Pesticide Column:	RTX-CLPesticides	#11139	(0.32mm)
Restek Pesticide Column:	RTX-CLPesticides2	#11324	(0.32mm)

5.4 GASES - ultra high purity (99.999%)
Helium - carrier gas
Nitrogen - make-up gas

5.5 MEASURING DEVICES
Syringes - 10µL-1000µL
Volumetric flasks, Class A with stoppers, 10mL-100mL

5.6 GC CONSUMABLES:

- Vials - National Scientific C4011-1, or equivalent

- Caps - National Scientific C4000-51B, or equivalent
- Inlet Seals, dual vespel ring - Restek 0.8mm #21243, or equivalent
- Septa, 11mm - Restek #20365 or equivalent
- O-ring, graphite, 6.5mm - Restek #20299, or equivalent
- O-ring, Viton - Restek #20377, or equivalent
- Liner, splitless, 4mm ID - Restek #20799-214.5, or equivalent
- Glass Wool, deactivated - Restek #20789, or equivalent
- Gold Seal - Restek #21306, or equivalent
- Universal Presstight Y - Restek #20469, or equivalent
- Vespel/Graphite Ferrule (detector) - Restek #20221, or equivalent
- Compact Vespel/Graphite Ferrule - Restek #20249, or equivalent
- Graphite Ferrules - various sizes
- Split Vent Trap (SW8081) - Agilent RDT-1023, or equivalent

6. REAGENTS

6.1 SOLVENTS - **Only pesticide residue grade or equivalent may be used.**
Hexane - Burdick and Jackson 216-4, or equivalent
Methanol - Burdick and Jackson 230-4, or equivalent

6.2 STANDARDS
All standards are stored following ALSLG-FC SOP 300 guidance, which is superseded by any guidance in this SOP. Generally after opening vials, the standards for this procedure are stored in the freezer (-10°C and -20°C), in PTFE-capped, or equivalent vials. Unopened stock standards in flame-sealed ampules are valid until the manufacturer's expiration date and may be stored at room temperature, if recommended by the manufacturer. Opened stock standards and intermediate standards expire six months from opening (preparation) or the manufacturer's expiration date, whichever is sooner. Standards may be replaced sooner if laboratory QC analyses or other factors indicate deterioration.

All stock and intermediate standards are documented in ALSLG-FC's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

6.2.1 Stock standards are generally purchased as mixes from vendors with certified concentrations. At a minimum, two independent sources of stock standards are needed for target analytes. An appropriate volume of stock standard is diluted (in hexane) to a specified volume to create intermediate standards. The intermediate standards are further diluted to volume using an appropriate solvent to create the working standards.

Working standards are prepared the day of use and documented in the analytical run log. A detailed description of the concentrations of the working standards and how they are used can be found in Section 8 of this SOP.

6.2.2 ICV Solution - Second source confirmation is required, this is accomplished by preparing an initial calibration verification (ICV) solution at a concentration near the midpoint of the calibration curve.

6.2.3 Endrin and 4,4'-DDT Standard (Breakdown Standard) - This standard is used to check inertness of injector system and columns prior to running standards or samples. Only one source is needed and primary, intermediate and working standards are created as described above and detailed in Section 8.

6.2.4 Surrogate Spike Solution - A primary standard containing tetrachloro-meta-xylene (TCMX) and decachlorobiphenyl (DCB) is purchased from a vendor. A solution containing 500ng/mL is prepared in methanol or other suitable solvent. This solution is used by the Organics Extraction Group to spike all samples for this test prior to extraction. Other concentrations or solvents may be used as needed (i.e., as defined in the applicable LIMS Program Specification).

6.2.5 Spike Solution - A primary standard (or standards) is used to prepare a solution to be used by the Organics Extractions Group in preparing laboratory control samples (LCS/LCSD) or matrix spiked samples (MS/MSD). This standard typically contains all the single component analytes listed in Section 1 at 400ng/mL in methanol. Other concentrations and solvents may be used as appropriate. Technical chlordane and toxaphene are not included in this matrix spike solution because either would interfere with the quantification of the single component pesticides. Technical chlordane and toxaphene-spiked samples are prepared separately when required (i.e., as indicated in the LIMS program specification).

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are generally not chemically preserved and must be collected in amber glass containers (generally 1000mL) with Teflon-lined lids. Samples must be maintained at 4±2°C and extracted within 7 days of collection. Sodium thiosulfate ($Na_2S_2O_3$) may be used to dechlorinate liquid samples that contain residual chlorine. This should be accomplished by the client in the field. The Project Manager may designate need for residual chlorine check of the sample upon receipt. Additionally, samples for Method EPA 608 may need to have pH adjusted upon receipt.

7.3 Solid samples are collected in 250mL wide mouth glass containers with Teflon-lined lids. Solid samples are not chemically preserved but must be maintained at 4±2°C. Solid samples must be extracted within 14 days of collection.

7.4 Extracts from solids or liquids must also be maintained at 4±2°C and analyzed within 40 days of preparation.

8. PROCEDURE

8.1 TYPICAL GAS CHROMATOGRAPHIC CONDITIONS

Carrier gas (He):	1.5mL/min (constant flow mode 9.3psi)
Make-up gas (N_2):	20-40mL/min
Injector temperature:	205°C
1µl injection:	splitless mode (purge off)
Purge:	on, 0.75min
Detector temperature:	325°C

Oven Temperature Program:

Initial temperature:	110°C, hold 0.5min
Oven ramp 1:	20°C/min to 140°C
Oven ramp 2:	11°C/min to 240°C, hold 4.09min
Oven ramp 3:	20°C/min to 300°C ,hold 8.00min

8.2 ROUTINE MAINTENANCE/ENDRIN AND 4,4'-DDT BREAKDOWN CHECK
Routine injector maintenance is performed, to limit and control both endrin and DDT breakdown, approximately once per 24 hours of system use. This includes septum replacement, liner (clean or replace), new deactivated glass wool, cut column (approximately 4cm), clean injection port and rinse of the gold seal.

Endrin and 4,4'-DDT breakdown must be checked and found acceptable before calibration or sample analyses may proceed. This check of system inertness must be performed at the start of any sequence. A working standard containing endrin and 4,4'-DDT at 100ng/mL and 200ng/mL, respectively, in hexane is injected. The peak areas of endrin, endrin aldehyde, endrin ketone, 4,4'-DDT, 4,4'-DDE and 4,4'DDD are integrated. Endrin and 4,4'-DDT breakdown as a percentage are calculated using the equations below:

$$endrin\ breakdown\,(\%) = (100)\left[\frac{peak\ area\ (endrin\,aldehyde + endrin\,ketone)}{peak\ area\,(endrin + endrin\,aldehyde + endrin\,ketone)}\right]$$

$$4,4'\text{–}DDT\ breakdown\,(\%) = (100)\left[\frac{peak\ area\ (4,4'\text{–}DDD + 4,4'\text{–}DDE)}{peak\ area\,(4,4'\text{–}DDT + 4,4'\text{–}DDD + 4,4'\text{–}DDE)}\right]$$

If the calculated breakdown of either endrin or 4,4'-DDT exceeds 15% on either column, corrective maintenance must be done before the analysis of any calibration standards or extracts may proceed. Endrin breakdown is typically indicative of injection port contamination. Other preventive maintenance such as clipping the guard column or analytical columns may be needed to bring the breakdown within criteria. Further injection port maintenance, such as cleaning the entire port and gas feeder lines, may also be needed.

ECD detector leak checks are performed semi-annually per the SOP 016.

8.3 INITIAL CALIBRATION

8.3.1 Prepare calibration standards as suitable for the requirements of the samples to be analyzed. A typical calibration sequence and preparation steps are shown below in Table 1. A one-point calibration at or below the report level for toxaphene and technical chlordane is performed unless these multi-component compounds are expected to be present in extracts. The concentrations of the single-point calibration for toxaphene and technical chlordane are typically 250 and 50ng/mL, respectively. When toxaphene or technical chlordane is known or expected to be present, a five-point calibration is performed to more accurately quantify these compounds. A typical calibration range for the single component pesticides is 5ng/mL to 75ng/mL, with the exception of methoxychlor at 15 to 375ng/mL. Calibration standards are prepared with surrogates at similar levels to target analytes. When toxaphene or technical chlordane curves are needed to quantify these compounds, a similar approach to that shown below for single component initial calibration is used.

TABLE 1
CALIBRATION STANDARDS

Working Standard	Hexane (µL)	Intermediate Std (or std specified) (µL)	Standard Concentration (ng/mL)
Breakdown Check	1000	250	DDT 0.2 Endrin 0.1
Toxaphene	975	25	250
Technical Chlordane	975	25	50
40% Standard	750	500	100
Single Component ICAL Level 7	250	750 of 40% std	75
Single Component ICAL Level 6	750	250	62.5
Single Component ICAL Level 5	1000	250	50
Single Component ICAL Level 4	500	500 of ICAL 7	37.5
Single Component ICAL Level 3	1000	250 of 40% Std	20
Single Component ICAL Level 2	500	500 of ICAL 3	10
Single Component ICAL Level 1	750	250 of ICAL 3	5
Single Component 2nd source ICV	varied over time	varied over time	typically 37.5

8.3.2 Note that because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore, the GC column may need to be primed by injecting a pesticide standard mixture at high concentration prior to calibration. The total chlorinated organic concentration of the solution should be approximately 5-10 ug/mL. Solvent blanks are typically injected following the priming in order to avoid contamination of later injections due to the high concentration levels of the priming standard.

8.3.3 Inject 1µL of calibration standard under the GC conditions listed previously. Each data file quantitation is accomplished via the external standard method of quantitation. Analyte Calibration Factors (CFs) are calculated as follows:

$$CF = \frac{\text{integrated peak area of analyte}}{\text{analyte concentration}}$$

Since each CF represents the slope of the line between the response for that standard and the origin, then if the observed deviation between the CF's is constant (i.e., ≤20% RSD), then the response is assumed to be invariant and the average (mean) CF may be used to quantitate sample content.

Relative Standard Deviation (RSD) is calculated as:

$$RSD\ (\%) = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean response factor}} \right)(100)$$

When %RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be ≥0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit", with perfect fit being a value of 1.0. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 calibration points, following the guidelines in SW-846 Method 8000C. A quadratic regression should not be used to compensate for detector saturation.

The mathematics used in least squares regression have a tendency to favor numbers of larger value over numbers of smaller value. The regression curves that are generated will therefore tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels. To compensate for this, a "weighting" factor which reduces this tendency can be used. The analyst may weight the curve to either the

inverse of the concentration or to the inverse of the square of the concentration.

The type of curve fit applied should be chosen to best represent the data.

NOTE: If an initial calibration point is not used for any reason, the analyst must clearly notate why the data point was not used for instrument calibration. "Picking and choosing" among calibration points in order to meet criteria is NOT acceptable. Generally, calibration points are only discarded due to easily demonstratable causes.

If regression criteria cannot be met, a new initial calibration must be performed.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is run after calibration. The concentration of the ICV should be different from that of the continuing calibration verification (CCV) and varied over time. The acceptance criteria for the ICV are identical to those of CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The concentration of the CCV is at or near the midpoint of the initial calibration. A CCV check is performed at the beginning (when initial calibration is not performed) and end, of each 12-hour analytical sequence (or batch of 20 samples). While QC samples are counted as part of the number of samples, solvent blanks are not.

NOTE: The CCV frequency given above should be considered a bare minimum, and some clients' LIMS program specifications may require more frequent CCV analysis. Even if this is not the case, a higher CCV frequency is strongly recommended. ALSLG-FC typically analyzes a CCV every 10 samples in order to reduce the amount of repeat injections necessary in the event of CCV failure.

Calibration is verified when all compounds are ≤20%D, when calculated as shown below:

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

If a compound shows *elevated* response (> 20%D) and is not detected in any samples associated with the CCV, re-analysis of those samples are not necessary. If a compound shows *low* response (> 20%D) and was not detected in the samples associated with the CCV, reinjection is necessary to ensure that a false negative

result is not reported.

If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

8.6 RETENTION TIME WINDOWS

Retention Time Windows (RTWs) are established by analyzing replicates (typically three injections) of a mid-level standard containing all single and multi-component analytes, non-consecutively, over a 72-hour period each time a new column is installed. The standard deviation of these analyses is calculated based on the absolute retention time yielded for each component. Each component's RTW is defined as the mean retention time $\pm 3\sigma$ such that the Upper Limit = $+3\sigma$ and the Lower Limit = -3σ.

RTWs should be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the beginning CCV when samples are not directly preceded by an initial calibration. Sample matrices may cause drift that requires further Analyst interpretation. In the chromatography data system, RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system. See Appendix I for chromatographic interpretation examples.

8.7 SAMPLE ANALYSIS, CALCULATIONS AND REPORTING

A constant volume, generally 1µL of each standard, blank, QC or field sample extract is directly injected into the GC via the automated injector. Sample extracts are diluted to maintain response within the linear range when necessary. All prepared extracts contain the surrogate (see Section 9). Extract concentration and sample concentration are determined as discussed below.

8.7.1 Note that ALSLG-FC employs a sample splitter that facilitates simultaneous dual column injections; therefore, both columns are calibrated in the same manner and either column may serve as the column for quantitation.

8.7.2 The tentative identification of an analyte occurs when a peak from a concentrated sample extract falls within the RTW of one column. If the retention time of the analyte falls within its RTW on the second column, the analyte's presence has been confirmed. Quantitation is calculated from both column responses and the best result is reported. The analyst considers performance data such as separation of interferences, calibration performance and matrix spike results in selecting the primary quantitation column for each analyte detected and reported. If results from both columns are comparable, the higher concentration is reported.

8.7.3 Multi-response compounds (e.g., toxaphene, chlordane) are identified through pattern recognition. Because samples may contain more than one multi-component analyte of interest and/or contain significantly weathered compounds, analyst expertise is crucial to the identification and quantitation of multi-response target compounds.

For multi-component analytes, four to eight peaks are used for identification and quantitation depending upon how many peaks are clearly defined. The same selected peaks ***must*** be consistently used for quantitation between the standard and sample set.

8.7.4 Extract concentration is calculated using the following equation:

$$\text{extract conc. (ng/mL)} = \frac{(\text{area} - \text{intercept})}{\text{slope}}$$

8.7.5 Sample concentration is calculated using the following equations:

$$\text{liquid sample conc. (ng/mL)} = \frac{(\text{extract conc.})(\text{extract volume})(\text{D})}{\text{sample volume}}$$

where:

extract conc. = ng/mL
extract vol. = mL
sample volume = mL
D = dilution factor (if applicable)

$$\text{solid sample conc. (ng/g)} = \frac{(\text{extract conc.})(\text{extract volume})(\text{D})}{\text{dry weight of sample}}$$

where:

extract conc. = ng/mL
extract vol. = mL
D = dilution factor (if applicable)
dry weight of sample = g and is the product of the weight extracted multiplied by the fraction solids in the sample.

8.7.6 If the dual column results for any analyte exceed 40% Relative Percent Difference (RPD; see calculation below), then it is necessary to investigate possible high bias of the greatest result by checking the chromatogram for apparent interferences and to check both results for appropriate integration. If no interference is evident, the highest result that is properly integrated and quantitated is reported. The elevated RPD is also discussed in the data package narrative or flagged in accord with the LIMS program specification.

$$RPD = \left[\frac{(concentration\ sample - concentration\ duplicate)}{1/2(concentration\ sample + concentration\ duplicate)} \right](100)$$

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

For this method, an analysis batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specification for additional or alternative requirements.

9.2 BLANKS

Method blanks are aliquots of matrix (i.e., organic-free water for liquids analyses; Ottawa sand for solids analyses) that have been prepared and analyzed in the same manner as the associated field samples. To be acceptable, concentrations of analytes of interest detected (if any) in the MB must be below the analyte reporting limit, or as otherwise specified in the LIMS program specification. If this criterion is not met, analyses should be halted and the source of the contamination found and corrected.

A reagent or instrument blank is an injection of solvent analyzed to demonstrate that the analytical system is free from contamination. These blanks are typically analyzed following extremely contaminated samples.

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percen**t** recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this analysis, either a field sample containing target compound contamination may be analyzed in duplicate (DUP), or the laboratory control sample (LCSD) or matrix spike analysis (MSD) can be performed in duplicate. The results of the duplicate analyses are evaluated in terms of RPD (calculation shown previously). See QC Table for evaluation criteria.

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. See QC Table for evaluation criteria. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \frac{A_{found} - A_{sample}}{A_{target}} \times 100$$

where:

A_{found} = Calculated analyte concentration in the MS or MSD sample

A_{sample} = Calculated analyte concentration in the unspiked field sample

A_{target} = The target (anticipated) concentration of the added analyte spike

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation will be made in the data package narrative.

9.6 SURROGATE RECOVERY AND ACCEPTANCE CRITERIA

The two surrogates (SUR) used for this procedure are suggested in SW8081. Both surrogates are added to all field and quality control samples prior to extraction; recovery is calculated per the recovery formula shown previously for the LCS. The two surrogates used were selected because they respond in a similar manner as the target compounds respond at the detector. Additionally these surrogates are not similar enough chemically to the target compounds to co-elute with the single component targets, nor do they suffer interferences from the multiple component targets. Tetrachloro-m-xylene (TCMX) elutes before any of the target compounds, and decachloro-biphenyl (DCB) elutes after all of the target compounds. However, because the surrogates are not deuterated analogs of targets as in GC/MS methods, they are not extracted with exactly the same efficiencies as the target compounds. Therefore, surrogate recovery problems may not be representative of target analyte recoveries.

Heavy co-extractive non-target compounds generally do not interfere with TCMX; light co-extractive non-target compounds generally do not interfere with DCB. However, some samples may produce matrix effects that cause surrogate recovery to be high or low; because of high concentrations of target and/or non-target compounds, quantification of the surrogates may even be precluded in some

samples. Muddy aqueous samples, for example, generally adsorb DCB after spiking and limit recovery to a few percent. High concentrations of heavy hydrocarbons in soils oftentimes have a similar matrix effect on DCB recovery.

The extraction process itself can have an effect on surrogate recovery. An example of this process-caused effect is use of Method SW3520 for extraction of aqueous samples and associated "low" recoveries of DCB. DCB is a heavy molecule and very hydrophobic. When spiked into water, this compound tends to rapidly adsorb to particulates at the liquid-liquid interface and thus exhibits a low recovery.

For the reasons listed above, ALSLG-FC does not view the evaluation of surrogate recovery in this procedure to be a straightforward process. Therefore, the following guidance for evaluating surrogate recovery is observed:

- Evaluate and report the recovery of both surrogates. When one or both surrogates are within laboratory control limits, the process is considered to be in control and no further action is taken (unless additional measures are stipulated in the LIMS program specification.

- When, due to elevated target concentrations, an extract requires a dilution of greater than 5X, the surrogate recoveries are not controlled; no further action is taken.

- When both surrogates are outside of laboratory control limits (or other limits specified in the LIMS program specification), the extract is re-injected to assure that instrument error was not the cause. If after re-injection the recoveries of both surrogates remain out of control, then re-extraction and re-analysis may be performed as directed by the client. A non-conformance report (NCR; SOP 928) to document the problems is required.

This process of evaluating surrogate recovery is based on several methods and guidance documents and has evolved in particular from Method SW8080 guidance as well as from the National Functional Guidelines for Data Review.

9.7 A METHOD DETECTION LIMIT (MDL) STUDY shall consist of the analysis of a minimum of seven replicate analyses for a target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at a minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM THE METHODS

10.1 This SOP meets the requirements of Method SW8081A and B. Note that ALSLG-FC analyzes a breakdown check every 24hrs, not every 12hrs.

10.2 Deviations from Method EPA 608

Because samples from several sites are usually batched together, only one spiking

level is used for each compound. It is impractical to match each compound's spike amount with the amount of the compound in the samples chosen for spiking and also matching the spike amount to the appropriate regulatory level for each compound. This difference must be stated in the data package narrative that accompanies each batch of samples.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), and when handling materials or equipment potentially contaminated with chemicals, or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 All flammable compounds must be kept away from ignition sources.

11.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.6 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport. The cylinder must be stored capped and secured at all times.

11.2 WASTE DISPOSAL

11.2.1 Any hexane or other nonhalogenated organic solvents that have not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste.

11.2.2 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.3 The extract vials, associated extracts, and any PCB contaminated debris that may contain PCBs in excess of 50ppm shall be disposed of intact in the PCB Debris Waste.

11.2.4 All empty solvent bottles are disposed of appropriately. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, "Method 8081A", Revision 2, December 1996.

12.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, Final Update IV, "Method 8081B", Revision 2, February 2007.

12.3 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, Final Update IV, "Method 8000C", Revision 3, March 2003.

12.4 40 CFR, Part 136, Appendix A, 7-1-99 Edition, "Method 608".

DOCUMENT REVISION HISTORY

7/5/06: Strengthened LIMS program specification references, analytical columns and consumables used, breakdown check and ICV concentrations, and dual column interpretation. Added DOCUMENT REVISION HISTORY.

3/19/09: Added methoxychlor comment to INTERFERENCES Section (4.6). Added reference to SOP 016 detector leak checks performance semi-annually to Section 8.2. Updated calibration discussion in Section 8.3.3, and CCV discussion in Section 8.5. Section 8.6 RTW discussion was also updated. Method references were updated to include SW8081B and 8000C (QC criteria were updated accordingly). Included in DEVIATIONS 10.1 that ALSLG-FC analyzes a breakdown check every 24hrs, not every 12hrs.

Analytical Method: SW8081, EPA 608	**Parameter:** Organochlorine Pesticides		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point; all analytes	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, use mean RFs and CFs to quantitate. If RSD >20% , calculate linear regression (not forced through origin); use for quantitation if coefficient of determination (r^2) is ≥ 0.990 or calculate quadratic regression (minimum of six points required); use for quantitation if COD (r^2) ≥0.990	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Endrin and DDT Breakdown Check; approx. midpoint of calibration	Daily prior to calibration verification	If ≤15% analyses may proceed.	Perform GC maintenance (e.g., change liner, clip column, inject primer, etc.); recalibrate.
Initial Calibration Verification (ICV); second source	After each initial calibration	≤20%D of each compound or as otherwise specified in applicable LIMS program specification	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV); first source	Brackets each set of 20 field sample analyses (standard practice is every 10 samples injections)	≤20%D of each compound or as otherwise specified in applicable LIMS program specification	Evaluate/correct instrument malfunction as needed (e.g., remove 1 meter from the guard column of the GC, prepare a new standard); reanalyze. - If CCV still non-compliant, recalibrate using a new curve. Samples analyzed after a failed CCV will be reanalyzed. - if target(s) in CCV fails high (>20%) and target is not present in samples, re-analyses of samples are not necessary. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW)	Whenever a new column is installed; based on at least 3	Column and compound specific. Window is ±3x the standard deviation of the 3-injection average	If SD=zero, then either do additional injections or use a default SD of 0.01 minutes. Experience of analyst weighs heavily in

Analytical Method: SW8081, EPA 608	**Parameter:** Organochlorine Pesticides		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
	injections throughout a 72-hour period.	for the respective column. Note that the ICV and CCV analyses are also used to monitor RTW shift.	interpretation of chromatograms (refer also to RT Shift).
Retention Time (RT) Shift	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate. Evaluate data based on a comparison with other standards run during the analytical sequence; consider the RTs for the surrogates and spiked compounds analyzed before and after the sample in question.
Method Blank (MB)	1 per each preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are outside the extraction holding time, then complete an NCR and contact PM for sample disposition.
Blank Spike; BS (Laboratory Control Sample; LCS)	1 per batch of ≤20 samples of like matrix	See laboratory limits; recoveries for the spiked compounds must be within the laboratory limits or other limits as specified in the LIMS program specification.	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions or analytical preparation was the cause. - if still non-compliant and the samples are within the extraction holding time, then request re-extraction using an NCR, and reanalyze all associated samples for the analyte that does not meet criteria. - if the samples are outside the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Matrix Spike (MS)	1 per batch of samples, not to exceed 20 samples of a	See laboratory limits; recoveries for the spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in

Analytical Method: SW8081, EPA 608	**Parameter:** Organochlorine Pesticides		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
	given matrix		narrative.
Matrix Spike Duplicate (MSD) or Duplicate	1 per batch of samples, not to exceed 20 samples of a given matrix.	See laboratory limits; see Matrix Spike information above for MSD recoveries. RPDs should be within advisory limits.	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). If no errors are found and, if analyzed, LCSD RPD is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Surrogate Spike	All extractions including field and laboratory QC samples.	See laboratory limits; recoveries should be within current limits for one or both surrogates; alternative criteria as defined in the LIMS program specifications may apply.	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with both surrogate recoveries outside the recovery limits, with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if both surrogate recoveries in the associated MB are not within limits, and the samples are within the holding time, then re-extract and reanalyze all associated samples. - if samples are outside the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study	As needed and at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If `criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Appendix I
Chlorinated Pesticide Data Interpretation Examples

- The presence of multi-component target analytes, such as toxaphene and/or chlordane, or non-target analytes such as Aroclors, in a sample may interfere with proper identification of target analytes by retention time and may cause false positives on both columns. Typically, the presence of either Aroclor 1254 or Aroclor 1260 result in peaks on both columns that are RT matches (potential false positives) for 4,4'-DDT. Aroclor 1254 also results in peaks on both columns that are RT matches for dieldrin. When either of these Aroclors is observed or suspected, the analyst may need to inject the appropriate Aroclor standard in order to better interpret the data with respect to presence or absence of single component pesticides.

- The retention times of surrogates in each extract injected provide useful information about the effects of sample matrices on retention times during each analysis. The surrogates used for this procedure have very early and very late retention times compared to the target analytes. If the observed TCMX and DCB retention times in sample analysis are the same as in bracketing CCVs, then it can be assumed that there is little or no matrix effect on the RT of target analytes. If, for example, DCB is 0.01 minutes later in a sample analysis than in surrounding calibration verifications, then the analyst may assume that late-eluting targets may also be eluting slightly later, and use this observation to assist with peak identification.

- Retention time difference between columns can also be used as an aid to identification. If both surrogates in a sample have the equivalent RTs to nearby standards and, for example, heptachlor is 0.03 minutes early on column 1 and 0.02 minutes late on column 2, then the analyst may decide that heptachlor is not confirmed as present and to not report heptachlor based on the relative retention time differences.

- The retention times and peak shapes of analytes in matrix spikes may be used as an aid to the analyst in identification in similar matrix samples. If endrin, for example, is identified on both columns and is 0.03 minutes later in the MS/MSD than in nearby calibration verifications, and this is consistent with other late-eluting peak RTs in the MS/MSD, then the analyst should use this information in evaluating and identifying targets in samples of similar matrix. If a sample has a peak that is within the RT window for example at 12.01 (column 1) and 13.07 (column 2), but the matrix spikes have peaks at 11.99 and 13.04, and both show evidence of a shoulder on the main peak, and the shoulder is on the later eluting side of the main peak, the analyst may document that the RT match appears to be a false positive match and not report the target as confirmed.

- The presence of alpha- and gamma-chlordane in a sample is a primary indicator of the presence of chlordane even if little or no pattern can be observed due to low concentrations of the technical mixture. ALSLG-FC does not analyze for individual components of toxaphene, so pattern recognition of toxaphene is the only mechanism of identifying this multi-component analyte. Weathered chlordane or toxaphene can produce patterns that are not good matches to fresh standards. Also, several producers manufactured multi-component pesticides, so patterns may not be identical between sources. The presence of moderate to high concentrations of single component pesticides such as 4,4'-DDT and its degradation products can also make pattern recognition of toxaphene or chlordane more difficult in real samples than in standards. Analyst experience is essential in properly identifying and quantifying such complex mixtures. For multi-component analytes, four to eight peaks are used for identification/quantitation, depending upon how many peaks are clearly defined. The same selected peaks must be consistently used for quantitation between the standard and sample set.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 404 REVISION 15

TITLE: **ANALYSIS OF NITROAROMATICS AND NITROAMINES (EXPLOSIVES RESIDUES) BY HPLC -- METHOD SW8330**

FORMS: **410 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8-13-07

QUALITY ASSURANCE MANAGER _____ DATE 8/12/07

LABORATORY MANAGER _____ DATE 8-13-07

HISTORY: Rev1, 1/28/92; Rev2, PCN #42, 12/17/93; Rev3, PCN #78, 1/10/94; Rev4, PCN #336, 1/23/95; Rev5, PCN #465, 4/24/95; Rev6, PCN #470, 8/10/95; Rev7, 1/23/96; Rev8, 9/21/99; Rev9, 3/6/02; Rev10, 3/26/03; Rev11, 4/16/04; Rev12, 3/13/06; Rev13, 7/24/06; Rev14, 2/8/07; Rev15, 8/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references – SW-846 Method 8330, are used to determine the concentration of certain nitroaromatics and nitroamines (i.e., explosives residues) in aqueous and solid matrices. The following compounds typically comprise Paragon's target analyte list:

HMX	4-Amino-2,6-Dinitrotoluene
RDX	2-Amino-4,6-Dinitrotoluene
1,3,5-Trinitrobenzene	2,6-Dinitrotoluene
1,4-Dinitrobenzene	2,4-Dinitrotoluene
1,3-Dinitrobenzene	2-Nitrotoluene
Tetryl	4-Nitrotoluene
Nitrobenzene	3-Nitrotoluene
2,4,6-Trinitrotoluene	

Other compounds may be analyzed if successful method detection limit (MDL) and demonstration of capability (DOC) studies are performed.

2. SUMMARY

Aqueous and solid matrix samples are extracted and concentrated using appropriate methods (SOP 665). Aqueous samples can also be analyzed by direct injection if concentrations are expected to be high. An aliquot of sample or extract is injected into a high performance liquid chromatograph (HPLC) that contains a C_{18} reverse phase (primary) chromatography column and/or an ether-linked phenyl phase (ELP) confirmation column. Target analytes are separated under isocratic (i.e., constant composition) solvent flow conditions on the primary column, and under gradient conditions on the confirmation column. The target analytes are then detected by an

ultraviolet (UV) detector using absorbance at 254nm. Detected analyte responses are recorded and calculated by a data acquisition system using the external standard method of quantitation. Solid matrix sample results are normally reported on an air-dried basis.

NOTE: Aqueous samples for direct injection must first be diluted 1:1 with methanol (preferred if HMX is an important target analyte) or acetonitrile, and filtered before this technique is applied.

All procedures must be conducted with care as the analytes of interest present an explosive hazard.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Analyst to perform the analysis according to the SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret results acceptably to utilize this method. Demonstration of performance may include Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Paragon Project Manager is responsible for directing a chlorine residual check to be performed upon sample receipt as applicable.

3.5 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of the measures taken to correct those errors.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Contaminants in reagents, from glassware or within the analytical system may

cause the appearance of discrete artifacts or elevated baselines. Use of high purity reagents, scrupulously cleaned glassware (SOP 334) and frequent maintenance of the analytical system minimizes these interferences.

4.2 Interferences coextracted from the sample matrix will vary considerably from source to source. If observed, the presence of significant interferences is discussed in the laboratory data package narrative.

4.3 Tetryl may decompose in water and with exposure to heat. Aqueous samples expected to contain tetryl should not be exposed to temperatures above room temperature.

4.4 Degradation products of tetryl may interfere with the quantification of 2,4,6-trinitrotoluene or 4-amino-2,6-dinitrotoluene. The degradation products of tetryl may impact quantitation of these compounds if tetryl is present at high concentrations relative to 2,4,6-trinitrotoluene and 4-amino-2,6-dinitrotoluene.

5. APPARATUS AND MATERIALS

5.1 HPLC, AUTOSAMPLER, DETECTORS

A Hewlett-Packard (HP) 1050 or 1090 or equivalent HPLC equipped with:

- gradient pumping system
- system controller
- column oven
- ultraviolet detectors
- autosampler

5.2 DATA SYSTEM

Any data acquisition system capable of acquiring, storing and processing HPLC data (e.g., LC ChemStation™ or equivalent)

5.3 COLUMNS - Equivalent columns may also be used

C_{18} column:	Phenomenex Ultracarb™	#00G-0206-E0	(5µ ODS (20); 250x4.6mm)
ELPcolumn:	Synergi POLAR-RP 80Å	#00G-4336-E0	(4µ Polar RP; 250x4.6mm)
Guard Cartridge Holder:	#KJO-4282		
Cartridge:	Phenomenex (C_{18})	#AJO-4287	(5µ ODS; 4.0 x 3.0mm)
	Synergi (Polar RP)	#AJO-6076	(4.0 x 3.0mm)

5.4 MEASURING DEVICES

Microsyringes, Hamilton Precision™ or equivalent, various µL sizes

Volumetric flasks, Class A with ground glass or Teflon™ stoppers, 10-100mL sizes

5.5 CONSUMABLES

- solvent inlet filter frit-1/4", 4.6mm, 2µm, Restek #25071 or equivalent

- HPLC pump maintenance kit, Restek #25270 or equivalent
- autosampler maintenance kit, Restek #25259, or equivalent
- PTFE syringe filters, 0.45µm
- autosampler vials
- glass pipets, disposable

6. REAGENTS

6.1 SOLVENTS - **Only HPLC grade solvents with acceptable UV cutoffs may be used!**

6.1.1 methanol (CH_3OH; MeOH), Burdick & Jackson #230-4 or equivalent

6.1.2 acetonitrile (ACN; CH_3CN), Burdick & Jackson #015-4 or equivalent

6.2 REAGENTS

6.2.1 HPLC grade water, Burdick & Jackson #365-4 or equivalent

6.2.2 sulfuric acid (H_2SO_4), concentrated, EMD #SX1244-5 or equivalent

6.2.3 HPLC grade water-acidified (use to prepare working standards): Create by adding 1 drop of conc. H_2SO_4 to 500mL HPLC grade water

6.3 STANDARDS

6.3.1 All standards are maintained per PAR SOP 300. Target analyte stock standards, typically 1,000µg/mL, are generally purchased as certified solutions, but may be prepared from pure standard materials dissolved in MeOH or ACN. For neat standards or standard materials of a purity <95%, adjust concentration for purity when calculating standard concentration. Two independent sources (first, second) of target analyte stock standards are needed. A (non-target analyte) surrogate stock standard is also purchased. The surrogate used for this method is 1,4-dinitrobenzene.

Intermediate standards are made by diluting an appropriate aliquot of stock standard to a specific volume using acetonitrile, and are stored in Teflon™-sealed vials. Typically, a 50-fold dilution is made, thus creating intermediate standards at a concentration of 20µg/mL. First source target analyte materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards (used by the Organics Extraction Group). Second source target analyte materials are used to create the initial calibration verification (ICV) solution. Typically, 1.0mL of intermediate surrogate standard is added into each calibration check, field and quality control (QC) sample. Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

Unopened stock standards are valid until the manufacturer's expiration

date. Transfer remainders of opened stock standards to Teflon™-sealed vials for storage. All stock and intermediate standards are stored in the freezer (i.e., dark, ˉ10 to ˉ20°C). Opened stock or prepared intermediate standards expire 30 days from opening (preparation), or per the manufacturer's expiration date (whichever is sooner). Standards may be replaced sooner if laboratory QC analyses or other factors indicate deterioration.

6.3.2 The intermediate target analyte standards are further diluted to create working standards. These working standards (ICAL, ICV, CCV) are prepared on the day of use, directly in analysis vials (µL injections), using portions of acidified water and acetonitrile as the diluents to create sufficient standard volume for analysis. The working standards must contain all target analytes and the surrogate. Calibration standards are documented in the analytical run log (Form 410). A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.3.3 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are not generally chemically preserved and must be collected in amber glass containers (typically 1L) with Teflon™-lined lids. Samples must be maintained at 4±2°C and extracted within 7 days of collection. Dechlorination using sodium thiosulfate ($Na_2S_2O_3$) may be necessary at the time of sampling if water is known to contain residual chlorine as part of a treatment process. The Project Manager may designate the need for residual chlorine check of the sample upon receipt.

7.3 Solid samples are collected in glass containers with Teflon™-lined lids. Solid samples are not chemically preserved and must be maintained at 4±2°C. Exception: Solid sample aliquots in the process of being prepared for analysis are air-dried, prior to subsequent extraction. Solid samples must be extracted within 14 days of collection.

7.4 Extracts, from liquid or solid samples, must be maintained in the dark at 4±2°C and analyzed within 40 days of preparation.

8. PROCEDURE

8.1 TYPICAL HPLC RUN CONDITIONS

Column 1: C_{18} isocratic analysis conditions with wash gradient, below:

Flow Rate: 0.8mL/min flow
MP A: 45% H_2O (±1.5%)
MP B: 55% CH_3OH (±1.5%)
Column Temperature: 28°C
Injection Volume: 50-100µL injections (no change during acquisition)

Linear Gradient Elapsed Time (min)	MP A: Water (%)	MP B: Acetonitrile (ACN) (%)
0	55	45
27	55	45
27.5	80	20
31.5	80	20
32	55	45
35 (equilibration)	55	45

Column 2: ELP analysis conditions (or as suitable):

Flow Rate: 1.6mL/min flow
Column Temperature: 32.0°C
Injection Volume: 50-100µL injections

Linear Gradient Elapsed Time (min)	MP A: Water (%)	MP B: Acetonitrile (ACN) (%)
0	70	30
27	45	55
30	70	30
35 (equilibration)	70	30

8.2 ROUTINE MAINTENANCE and PRE-RUN CHECK

Prior to analyzing samples or establishing calibration curves, the following suggested maintenance can be performed to aid in achieving more consistent results:

- Change the column frits as needed (i.e., if pressure increase is observed).
- Change the cartridge on the guard column as necessary (i.e., pressure increase or poor chromatography).
- Install fresh HPLC water for every run.
- Restart the computer and instrument before starting equilibration and analysis.

- Minimize air currents blowing on the instrument and vials loaded on the autosampler tray.
- Replace lamps at 2yr or upon observation of degraded signal.
- Major repairs on contract (by Full Spectrum or equivalent).
- Ensure that instrument is equilibrated and retention times have stabilized; instrument may be primed with one or more injections of the CCV solution prior to initiation of the CCV for the acquisition sequence.

8.3 INITIAL CALIBRATION

8.3.1 Set pump at flow rate used for the column in use. Turn on the detector lamp. Allow the HPLC system to equilibrate for a minimum of 15min.

8.3.2 Prepare a minimum of 5 concentrations of calibration standards (typically 6 are used) as shown below in Table 1 or as required for each sample set to be analyzed. The purpose of the initial calibration (ICAL) is to define the linear range of the detector. The ICAL can be used for analysis of both soil or water extracts. Each ICAL standard must include all target analytes and the surrogate. The lowest standard's concentration standard shall be at or below the reporting limit (RL) of each analyte. Create calibration standards by diluting aliquots of the first source intermediate calibration standard using an acetonitrile/acidified water mix. The mid-range calibration standard is used for continuing calibration verification (CCV).

TABLE 1
CALIBRATION STANDARDS

ACN (µL)	Acidified HPLC H_2O (µL)	5µg/mL Intermediate (µL)	Final Conc. (µg/mL)
0	500	500	2.5
300	500	200	1.0
400	500	100	0.5
480	500	20	0.1
495	500	5	0.025
498	500	2	0.01
400 CCV	500	100	0.5
480 ICV	500	20	0.1

8.3.3 Inject an appropriate volume (50µL) of each ICAL standard into the HPLC and analyze. Alternatively, a 100µL injection may be used for

all blank, standard, quality control and field sample injections. The data system accomplishes quantitation via the external standard method (i.e., area responses are tabulated against the concentration injected). Analyte Calibration Factors (CFs) are calculated as follows:

$$CF = \frac{\text{Peak Area}}{\text{Concentration of Analyte}}$$

If the CFs over the working range of the detector are constant (i.e., $\leq$20% RSD), then response can be assumed to be invariant (linear through zero) and the average (mean) CF may be used to quantitate sample content.

Relative Standard Deviation (RSD) is calculated as:

$$\text{RSD (\%)} = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean response factor}} \right)(100)$$

When RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first (minimum of 5 ICAL points used, r) or second (minimum of 6 ICAL points used, r^2) order regression curve fit that does not pass through zero (e.g., least squares method) may be constructed. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000B. A quadratic regression should not be used to compensate for detector saturation. Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

If a first order regression fit is applied, the correlation coefficient (r) value yielded must be $\geq$0.995. If a second order regression fit is applied, the coefficient of determination (COD, r^2 value) yielded must be $\geq$0.99. Note that the curve fit value expresses "goodness of fit", with perfect fit being a value of 1.0.

If the curve fit value does not meet criteria, check that the calibration standards were prepared properly, reanalyze and generate a new initial calibration curve.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The acceptance criteria for the ICV is the same as for the CCV (described below). If the control criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new

initial calibration must be generated. See QC Summary Table for further details.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

The percent difference (%D) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when responses for all analytes are within $\leq$15%. If a CCV does not meet acceptance criteria, reanalyze the CCV. See QC Summary Table for further details and corrective action to be taken should the CCV still fail.

So long as CCV analyses yield compliant results, and other QC samples are analyzed as required, the series of ten sample analyses bracketed before and after by successful CCV analyses may continue as long as the reserve of solvents lasts.

8.6 RETENTION TIME WINDOWS

For chromatographic methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used to compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (σ) of the absolute retention time yielded for each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time $\pm 3\sigma$, such that the Upper Limit = $+3\sigma$ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time shifts). Sample matrices may cause RT differences that require further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system

8.7 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATIONS, REPORTING)

The calibration of the analytical system is verified. A constant volume, generally

50 or 100uL of each standard, blank, QC or field sample extract is injected into the HPLC via the automated injector. All prepared extracts contain the surrogate (see Section 9). Sample extracts are diluted to maintain response within the linear range when necessary. Note that where sample concentrations are expected to be significant enough, filtered aqueous sample aliquots may be directly injected into the HPLC. Allow the HPLC system to equilibrate after each injection/analysis.

8.7.1 Tentative identification occurs when a peak's response falls within the RTW of the C_{18} column. Confirmation occurs when the peak's response also falls within the RTW on the ELP confirmation column. Note that per LIMS program specification, diode array detection spectral confirmation may also be used.

8.7.1 Sample concentration may be calculated using the average calibration factor or using the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

Average CF:

$$\text{Concentration}_{(ug/L,\ ug/kg)} = \frac{(A_x)(V_t)(DF)}{(\text{Average CF})(V_s \text{ or } W_s)}$$

where:

A_x = analyte response (area units)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Average CF = average calibration factor

V_s or W_s = volume or weight of sample extracted (mL or g)

Linear Curve Equation:

$$x = \frac{(y - b)\,(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte in ng/mL, ng/g (equal to ug/L, ug/Kg)

y = analyte instrument response (area units)

b = calculated intercept (area units)

m = calculated slope of the line (area units/conc. units-ng/mL)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples of like matrix that is associated with one unique set of QC samples and processed together as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS) and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Check LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method blanks (MBs) are aliquots of matrix (i.e., HPLC water for liquid analyses; Ottawa sand for solid analyses) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is processed, or there is a change in reagents, an MB must be prepared. Concentrations of target analytes, if any, must be less than the analyte reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this requirement is not met, analyses must be halted and the source of the contamination found and corrected. See also QC Table.

As the analyst deems necessary, aliquots of solvent may be injected to clean the analytical system and demonstrate that it is free from contamination.

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below:

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

See QC Table for evaluation criteria.

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical

results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below:

$$\text{RPD} = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

See QC Table for evaluation criteria.

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%\text{R} = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

See QC Table for evaluation criteria.

9.6 SURROGATE RECOVERY AND ACCEPTANCE CRITERIA

Paragon uses the compound 1,4-dinitrobenzene as the surrogate for this method. Surrogates are selected for chemical structure and detection characteristics that are similar to the target analytes, but not so much so that it co-elutes with any of the single component targets. It should be noted, however, that because the surrogate is not a deuterated analog of a target analyte, as in GC/MS methods, it is not extracted with exactly the same efficiency as the target compounds. Therefore, surrogate recovery problems are not entirely representative of target analyte recoveries.

The %R of the surrogate is calculated (see equation shown for LCS recovery above) for all field and QC samples. If the recovery is outside QC limits, the

sample is reanalyzed to verify that analytical error was not the problem. If after re-injection the recovery is still out-of-control, initiate an NCR (SOP 928) to consult with the Project Manager (and client as needed), and apply the decided upon action.

9.7 A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses for each target analyte at a concentration level near to the capabilities of the method. The MDL study should be performed as needed, at a minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW8330. There are no known deviations from the method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 ***Samples containing explosive material may under no circumstances be heated in any fashion (e.g., boiling a solution; drying in an oven).***

11.1.2 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.3 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.4 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.5 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.6 All flammable compounds must be kept away from ignition sources.

11.1.7 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.8 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Any rinse waters used for rinsing syringes or other devices prior to

sample contact may be disposed of in the Aqueous Lab Waste.

11.2.2 The ACN-Water HPLC waste may be discarded into the ACN Waste Stream container.

11.2.3 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.4 The extract vials, associated extracts, and any PCB-contaminated debris that may contain PCBs in excess of 50ppm, shall be disposed of intact in the PCB Debris Waste.

11.2.5 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be removed or defaced prior to disposal.

12. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 8330, Revision 2, December 1996.

DOCUMENT REVISION HISTORY

7/23/06: LIMS program specification references strengthened; analytical columns used clarified; consumables list added; standards discussion revamped storage temperatures confirmed to reflect actual practice. DOCUMENT REVISION HISTORY Section added.

2/8/07: Format updated. References to RFs changed to CFs. STANDARDS section updated, ICV added to standards table. Calculations updated.

8/12/07: Calibration discussion further clarified, Section 8.3.3 and QC Table.

Analytical Method: SW8330	**Parameter:** Nitroaromatics and Nitroamines by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
Initial Calibration (ICAL); minimum 5-points, all analytes	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate If RSDs over calibrated range exceed 20%, first order linear regression (using a minimum of 5 ICAL points) may be applied; $r \geq 0.995$ Higher order regression fits may be applied if more than 6 ICAL points are used; $r^2 \geq 0.99$	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Initial Calibration Verification (ICV); conc. not equal to midpoint of calibration curve; second source	After each ICAL	If ≤15%, analyses may proceed	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8330 allows bracketing of 20 field sample analyses)	If ≤15%, analyses may proceed	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of variation	Whenever a new column is installed	Column and compound specific. Window is ±3x the standard deviation of the 3-injection average for the respective column Note that the ICV and CCV analyses are also used to	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms (refer also to RT Shift).

Analytical Method: SW8330	**Parameter:** Nitroaromatics and Nitroamines by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
		monitor RT drift	
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per each preparation batch of ≤20 samples of like matrix	See laboratory oir other applicable limits; recoveries for spiked compounds must be within these limits	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the

Analytical Method: SW8330	**Parameter:** Nitroaromatics and Nitroamines by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
			samples are within the extraction holding time, then initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per batch, not to exceed 20 samples of like matrix	See laboratory or other applicable limits; recoveries for spiked compounds should be within these advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per batch , not to exceed 20 samples of like matrix	See Matrix Spike information above for MSD recoveries. RPDs should not exceed value specified in LIMS program specification (typically 20%)	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers.
Surrogate Spike	All extractions including field and laboratory QC samples	See laboratory or other applicable limits; recoveries should be within these limits	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with surrogate recovery outside the QC limits with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if surrogate recovery in the associated MB and LCS is not within limits and the samples are

Analytical Method: SW8330	**Parameter:** Nitroaromatics and Nitroamines by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
			within the holding time, then re-extract and reanalyze all associated samples - if samples are beyond the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study; run at analyte concentrations near to the minimum detection capability of the method	As needed, at minimum, annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

_____A

daily calibration standard preparation form 410r7a.xls (03/01/05)

date_____ preparer_____ method-SW-846_**8330**_ SOP__**404**_ Rev___

primary source standard tracking #_____ expiration date_____

target compound conc._____µg/ml (5.0) surrogate conc._____µg/ml (5.0)

conc. µg/ml	dilution factor	acidified water µl required	acidified water µl actual	acetonitrile µl required	acetonitrile µl actual	standard µl required	standard µl actual
0.5	10	500		400		100	

10-fold dilution example calculation:
100µl = 0.1ml (0.1ml) X (5µg/ml) = 0.5µg
500µl + 400µl + 100µl = 1000µl = 1ml (0.5µg) / (1ml) = 0.5µg/ml

Instrument Name _____ **Paragon Analytics** Logbook No./Page _____ **B**

Date Analyzed _____ Operator _____ Method _____ SOP _____ Rev. _____ **Reviewed by / date** _____

Sequence File: C:\HPCHEM_____\SEQUENCE_____ ICAL Date _____ Processing Method _____

Data Path:
C:\HPCHEM_____\DATA_____ Date Archived _____

CH_3OH Lot # _____ H_2O Lot # _____ H_2O w H_2SO_4 Lot # _____ CH_3CN Lot # _____ Col. Type & Serial No. _____

Vial	Inst. Method	Data File	Sample Name	Rerun?	Comments

Comments: _____ Form 410r7b.xls (03/01/05)

Must Discard 30 Days from _____ (date printed)

ALS LABORATORY GROUP - FORT COLLINS
STANDARD OPERATING PROCEDURE 406 REVISION 14

TITLE: **EXTRACTABLE PETROLEUM HYDROCARBONS ANALYSIS BY GAS CHROMATOGRAPHY (TEPH, DRO)**

FORMS: **531** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2.12.09

QUALITY ASSURANCE MANAGER _____ DATE 2/12/09

LABORATORY MANAGER _____ for KOC DATE 2/12/09

HISTORY: Rev0, 2/11/92; Rev1, PCN #243, 7/15/94; Rev2, 12/12/95; Rev3, 7/19/96; Rev4, 2/01/99; Rev5, 6/15/99; Rev6, 2/17/00; Rev7, 1/15/02; Rev8, 3/2/02; Rev9, 3/14/03; Rev10, 2/25/04; Rev11, 11/22/04; Rev12, 9/1/06; Rev13, 7/18/08; Rev14, 2/12/09.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the determination of extractable petroleum hydrocarbons in aqueous and solid matrices, using analysis by gas chromatograph (GC) with flame ionization detection (FID). This basic GC-FID technique is comparable to analysis protocols such as SW-846 Method SW8015B or D, Cal LUFT, and various State-specific protocols such as FL-PRO.

Note that the various analytical protocols may define the quantitated hydrocarbon range differently. For example, Method SW8015B defines the alkane range corresponding to diesel range organics (DRO) as approximately C_{10} to C_{28}. The FL-PRO method defines the extractable petroleum hydrocarbon range of interest as C_8 to C_{40}. The following substances can be analyzed using this method:

diesel #1	mineral spirits
aviation jet fuel (JP-4)	miscellaneous extractable petroleum products
diesel #2	Stoddard solvent
jet fuel (JP-5)	motor oil

Analyst expertise is crucial to this method as multiple petroleum hydrocarbon patterns may be present in a sample. Also, pattern responses in environmental samples may differ from textbook characterizations because of weathering. The alkane range of hydrocarbons present in a sample is reported to the client if concentrations are greater than or equal to the reporting limit (RL).

2. SUMMARY

Concentrated sample extracts prepared via SOP 603 (e.g., SW8015, FL-PRO) and SOP 626 (e.g., SW3510, Cal LUFT), are injected into a GC-FID chromatographic system that is temperature programmed. Detector responses are recorded by a data acquisition system to facilitate processing of data. The total peak area from the designated petroleum hydrocarbon retention time window (RTW) is measured using baseline-to-baseline

integration. Quantitation is accomplished using the external standard method of quantitation. Performance of a surrogate (s) is also monitored. RLs are set at or above the concentration of the low standard incorporated into the calibration curve. Typically, both the amount and type of petroleum hydrocarbon observed are reported.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 ALSLG-FC's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALSLG-FC's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the handling or analysis of the samples. Any discrepancies found must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Interference from phthalate esters can be minimized by using plastic-free solvent containers and scrupulously cleaned glassware (SOP 334) that has been kiln-baked or solvent-rinsed prior to use. Use of low phthalate gloves, such as nitrile, may also be important. These practices are important both in the field and in the laboratory.

4.2 Column compensation may be used because the chromatographic conditions employed for extractable petroleum hydrocarbon analysis can result in significant column bleed and a resultant rise in the baseline, it is appropriate to perform a

subtraction of the column bleed from the area of the petroleum hydrocarbon chromatogram. A column comparison is performed on a dry run (no solvent injected, temperature program executed) to determine the area caused by column bleed. This area is subsequently stored by the GC system and used to correct the baseline for all associated standards and samples. This procedure is acceptable provided that the column bleed is consistent throughout the run. A consistent dry run or blank baseline confirms proper column compensation.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH (GC), AUTOSAMPLER, DETECTORS
Hewlett Packard (HP) 7673 Automated Injection System; HP 5890 Series II GC equipped with a flame ionization detector (FID), or equivalents

NOTE: An FID must be used because FID response is essentially proportional to the number of carbons and can, therefore, provide a useful total area for evaluation of total hydrocarbon concentration; other detectors will not produce adequate quantitative results.

5.2 COLUMN - Equivalent columns may also be used

J&W Capillary Column:	DB-5.625 # 200-0056*	30m x 0.250mm ID, 0.5µm film thickness

*J&W columns are available through Agilent, part numbers are Agilent numbers

5.3 DATA SYSTEM
Agilent EzChrome Elite, or equivalent

5.4 GASES - **Use only high purity gases!**
Helium - carrier gas
Hydrogen - to supply FID
Compressed Air - to supply FID

5.5 MEASURING DEVICES

5.5.1 Microsyringes, Hamilton Precision™ or equivalent, 1µL-1.0mL sizes

5.5.2 Top loading balance, capable of weighing to ±0.01g

5.5.3 Volumetric flasks, Class A with ground glass stoppers, 10-500mL sizes

5.6 GC CONSUMABLES

- Vials and caps, National Scientific #C4011-1 and # C4000-51B or equivalents
- Inlet seal, dual Vespel ring, 0.8mm, Restek #21243 or equivalent
- Septa, 11mm, Restek #20365 or equivalent
- O-ring, graphite, 6.5mm, Restek #20299 or equivalent
- Liner, splitless, 4mm ID, Restek #20799-214.5 or equivalent
- Glass wool, deactivated, Restek #20789 or equivalent
- Gold seal, Restek #21306 or equivalent

- Vespel/graphite ferrule (detector), Restek #20221 or equivalent
- Compact Vespel/graphite ferrule, Restek #20249 or #20264 or equivalent
- Graphite ferrules, various sizes

6. REAGENTS

6.1 SOLVENTS - **Only chromatography grade or higher quality solvents may be used**

n-hexane, Burdick & Jackson #216-4 or equivalent

methanol, Burdick & Jackson #230-4 or equivalent

methylene chloride, Burdick & Jackson #299-4 or equivalent

6.2 STANDARDS

NOTE: All standards are maintained per PAR SOP 300

6.2.1 Target analyte stock standards are generally acquired through locally available commercial sources. Two independent sources (first, second) of target analyte stock standards are needed. To set correct integration windows, ALSLG-FC currently makes use of a TRPH Standard (Ultra-Scientific TRPH Florida Standard or equivalent) that contains even numbered alkanes C_8-C_{40}. Alternate standards may be used if required by the LIMS program specification.

A non-target analyte surrogate stock standard is also purchased. The surrogate used in this procedure is o-terphenyl.

Unopened stock standards are valid until the manufacturer's expiration date, and may be stored at room temperature in flame-sealed ampules, if recommended by the manufacturer. After ampules are opened, stock standards are transferred to Teflon™-lined septum seal vials for storage. Opened stock standards and prepared intermediate standards are stored in the freezer (dark, ˉ10 to ˉ20°C). Open stock standards expire 3 months from opening (preparation), or per the manufacturer's expiration date (whichever is sooner). Intermediate standards must be made monthly. Standards may be replaced sooner if laboratory QC analyses or other factors indicate deterioration.

6.2.2 Intermediate standards are made by diluting an appropriate aliquot of stock standard to a specific volume using hexane, and are stored in Teflon™-sealed vials. First source target analyte materials are used to create calibration, continuing calibration verification (CCV) and quality control (QC) sample spike standards (used by the Organics Extraction Group). Second source target analyte materials are used to create the initial calibration verification (ICV) solution.

6.2.3 The intermediate target analyte standards are further diluted using an appropriate solvent (hexane) to create working standards. These working calibration/check standards (ICAL, ICV, CCV) are prepared

on the day of use and documented in the analytical run log (Form 531). They must contain all target analytes and the surrogate. A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.2.4 Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

6.2.5 All stock and intermediate standards are documented in ALSLG-FC's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials, and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Aqueous samples are collected in 1L amber-glass bottles with screw-top caps equipped with Teflon™ liners. Aqueous samples are usually preserved in the field immediately after sampling with the addition of enough hydrochloric acid (HCl) to adjust to pH<2. The samples must be maintained chilled (4±2°C).

7.3 Soil samples are collected in wide-mouth glass containers with Teflon™-lined lids. Samples are not chemically preserved and must be maintained chilled (4±2°C).

7.4 The holding time to extraction for aqueous extractable petroleum hydrocarbon samples is 7 days (unpreserved) or 14 days (preserved with HCl) from collection. The hold time to extraction for solid matrix extractable petroleum hydrocarbon samples is 14 days from collection. Consult the LIMS program specification as other hold times may be specified.

7.5 Extracts, from liquid or solid samples, must be maintained chilled (4±2°C) and analyzed within 40 days of preparation.

8. PROCEDURES

8.1 TYPICAL GC CONDITIONS

Note that conditions may be altered to improve resolution, or simplified if a single product, such as motor oil, is to be analyzed.

Carrier Gas Flow Rate:	3-5mL/min
FID H_2 Flow Rate:	30mL/min
FID Air Flow Rate:	350mL/min
Injector Temperature:	320°C

Initial Oven Temperature:	60°C for 3min
Oven Ramp:	17°C/min to 320°C
Hold:	320°C for 15min
FID Temperature:	320°C

8.2 CHROMATOGRAPHIC MAINTENANCE

8.2.1 Reagent blanks are an injection of solvent analyzed to show that the analytical system is free from contamination. They may be injected following samples of unusually high concentration to check the status of the analytical system and to facilitate re-equilibration of the system. Reagent blank results should be below the RL.

8.2.2 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Oxidized columns will exhibit baselines that rise rapidly during temperature programming.

8.2.3 Peak tailing for all components will be exacerbated by a dirty injector.

8.2.4 If the instrument has sat idle for a period of time, it may be primed with one or more injections of hexane prior to initiation of the acquisition sequence.

8.3 INITIAL CALIBRATION

8.3.1 Create multi-concentration level (i.e., spanning the calibration range) DRO, or other window-defining standard such as motor oil, using hexane or methylene chloride per methods SW8000C and SW8015D. Hexane is less volatile than methylene chloride, hence standards prepared in hexane are less prone to concentration. Each standard must contain the surrogate. A minimum of five concentration levels are required, typically seven standards are prepared, as shown below:

Level	Petroleum Hydrocarbon Concentration (µg/mL)	Surrogate Concentration (µg/mL)
7	5000	500
6	2500	250
5	1000	100
4	500	50
3	100	10
2	50	5
1	20	2

ICV	100	10
CCV	500	50

8.3.2 Typically 1µL of standard or field or QC sample extract is injected by automated injector for analysis. TEPH is identified by pattern recognition.

8.3.3 For each data file, quantitation is accomplished via the external standard method of quantitation using baseline-to-baseline integration across the hydrocarbon range of interest. The surrogate area is subtracted from the total area integrated in order to obtain the area associated with the injected extract.

8.3.4 A calibration factor (CF) for each standard is calculated as follows:

$$CF = \frac{\text{TEPH Area Total}}{\text{Concentration of TEPH Injected (mg/mL)}}$$

If the CFs over the working range of the detector are constant (i.e., ≤20% RSD), then response can be assumed to be invariant and the average (mean) CF may be used to quantitate sample content. Relative Standard Deviation (RSD) is calculated as:

$$\text{RSD (\%)} = \frac{\text{Standard Deviation (SD)}}{\text{Average (mean) CF}} \times 100$$

When RSD over the calibration range is >20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be >0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit", with perfect fit being a value of 1.0. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW8000C. However, a quadratic regression should not be used to compensate for detector saturation.

Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV

are identical to those of CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or near the midpoint of the initial calibration. Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

NOTE: Method SW8015D specifies that the CCV must be analyzed at the beginning of each 12-hour shift (allows approximately 20 samples to be analyzed between CCVs). ALSLG-FC commonly analyzes 10 samples between CCVs to reduce the amount of repeat injections, should they be required.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when all compounds are within 20%D. If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed. So long as CCV analyses yield compliant results, and other QC samples are analyzed as required, the series of ten sample analyses bracketed before and after by successful CCV analyses may continue indefinitely.

NOTE: When analyzing samples by the Cal LUFT method, for California compliance reporting, the CCV criteria of $\pm$10%D **must** be observed (electronically controlled via the specific test code used in association with ALSLG-FC's LIMS program specification system).

8.6 RETENTION TIME WINDOWS

8.6.1 Evaluate bracketing standards and set the retention time window (RTW) to include the designated petroleum hydrocarbon pattern. The standard contains the even numbered aliphatic hydrocarbons from C_8 – C_{40}. The default window is typically set from C_{10} through C_{32}, and needs to be adjusted to meet project requirements.

8.6.2 RTWs are used to define the integration envelope for quantifying various products in samples. Peak area integration will begin

immediately prior to elution of the first chromatographic peak of interest and will stop after the last peak of interest.

8.6.3 The experience of the analyst weighs heavily in interpretation of the chromatogram. Environmental samples may contain more than one type of product, and loss of light end components may indicate weathering or poor extraction techniques.

8.7 SAMPLE ANALYSIS, IDENTIFICATION, CALCULATIONS, REPORTING

8.7.1 Prior to initiating acquisition, ensure that that there is an adequate supply of gases and rinse solvents to complete the run.

8.7.2 When necessary, sample extracts are diluted to maintain response within the linear range.

8.7.3 If the average CF is used for quantitation, the sample concentration is calculated using the following equation:

$$\text{Concentration}_{(\text{ug/L, ug/kg})} = \frac{(A_x)(V_t)(DF)}{(\text{Average CF})(V_s \text{ or } W_s)}$$

where:

A_x = analyte response (area units)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Average CF = average calibration factor (area/concentration in mg/mL)

V_s or W_s = volume or weight of sample extracted (L or kg)

8.7.4 Sample concentration, in ppm (mg/L or mg/kg), is calculated using the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte (TEPH, ppm)

y = intercept for analyte instrument response (area)

b = calculated intercept (area)

m = calculated slope of the line (area/concentration in mg/mL)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (L or kg)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with

one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All QC samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specification for additional or alternative requirements.

9.2 BLANKS

MBs are aliquots of matrix (i.e., organic-free water for liquids, Ottawa sand for solids) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the RL, or as otherwise prescribed in the LIMS program specification. If this criterion is not achieved, then analyses must be halted and the source of the contamination found and corrected.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

MSs consist of field samples into which known concentrations of target analytes are spiked and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. See QC Table for evaluation criteria. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

NOTE: Typically, one MS/MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate the MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.6 SURROGATE RECOVERY

The %R of the surrogate is calculated (see equation shown for LCS recovery above) for all field and QC samples. See QC Table for evaluation criteria.

9.7 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicate analyses of an extractable petroleum hydrocarbon standard at a concentration level near the sensitivity limit of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of SW8015D; there are no known deviations from the method. Cal LUFT method criteria are also met with the following exception: Cal LUFT specifies a %D criteria of ±10% for daily calibration verification. ALSLG-FC defaults to the criteria listed in SW8015D of ±20% D, unless client or regulatory contractual needs dictate otherwise. ALSLG-FC notes that the SW-846 suggested carbon range for diesel (C_{10} to C_{28}) may be modified to meet our client's requirements.

11. SAFETY HAZARDS AND WASTE

11.1 SAFETY HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents

and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.1.8 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Any methanol, hexane or other nonhalogenated organic solvents that has not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste.

11.2.2 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

11.2.4 Any rinse waters used for rinsing syringes or other devices prior to contact with samples must be disposed of in the Aqueous Lab Waste.

11.2.5 Halogenated wastes (if any) are disposed of in the halogenated waste stream.

12. REFERENCES

12.1 EPA SW-846, Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, 3rd edition, Final Update III, "Method 8015D", June 2003.

12.2 EPA SW-846, Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, 3rd edition, Final Update III, "Method 8000C", Revision 3. March 2003.

12.3 California LUFT Field Manual, October 1989 update.

12.4 "Method for Determination of Petroleum Range Organics (FL-PRO)", Revision 1. Florida Department of Environmental Protection. November, 1995.

12.5 EPA SW-846, Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, 3rd edition, Final Update III, "Method 3510C", Revision 3, December 1996.

12.6 EPA SW-846, Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, 3rd edition, Final Update III, "Method 3540C", Revision 3, December 1996.

12.7 EPA SW-846, Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, 3rd edition, Final Update III, "Method 3550B", Revision 2, December 1996.

DOCUMENT REVISION HISTORY

9/1/06: LIMS program specification language strengthened. Calculations reformatted. DOCUMENT REVISION HISTORY section added.

7/18/08: Corrections to Section 2 SUMMARY made. Methanol is not used and was removed from the reagents list, Section 6. No technical revisions were made.

12/18/08: Section 8.6 amended to establish typical DRO quantitation range as C_{10}-C_{38}.

2/12/09: Changed Title, Sections 1 and 2, as needed throughout, and QC Table Method Reference header to indicate petroleum hydrocarbons more generically. Added SW8015D and FL-PRO to REFERENCES. Added Appendix A (FL-PRO).

Analytical Method: Extractable Petroleum Hydrocarbons by GC-FID	**Parameter:** Total Extractable Petroleum Hydrocarbons Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum 5-point, all analytes	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate Calculate linear regression (not forced through origin); use for quantitation if coefficient of determination (r^2) ≥0.99 or Calculate quadratic regression (minimum of six points required); use for quantitation if COD ≥0.99	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Initial Calibration Verification (ICV); conc. not equal conc. to midpoint of calibration curve; second source	After each ICAL	≤20%D of each compound	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8015B allows bracketing of 20 field sample analyses)	≤20%D of each compound **NOTE:** Cal LUFT method requirements state that analyses may continue only when CCV is ±10%D. Check the LIMS Project Specification to ensure that appropriate criteria are applied.	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. - Samples analyzed before and after a failed CCV (bracketing with acceptable calibration fails) must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV (bracketed by acceptable CCVs) will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition..
Retention Time Window (RTW); set to include the designated extractable petroleum	Whenever a new column is installed or if a new extractable petroleum hydrocarbon	Brackets appropriate hydrocarbon elution range Note that the ICV and CCV analyses are also used to	Perform system maintenance to correct drift. Experience of analyst weighs heavily in interpretation of chromatograms.

Analytical Method: Extractable Petroleum Hydrocarbons by GC-FID	**Parameter:** Total Extractable Petroleum Hydrocarbons Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
hydrocarbon reference standard	range is required	monitor RT drift	
Retention Time Shift; RT of pattern in CCV is evaluated against the midpoint of the ICAL or the preceding CCV	Each CCV; RT of analytes evaluated against the ICAL or preceding CCV to ensure that the designated extractable petroleum hydrocarbon range has not significantly shifted	Instrument performance supports accurate quantitation of TEPH	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition.
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be

Analytical Method: Extractable Petroleum Hydrocarbons by GC-FID	**Parameter:** Total Extractable Petroleum Hydrocarbons Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; see Matrix Spike information above for MSD recoveries RPDs should be within advisory limits	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. Note in narrative. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers.
Surrogate Spike	All field and laboratory QC samples	See laboratory limits; recoveries should be within current limits alternative criteria as defined in the LIMS program specifications may apply	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if surrogate recovery in the associated MB is not within limits and the samples are within the holding time, then re-extract and reanalyze all associated samples - if samples are beyond the holding time, then contact the PM via an

Analytical Method: Extractable Petroleum Hydrocarbons by GC-FID	**Parameter:** Total Extractable Petroleum Hydrocarbons Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

APPENDIX A

EXTRACTABLE PETROLEUM HYDROCARBON ANALYSIS VIA THE FL-PRO METHOD

1. SCOPE AND APPLICATION

SUMMARY

The procedural particulars given in this Appendix supercede the guidance given in the main body of SOP 406. The procedures depicted in this Appendix are applicable to the GC-FID analysis of aqueous and solid matrix sample extracts using the Florida Residual Petroleum Organic Method (FL-PRO).

The FL-PRO Method is designed to measure concentrations of extractable petroleum hydrocarbons in water and soil in the alkane range of C_8-C_{40}. Other organic compounds, including chlorinated hydrocarbons, phenols, and phthalate esters, are measurable by this procedure, thus the resultant EPH results include these compounds.

The MDL is approximately 0.1 mg/L for water, and 4 mg/kg for soil (each laboratory must establish a laboratory-specific MDL for all matrices prior to analyzing any sample).

2. RESPONSIBILITIES
INTERFERENCES
APPARATUS AND MATERIALS

Refer to SOP 406 main text.

3. REAGENTS, SOLVENTS, STANDARDS

Note that both the surrogate and spike standard is specific to this test. The surrogate standard contains o-terphenyl at 100ug/mL, and nonatriacontane at 600ug/mL (in acetone). [These concentrations are 2X those specified in the Method (Section 7.4.1), which directs the addition of 2mL surrogate solution. ALSLG-FC will add 1mL, therefore the doubling in concentration.]

The QC spike solution contains even-numbered straight-chain alkanes from C_8 to C_{40}. The water spiking solution should be 5000ug/mL Total PHS (Petroleum Hydrocarbon Standard), and the soil spike should be 3000ug/mL Total PHS. 1mL of spike will give the required concentrations in the sample.(Method Sections 7.4.3, 7.4.4). Acceptance criteria for surrogate, LCS, and MS recoveries are method criteria and can be found in the Method (Table 2, p.28), or the LIMS test code (see SOP 3.4 for a discussion of ALSLG-FC LIMS program specifications).

4. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Certain sampling considerations apply, refer to Method for more details.
Water samples must be acidified to pH<2 with HCl or H_2SO_4.
All samples must be stored at 4±2°C until extraction.
Extraction must be performed within 7 days of collection for aqueous samples, and within 14 days of collection for solid samples.
All analyses must be performed within 40 days of extraction.

5. CALIBRATION

5.1. INSTRUMENT CONDITIONS

Recommended instrument conditions are given in Method Section 9.2.1. Other conditions may by used as long as satisfactory performance is achieved (C_8 must be resolved from the solvent front, and the surrogate must be separated from the petroleum hydrocarbon components). Refer to Method Sections 9.2.1 through 9.2.2.3 for further details.

5.2. RETENTION TIME WINDOWS (RTWs)

Method Sections 9.3.2.2 through 9.4.3 direct that RTWs must be established on each GC column by making 3 injections of the method standard throughout the course of a 72-hour period. The standard deviation of the absolute RTs for the two surrogates, and for the C_8 and C_{40} peaks are then calculated, and the RTW for individual peaks is established as the mean RT +/- 3 times the standard deviation. Instead, ALSLG-FC utilizes the results of the first daily CCV run prior to sample analysis, and establishes the hydrocarbon region of interest window as just prior to the RT of the first designated peak and just beyond the RT of the last designated peak of interest.

5.3. INITIAL CALIBRATION

5.3.1. For both qualifying (setting retention times) and quantifying, this Method (Section 3.2), uses a 17-component mix of (even numbered) straight-chain alkanes from C_8 thru C_{40} (ALSLG-FC already uses this standard for setting retention time window).

5.3.2. Although the Method (Section 7.4.3) states that surrogates are to be kept at constant concentration in the different ICAL points (50ug/mL for oTP and 300ug/mL for C_{39}), ALSLG-FC will vary their concentrations (like targets) in order to be able to quantitate surrogate recoveries in extracts that have to be diluted.

5.3.3. Note that a blank must be analyzed with the ICAL (Method Section 9.3.1). The blank may be analyzed before the ICAL to demonstrate that the system is free of interferences.

5.3.4. Per Method Section 9.3.1, integration should be continuous and encompass all peaks (excluding surrogates) beginning from a point just prior to elution of the C_8 peak and ending just subsequent to elution of the C_{40} peak.

5.3.5. Initial calibration may be by average calibration factor (%RSD must be **≤20%),** or linear regression (correlation coefficient, r, must be **≥0.995**). Note that although this Method (Sections 9.3.1.1 through 9.3.1.2) does not contain provision for a quadratic regression, ALSLG-FC may use a quadratic fit if it best represents the data (quadratic fit will NOT be used to compensate for detector saturation).

5.3.6. The Initial Calibration Verification (ICV) standard (2nd source), should be prepared at the midpoint of the curve, and must quantitate within **20%** of the expected value. (Method Section 9.3.1.3).

5.4. CONTINUING CALIBRATION

The Continuing Calibration Verification (CCV) standard should be prepared at the midpoint of the curve, and must quantitate within **25%** of the expected value. Although the Method (Sections 9.3.2; 9.3.2.1; 9.5.3) states that a CCV's failure to meet this criteria automatically necessitates analysis of a new ICAL, ALSLG-FC may analyze a 2nd CCV as a precaution against a bad injection in the case of the first (if the 2nd CCV passes critieria, analyses may continue).

RTs for the surrogates and C_8 and C_{40} should be within the established RTWs for these 4 compounds. The windows will be 'reset' on these four compounds, and the 'reset' windows will apply to all field, QC, and standard analyses in that analytical sequence. (see Method Section 9.3.2.2).

CCVs should be analyzed at the beginning and end of each analytical sequence. Additionally, a CCV should be analyzed every 10 field or QC samples (solvent blanks excluded). The concentration of the CCVs should vary, based on *expected* concentrations of target in the samples. At least one of the CCVs should be at a level 1 to 2 times the RL as a verification of sensitivity. (see Method Section 9.5.2).

6. ANALYSIS

Dilutions may be performed as necessary to put the chromatographic envelope within the linear range of the method (dependent in part upon column type, detector sensitivity and injection volume; typically 170-17,000ng on column of Total PHS). Each laboratory must establish and document the linear range for the instrument(s) in use. A Dilution Technique is specified, to be used for product or waste samples which are soluble in Methylene Chloride (refer to Method for further details).

Per Method Section 9.5.4, a dichloromethane blank must be run in every sequence to determine the area generated from normal baseline bleed. This blank is integrated in the same manner as standards and samples, and the calculated quantitation should be less than the MDL of the method.

Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for instrument contamination.

7. QUALITY CONTROL

See Method (Table 2, p.28), or the LIMS test code.

8. DEVIATIONS FROM THE METHOD

No technical deviations.

9. HEALTH, SAFETY, AND WASTE DISPOSAL

See SOP 406 main text.

10. REFERENCES

"Method for Determination of Petroleum Range Organics (FL-PRO)", Revision 1. Florida Department of Environmental Protection. November, 1995.

DOCUMENT REVISION HISTORY

2/12/09: New

Must Discard 30 Days from _______ (date printed)

Instrument Name __________ **Paragon Analytics** Logbook No./Page ______________

Sequence File: C:\HPCHEM___\SEQUENCE_________________ Date Analyzed __________ Operator ______ GC Method _________

Data Path: C:\HPCHEM___\DATA_____________ Analytical Method _________ SOP ______ Rev. ___

Hexane Lot _______ Dichloromethane Lot _______ **Reviewed by / date** ___________________ Form 531r2.xls (9/14/2001)

Vial	Data File	Method	Sample Name	Comments	rr?

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 407 REVISION 8

TITLE: **ORGANOPHOSPHOROUS COMPOUNDS BY GAS CHROMATOGRAPHY -- METHODS SW8141A AND EPA 614**

FORMS: **530 (use current iteration)**

APPROVED BY:
TECHNICAL MANAGER Dag Shenerman DATE 08/4/06
QUALITY ASSURANCE MANAGER Del Sabert DATE 8/4/06
LABORATORY MANAGER [signature] DATE 8-4-06

HISTORY: Rev0, 8/4/92 and 4/13/94 (updated format); Rev1, PCN #494, 5/30/95; Rev2, 3/25/96; Rev3, 6/12/96; Rev4, 6/24/99; Rev5, 11/22/02; Rev6, 3/6/04; Rev7, 3/13/06; Rev8, 7/24/06.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- SW8141A and EPA 614, are used to determine the concentrations of organophosphorous pesticides in extracts from liquid or solid matrices. Method SW8141A addresses liquid and solid matrices and Method EPA 614 addresses liquid matrices (municipal and industrial wastewater). Currently, Paragon analyzes the following compounds using this SOP:

Azinphos methyl	Merphos (including its degradation product)
Chlorpyrifos	Methyl parathion
Coumaphos	Mevinphos
Demeton (total o- and s-)	Naled
Diazinon	Phorate
Dichlorovos	Ronnel
Disulfoton	Tetrachlovinphos
Ethoprop	Tokuthion
Fensulfothion	Trichloronate
Fenthion	Sulprofos
Malathion	

Other compounds may be analyzed if successful method detection limit (MDL) and demonstration of capability (DOC) studies are performed.

2. SUMMARY

Samples are extracted and the extracts concentrated and solvent exchanged using appropriate Paragon Analytics SOPs (i.e., PAR 617, 625, 622, 607, 637). The extracts are injected into a gas chromatograph (GC) containing a sample splitter and two columns of varying selectivity (i.e., dissimilar RT elution properties). The target analytes are

separated in the columns and detected by two flame photometric detectors (FPDs). This chromatography system allows tentative identification by one column and confirmation by the other column to be performed simultaneously. Quantitation is performed using the best column for each analyte. The analyst considers performance data such as separation of interferences, calibration performance and matrix spike results in selecting the primary quantitation column for each analyte detected and reported. If results from both columns are comparable, the highest result is reported.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon’s standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Use of flame photometric detectors in phosphorous mode will minimize interferences from materials that do not contain phosphorous. Method SW8141A states that elemental sulfur may interfere with the determination of certain organophosphorous compounds by flame photometric gas chromatography.

4.2 If a sulfur cleanup is employed, only the tetrabutylammonium (TBA)-sulfite option should be chosen, because copper may destroy organophosphorous pesticides. The stability of each analyte must be tested to ensure that the recovery from the TBA-sulfite cleanup step is not less than 85%.

4.3 Analytical difficulties encountered for target analytes include:

4.3.1 The water solubility of dichlorvos is 10g/L at 20°C and recovery may be poor from aqueous solutions.

4.3.2 Naled is converted to dichlorvos in water or by injection on column by debromination. This reaction may also occur during sample extraction and preparation. The extent of debromination will depend upon the nature of the matrix being analyzed. The analyst must consider the potential for debromination when naled is to be determined or when dichlorovos is detected.

4.3.3 Trichlorfon can rearrange by hydrodechlorination in acidic, neutral, or basic media to form dichlorvos and hydrochloric acid. If this method is to be used for the determination of organophosphates and the presence of trichlorfon is known, the analyst should be aware of the possibility of rearrangement to dichlorvos if dichlorovos is detected.

4.3.4 Demeton (Systox) is a mixture of two compounds - O, O-diethyl O- [2-(ethylthio) ethyl] phosphorothioate (demeton-O) and O, O-diethyl S-[2-(ethylthio) ethyl] phosphorothioate (demeton-S). Two peaks are observed in demeton standards. The two peaks correspond to the two isomers.

4.3.5 Merphos (tributyl phosphorotrithioite) is readily oxidized to its phosphorotrithioate (merphos oxone). Chromatographic analysis of merphos almost always results in two peaks (unoxidized Merphos elutes first). As the relative amounts of oxidation of the sample and the standard are probably different, quantitation based on the sum of both peaks is most appropriate.

4.3.6 Many analytes will degrade on reactive sites in the chromatographic system. Analysts must ensure that injectors and splitters are free from contamination. Columns should be installed and maintained properly.

4.4 Interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that leads to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the condition of the analysis by analyzing reagent blanks with every batch of 20 or fewer field samples. Because

the FPD with P filter is an element-specific detector, the probability of non-target contamination is minimal.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH (GC), AUTOSAMPLER AND DETECTORS
Hewlett Packard (HP) 5890 Series II GC equipped with HP 7673A autosampler and dual FPD detectors (complete with accessories for on-column or split/splitless injection), or equivalents

5.2 CHROMATOGRAPHIC DATA ACQUISITION AND PROCESSING SYSTEM
Hewlett Packard ChemStation (Enviroquant™), or equivalent

5.3 COLUMNS - Equivalent columns may also be used

Restek Column: RTX-1 #10139 (30m x 0.32mm ID, 0.5µm film thickness)
Restek Column: RTX-OP Pesticides #11239 (30m x 0.32mm ID, 0.5µm film thickness)

5.4 GASES - ultra high purity (99.999%)
Helium - carrier gas
Nitrogen - make-up
Air -detector
Hydrogen -detector

5.5 MEASURING DEVICES
Syringes - 10µL-1000µL
Volumetric flasks, Class A with stoppers, 10mL-100mL

5.6 GC CONSUMABLES

- Vials - National Scientific C4011-1, or equivalent
- Caps - National Scientific C4000-51B, or equivalent
- Inlet Seals, dual Vespel ring - Restek 0.8mm #21243, or equivalent
- Septa, 11mm - Restek #20365 or equivalent
- O-ring, graphite, 6.5mm - Restek #20299, or equivalent
- O-ring, Viton - Restek #20377, or equivalent
- Liner, splitless, 4mm ID - Restek #20799-214.5, or equivalent
- Glass Wool, deactivated - Restek #20789, or equivalent
- Gold Seal - Restek #21306, or equivalent
- Universal Presstight Y - Restek #20469, or equivalent
- Vespel/Graphite Ferrule (detector) - Restek #20221, or equivalent
- Compact Vespel/Graphite Ferrule - Restek #20249, or equivalent
- Graphite Ferrules - various sizes

- Split Vent Trap (SW8081) - Agilent RDT-1023, or equivalent

6. REAGENTS

6.1 SOLVENTS - Only pesticide residue grade or equivalent may be used!

Hexane (C_6H_{14}), Burdick and Jackson #216-4, or equivalent

Methanol (CH_3OH, MeOH), Burdick and Jackson #230-4, or equivalent

6.2 STANDARDS

6.2.1 All standards are maintained per PAR SOP 300, which supercedes any guidance in this SOP. Unopened stock standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules, if recommended by the manufacturer. Generally after opening ampules, the standards for this procedure are stored in the freezer (-10--20°C), in PTFE-capped, or equivalent, vials. Opened stock standards and intermediate standards expire six months from opening (preparation) or per the manufacturer's expiration date (whichever is sooner). Standards may be replaced sooner if laboratory quality control (QC) analyses or other factors indicate deterioration.

6.2.2 Two independent sources of commercial stock standards are required for target analytes. These certified stock standards are purchased from suitable vendors. First source materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards. Second source materials are used to create the initial calibration verification (ICV) solution. A (non-target analyte) surrogate stock standard is also purchased. The surrogate used for this method is triphenylphosphate. Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

An appropriate volume of stock standard is diluted (in hexane) to a specific volume to create intermediate standards (the QC sample and surrogate spike standards, used by the Organics Extraction Group, are intermediate standards). The intermediate calibration standards are further diluted to volume using an appropriate solvent to create working standards. Working standards are prepared on the day of use and documented in the analytical run log (Form 530). A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.2.3 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures

traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Aqueous samples must be collected in amber glass containers (generally 1000mL) with Teflon™-lined lids. Samples must be maintained at 4±2°C and extracted within 7 days of collection. Additionally, samples for EPA Method 614 may need to have pH adjusted to be between 5 and 8, using sodium hydroxide or sulfuric acid solution, upon receipt.

7.3 Solid samples are collected in wide-mouth glass containers with Teflon™-lined lids. Solid samples are not chemically preserved and must be maintained at 4±2°C. Solid samples must be extracted within 14 days of collection.

7.4 Extracts, from liquid or solid samples, must be maintained between 4±2°C and analyzed within 40 days of preparation.

8. PROCEDURE

8.1 TYPICAL GC OPERATING CONDITIONS

Carrier gas:	Helium
Hydrogen (detector fuel gas)	75mL/min
Air (detector oxidizing gas)	100mL/min
Injection port temperature	210°C
Injection volume	3µL
Detector temperatures	275°C
Initial oven temperature	105°C, hold 1min
Purge	On, 1min
Initial oven ramp	20°C/min to 185°C, hold 5min
2nd oven ramp	2°C/min to 205°C, hold 2min
3rd ramp	20°C/min to 300°C, hold 8.25min

8.2 CHROMATOGRAPHIC MAINTENANCE

8.2.1 Dual columns are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector. Reattach the columns after cleanly cutting off at least two loops from the injection port side of the column using a capillary cutting tool or scribe. The accumulation of high boiling residues may change split ratios between dual columns and thereby change calibration factors. Clip a loop from the guard column or replace as necessary.

8.2.2 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Polar columns (including DB-210, DB-1701 and DB-608) are more prone to oxidation. Oxidized columns will exhibit baselines that rise rapidly during temperature programming.

8.2.3 Peak tailing for all components will be exacerbated by dirty injectors, dirty guard columns, and dirty glass Y's. Components such as fensulfothion, naled, methyl azinphos, dimethoate, and triphenyl phosphate are good indicators of system performance.

8.2.4 FPDs may be susceptible to stray light in the photomultiplier tube compartment. This stray light will decrease the sensitivity and the linearity of the detector. Analysts may check for leaks by initiating an analysis is a dark room and turning on the lights. A shift in the baseline indicates that light may be leaking into the photomultiplier tube compartment. Additional shielding should be applied to eliminate light leaks and minimize stray light interference.

8.2.5 FPDs use a flame to generate a response. Flow rates of air and hydrogen should be optimized to give a sensitive, but linear detector response for target analytes.

8.2.6 If the instrument has sat idle for a period of time, it may be primed with one or more injections of the CCV prior to analysis of the CCV for the acquisition sequence.

8.3 INITIAL CALIBRATION

8.3.1 Prepare a minimum of 5 concentrations of calibration standards (generally 8 or 9 are used), defining the linear range of the detector (SW8141A). Fewer calibration levels are required by EPA 614, but the use of 8 or 9 calibration levels is recommended. Create calibration standards by diluting aliquots of the intermediate calibration standard using hexane. Each ICAL standard must include all target analytes and the surrogate (at a level similar to the target analytes). The typical range of the calibration is 50ng/mL to 10000ng/mL. The lowest concentration standard shall be at a level at or below the reporting limit (RL) of each analyte. Not all compounds can be detected at the lowest levels of the calibration. Reporting limits are higher for compounds that do not respond well and cannot be detected in the lowest calibration standards. The mid-range calibration standard is used for continuing calibration verification (CCV). A typical calibration sequence and preparation steps are shown below in Table 1.

TABLE 1
CALIBRATION STANDARDS

Working Standard	Hexane (µL)	10,000 PPB Primary Standard (µL)	Standard Concentration (µg/L)
ICAL Level 1 (100%)	0	500	10,000
ICAL Level 2 (80%)	100	400	8,000
ICAL Level 3 (60%)	200	300	6,000
ICAL Level 4 (50%)	250	250	5,000
ICAL Level 5 (40%)	300	200	4,000
ICAL Level 6 (20%)	400	100	2,000
ICAL Level 7 (10%)	450	50	1,000
ICAL Level 8 (5%)	475	25	500
ICAL Level 9 (0.5%) (diazinon only)	995	5	50
2nd source ICV (40%)	300	200	4,000
CCV (50%)	250	250	5,000

8.3.2 Inject and analyze 1µL of each calibration standard. Each data file quantitation is accomplished via the external standard method of quantitation. Analyte Calibration Factors (CFs) are calculated as follows:

$$CF = \frac{\text{Selected Peak Areas}}{\text{Mass of Analyte Injected On-Column (ng)}}$$

If the CFs over the working range of the detector are constant (i.e., ≤20% RSD), then response can be assumed to be invariant and the average (mean) CF may be used to quantitate sample content. Relative Standard Deviation (RSD) is calculated as:

$$RSD\ (\%) = \frac{\text{Standard Deviation (SD)}}{\text{Average (mean) CF}} \times 100$$

When RSD over the calibration range is >20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The type of curve fit applied should be chosen to best represent the data. The regression calculation will yield a coefficient of determination (r2 value) that must be >0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit" with perfect fit being a value of 1.0. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of

6 points, following the guidelines in SW-846 Method 8000. A quadratic regression should not be used to compensate for detector saturation.

Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV are identical to those of CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is near the midpoint of the initial calibration. Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

NOTE: Method SW8141A allows 20 samples to be analyzed between CCVs. Paragon commonly analyzes 10 samples between CCVs to reduce the amount of repeat injections.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when all compounds are within 15%D or when the average of the %Ds for all compounds is $\leq$15% (individual compounds that exceeded 15% are noted in the data package narrative). If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

8.6 RETENTION TIME WINDOWS

For GC methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used to compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a

mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (σ) of the absolute retention time yielded for each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time $\pm 3\sigma$, such that the Upper Limit = $+3\sigma$ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time drift). Sample matrices may cause drift that requires further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system.

8.7 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATIONS, REPORTING)
A constant volume, generally 1µL of each standard, blank, QC or field sample extract is directly injected into the GC via the automated injector. Sample extracts are diluted to maintain response within the linear range when necessary. All prepared extracts contain the surrogate (see Section 9). Extract concentration and sample concentration are determined as discussed below.

8.7.1 Note that Paragon employs a sample splitter that facilitates simultaneous dual column injections; therefore, both columns are calibrated in the same manner and either column may serve as the column for quantitation.

8.7.2 Tentative identification occurs when a peak from a sample extract falls within the RTW of one column. If the peak also falls within the RTW of the second column, then the analyte's presence has been confirmed. Quantitation is calculated from both column responses and the best result is reported. The analyst considers performance data such as separation of interferences, calibration performance and matrix spike results in selecting the quantitation column for each analyte detected and reported. If there are interferences present on one column, these need to be documented by printouts of that region of the chromatogram; the lower (i.e., other column's) results may be reported in this case. If results from both columns are of comparable quality, the higher concentration is reported (per SW8000).

8.7.3 Sample concentration is calculated using the equation of the linear curve generated during initial calibration (i.e., $y = mx + b$), as follows:

$$x = \frac{(y - b)\,(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte

y = analyte instrument response (area units)

b = calculated intercept

m = calculated slope of the line

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (mL or g)

If the average CF is used for quantitation, the sample concentration is calculated using the following equation:

$$\text{Concentration}_{(ug/L,\ ug/kg)} = \frac{(A_x)(V_t)(DF)}{(\text{Average CF})(V_s \text{ or } W_s)}$$

where:

A_x = analyte response (area units)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Average CF = average calibration factor

V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 METHOD BLANKS

MBs are aliquots of matrix (i.e., organic-free water for liquids, boiling chips for solids) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this criterion is not achieved, then analyses must be halted and the source of the contamination found and

corrected. As the analyst deems necessary, aliquots of solvent may be injected to clean the analytical system and demonstrate that it is free from contamination.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. See QC Table for evaluation criteria. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.6 SURROGATE RECOVERY

The %R of the surrogate is calculated (see equation shown for LCS recovery above) for all field and QC samples. If the recovery is outside QC limits, the sample is reanalyzed to verify that analytical error was not the problem. If after re-injection the recovery is still out-of-control, initiate an NCR (SOP 928) to consult with the Project Manger (and client, as needed) and apply the decided upon action.

9.7 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM THE METHOD

10.1 This SOP meets the requirements of Method SW8141A. There are no known deviations from the method.

10.2 As of this writing, Paragon does not analyze wastewater samples for compliance monitoring purposes. Paragon extracts aqueous samples according to SW-846 protocol. Following are deviations from EPA Method 614:

10.2.1 EPA Method 614 prescribes preparation via a separatory funnel shakeout. Paragon extracts samples using continuous liquid-liquid extractors (CLLEs).

10.2.2 EPA Method 614 prescribes an extraction mixture of 15% methylene chloride and 85% hexane. Paragon extracts samples with methylene chloride only, per SW3520C protocol.

10.2.3 EPA Method 614 requires a relative standard deviation (RSD) of less than 10% in order to quantify samples by the average response factor. Paragon requires an RSD of less than 20% to quantify samples by the average response factor, per SW8141A protocol.

10.2.4 EPA Method 614 requires a percent difference of ±10% for continuing calibration standards. Paragon requires a percent difference of ±15%, per SW8141A protocol.

10.2.5 Paragon does not analyze the full list of compounds from EPA Method 614.

10.2.6 For Health & Safety and waste stream management reasons, Paragon does not support use of mercuric chloride as a preservative.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.5 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.2 WASTE DISPOSAL

11.2.1 Any hexane, acetone, or other nonhalogenated organic solvents that have not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste stream.

11.2.2 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.3 The extract vials, associated extracts, and any PCB contaminated debris that may contain PCBs in excess of 50ppm shall be disposed of intact in the PCB Debris Waste stream.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be removed or defaced prior to disposal.

12. REFERENCES

12.1 USEPA, SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, Volume 1B, Method 8141A, Revision 1, September 1994.

12.2 USEPA, SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, Volume 1B, Method 8000B, Revision 2, December 1996.

12.3 USEPA, EPA 821 RR-92-002, April 1992. Method 614. "The Determination of Organophosphorous Pesticides in Municipal and Industrial Wastewater".

DOCUMENT REVISION HISTORY

7/18/06: LIMS program specification language strengthened. Dual column identification and interpretation of results clarified. List of consumables added. DOCUMENT REVISION HISTORY section added.

Analytical Method: SW8141A, EPA614	**Parameter:** Organophosphorous Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum 5-points, all analytes (SW 8141A); Methods EPA 614 does not require 5-points	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean CF to quantitate Calculate linear regression (not forced through origin); use for quantitation if correlation coefficient (r^2) ≥0.99 or Calculate quadratic regression (minimum of six points required); use for quantitation if COD ≥0.99	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Initial Calibration Verification (ICV); conc. not equal to midpoint of calibration curve; second source	After each ICAL	≤15%D of each compound or mean %D ≤15%	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8141A allows bracketing of 20 field sample analyses)	≤15%D of each compound or mean %D ≤15%	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of	Whenever a new column is installed	Column and compound specific Window is ±3x the standard deviation of the 3-injection average for the respective column	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms

Analytical Method: SW8141A, EPA614	**Parameter:** Organophosphorous Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
variation		Note that the ICV and CCV analyses are also used to monitor RT drift	(refer also to RT Shift).
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction

Analytical Method: SW8141A, EPA614	**Parameter:** Organophosphorous Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per batch, not to exceed 20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per batch not to exceed 20 samples of like matrix	See laboratory limits; see Matrix Spike information above for MSD recoveries. RPDs should be within advisory limits.	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. Note in narrative. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers.
Surrogate Spike	All extractions including field and laboratory QC samples	See laboratory limits; recoveries should be within current limits, alternative criteria as defined in the LIMS program specifications may apply	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if surrogate recovery in the

Analytical Method: SW8141A, EPA614	**Parameter:** Organophosphorous Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			associated MB is not within limits and the samples are within the holding time, then re-extract and reanalyze all associated samples - if samples are beyond the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Paragon Analytics

Logbook No./Page _____________

Instrument Name _________ Sequence File: C:\HPCHEM___\SEQUENCE_______________ Date Analyzed ________ Operator _____ GC Method _______

Data Path: C:\HPCHEM___\DATA_____________ Analytical Method __________ SOP ____ Rev ___ Hexane Lot _______________

Form 530r6fpd.xls (7/24/2002) **Reviewed by / date ____________________**

Vial	Data File	Method	Sample Name	Comments	rr?

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 408 REVISION 11

TITLE: **ANALYSIS OF NITROGLYCERIN AND/OR PETN BY HPLC -- METHOD SW8332**

FORMS: **410 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8-13-07

QUALITY ASSURANCE MANAGER _____ DATE 8/12/07

LABORATORY MANAGER _____ DATE 8-13-07

HISTORY: Rev0, 2/21/92; Rev1, 2/18/93; Rev2, PCN #109, 4/4/94; Rev3, 9/21/99; Rev4, 3/2/02; Rev5, 3/28/03; Rev6, 4/16/04; Rev7, 7/26/05; Rev8, 3/13/06; Rev9, 8/24/06; Rev10, 2/8/07; Rev11, 8/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references – SW-846 Method 8332 -- is used to determine the concentration of nitroglycerin (NG) and/or pentaerythrite tetranitrate (PETN) in liquid and solid matrices.

2. SUMMARY

Aqueous and solid matrix samples are extracted and concentrated using appropriate methods (SOP 665). Aqueous samples can also be analyzed by direct injection if concentrations are expected to be high. An aliquot of sample or extract is injected into a high performance liquid chromatograph (HPLC) containing a C_{18} (primary) column and an ether-linked phenyl phase (ELP) confirmation column. Target analytes are separated under isocratic (i.e., constant composition) solvent flow conditions on the primary column, and under gradient conditions on the confirmation column. The target analytes are then detected by an ultraviolet (UV) detector using absorbance at 215nm. Detected analyte responses are recorded and calculated by a data acquisition system using an external standard method of quantitation. Solid matrix sample results are normally reported on an air-dried basis.

NOTE: Aqueous samples for direct injection must first be diluted 1:1 with methanol or acetonitrile, and filtered before this technique is applied.

CAUTION: Use extreme care at all times. Target analytes present an explosive hazard. Nitroglycerin at concentrations over 1% is particularly unstable and explosion may be initiated by concussion or heat.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform this determination according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review or the performance of precision and accuracy tests.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Paragon Project Manager is responsible for directing a chlorine residual check to be performed upon sample receipt as applicable.

3.5 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Contaminants in reagents, from glassware or within the analytical system may cause the appearance of discrete artifacts or elevated baselines. Use of high purity reagents, scrupulously cleaned glassware (SOP 334) and frequent maintenance of the analytical system minimizes these interferences.

4.2 Interferences co-extracted from the sample matrix will vary considerably from source to source. If observed, the presence of significant interferences is discussed in the laboratory data package narrative.

5. APPARATUS AND MATERIALS

5.1 HPLC, AUTOSAMPLER, DETECTORS

A Hewlett-Packard (HP) 1050 or 1090 (or equivalent) HPLC equipped with:

- gradient pumping system
- system controller
- column oven

- ultraviolet detectors
- autosampler

5.2 DATA SYSTEM

Data acquisition system capable of acquiring, storing and processing HPLC data (e.g., LC ChemStation™ or equivalent).

5.3 COLUMNS - Equivalent suppliers, columns may also be used

C_{18} column:	Phenomenex Ultracarb™	#00G-0206-E0	(5µ ODS (20); 250x4.6mm)
ELPcolumn:	Synergi POLAR-RP 80Å	#00G-4336-E0	(4µ Polar RP; 250x4.6mm)
Guard Cartridge Holder:	#KJO-4282		
Cartridge:	Phenomenex (C_{18})	#AJO-4287	(5µ ODS; 4.0 x 3.0mm)
	Synergi (Polar RP)	#AJO-6076	(4.0 x 3.0mm)

5.4 MEASURING DEVICES

Microsyringes, Hamilton Precision™ or equivalent, various µL sizes
Volumetric flasks, Class A with ground glass or Teflon™ stoppers, 10-100mL sizes

5.5 CONSUMEABLES

- solvent inlet filter frit, 1/4", 4.6mm, 2µm, Restek #25071 or equivalent
- HPLC pump maintenance kit, Restek #25270 or equivalent
- autosampler maintenance kit, Restek #25259 or equivalent
- PTFE syringe filters, 0.45µm
- autosampler vials
- glass pipets, disposable

6. REAGENTS - Only HPLC grade solvents with acceptable UV cutoffs may be used!

6.1 SOLVENTS

6.1.1 methanol (CH_3OH; MeOH), Burdick & Jackson #230-4 or equivalent

6.1.2 acetonitrile (ACN; CH_3CN), Burdick & Jackson #015-4 or equivalent

6.2 REAGENTS

6.2.1 HPLC grade water, Burdick & Jackson #365-4 or equivalent

6.2.2 sulfuric acid (H_2SO_4), concentrated, EMD #SX1244-5 or equivalent

6.2.3 HPLC grade water-acidified (use to prepare working standards): Create by adding 1 drop of conc. H_2SO_4 to 500mL HPLC grade water

6.3 STANDARDS

6.3.1 All standards are maintained per PAR SOP 300. Target analyte stock standards, typically 1,000µg/mL, are generally purchased as certified solutions, but may be prepared from pure standard materials dissolved in MeOH or ACN. For neat standards or standard materials of a purity

<95%, adjust concentration for purity when calculating standard concentration. Two independent sources (first, second) of target analyte stock standards are needed. A (non-target analyte) surrogate stock standard is also purchased. The surrogate used for this method is 1,4-dinitrobenzene.

Intermediate standards are made by diluting an appropriate aliquot of stock standard to a specific volume using acetonitrile, and are stored in Teflon™-sealed vials. Typically, a 50-fold dilution is made, thus creating intermediate standards at a concentration of 20µg/mL. First source target analyte materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards (used by the Organics Extraction Group). Second source target analyte materials are used to create the initial calibration verification (ICV) solution. Typically, 1.0mL of intermediate surrogate standard is added into each calibration check, field and quality control (QC) sample. Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

Unopened stock standards are valid until the manufacturer's expiration date. Transfer remainders of opened stock standards to Teflon™-sealed vials for storage. All stock and intermediate standards are stored in the freezer (i.e., dark, ˉ10 to ˉ20°C). Opened stock or prepared intermediate standards expire 30 days from opening (preparation), or per the manufacturer's expiration date (whichever is sooner). Standards may be replaced sooner if laboratory QC analyses or other factors indicate deterioration.

6.3.2 The intermediate target analyte standards are further diluted to create working standards. These working standards (ICAL, ICV, CCV) are prepared on the day of use, directly in analysis vials (µL injections), using portions of acidified water and acetonitrile as the diluents to create sufficient standard volume for analysis. The working standards must contain all target analytes and the surrogate. Calibration standards are documented in the analytical run log (Form 410). A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.3.3 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are not generally chemically preserved and must be collected in amber glass containers (typically 1L) with Teflon™-lined lids. Samples must be maintained at 4±2°C and extracted within 7 days of collection. Dechlorination using sodium thiosulfate ($Na_2S_2O_3$) may be necessary at the time of sampling if water is known to contain residual chlorine. The Project Manager may designate the need for residual chlorine check of the sample upon receipt.

7.3 Solid samples are collected in glass containers with Teflon™-lined lids. Solid samples are not chemically preserved and must be maintained at 4±2°C. Exception: Solid sample aliquots in the process of being prepared for analysis are air-dried, prior to subsequent extraction. Solid samples must be extracted within 14 days of collection.

7.4 Extracts, from liquid or solid samples, must be maintained in the dark at 4±2°C and analyzed within 40 days of preparation.

8. PROCEDURE

8.1 TYPICAL HPLC CONDITIONS

Column 1: C_{18} isocratic analysis conditions with wash gradient, below:

Flow Rate:	0.8mL/min flow
MP A:	40% H_2O (±1.5%)
MP B:	60% CH_3OH (±1.5%)
Column Temperature:	28°C
Injection Volume:	50µL injections

Linear Gradient Elapsed Time (min)	MP A: Water (%)	MP B: MeOH (%)
0	40	60
21.5	30	70
23.5	30	70
25	40	60
28 (equilibration)	40	60

Column 2: ELP analysis conditions (or as suitable):

Flow Rate:	1.6mL/min
MP A	65% H_2O (±1.5%)
MP B	35% ACN (±1.5%)
Column Temperature:	30.0°C
Injection Volume:	50µL injections

Linear Gradient Elapsed Time (min)	MP A: Water (%)	MP B: Acetonitrile (ACN) (%)
0	65	35
21	60	40
22	35	65
23 (equilibration)	35	65

8.2 CHROMATOGRAPHIC MAINTENANCE

Prior to analyzing samples or establishing calibration curves, the following suggested maintenance might be performed to aid in achieving more consistent results:

- Change the column frits as needed (i.e., control pressure).
- Change the cartridge on the guard column as necessary (i.e., correct pressure increase or poor chromatography).
- Install fresh HPLC water for every run.
- Restart the computer and instrument before starting analysis.
- Minimize air currents blowing on the instrument and vials loaded on the autosampler tray.
- Replace lamps at 2yr or upon observation of degraded signal.
- Major repairs on contract (by Full Spectrum or equivalent).
- When installing a new column, any column deficiencies with the old column should be documented, at a minimum, on the column box.
- Ensure that instrument is equilibrated and retention times have stabilized; instrument may be primed with one or more injections of the CCV solution prior to initiation of the CCV for the acquisition sequence.

8.3 INITIAL CALIBRATION

8.3.1 Set pump at flow rate used for the column in use. Turn on detector lamp. Allow the HPLC system to equilibrate for a minimum of 15min.

8.3.2 Prepare a minimum of 5 concentrations of calibration standards (typically 6 are used) as shown below in Table 1 below or as required for each sample set to be analyzed. The purpose of the initial calibration (ICAL) is to define the linear range of the detector. The ICAL can be used for analysis of both soil or water extracts. Each ICAL standard must include all target analytes and the surrogate. The lowest standard's concentration standard shall be at or below the reporting limit (RL) of each analyte. Create calibration standards by diluting aliquots of the first source intermediate calibration standard using an acetonitrile/acidified water mix. The mid-range calibration standard is used for continuing calibration verification (CCV).

Table 1
CALIBRATION STANDARDS

ACN (µL)	Acidified HPLC H_2O (µL)	Intermediate (µL)	Final Conc. (µg/mL)
0	500	500	2.5
300	500	200	1.0
400	500	100	0.5
480	500	20	0.1
495	500	5	0.025
498	500	2	0.01
400 CCV	500	100	0.5
300 CCV	500	200	1.0
400 ICV	500	100	0.5

8.3.3 Inject an appropriate volume (50µL) of each ICAL standard into the HPLC and analyze. The data system accomplishes quantitation via the external standard method (i.e., area responses are tabulated against the concentration injected). Analyte Calibration Factors (CFs) are calculated as follows:

$$CF = \frac{\text{Peak Area}}{\text{Concentration of Analyte}}$$

If the CFs over the working range of the detector are constant (i.e., ≤20% RSD), then response can be assumed to be invariant (linear through zero) and the average (mean) CF may be used to quantitate sample content.

Relative Standard Deviation (RSD) is calculated as:

$$\text{RSD (\%)} = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean response factor}} \right)(100)$$

When RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first (minimum of 5 ICAL points used, r) or second (minimum of 6 ICAL points used, r^2) order regression curve fit that does not pass through zero (e.g., least squares method) may be constructed. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000B. A quadratic regression should not be used to compensate for detector saturation. Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

If a first order regression fit is applied, the correlation coefficient (r)

value yielded must be ≥0.995. If a second order regression fit is applied, the coefficient of determination (COD, r^2 value) yielded must be ≥0.99. Note that the curve fit value expresses "goodness of fit", with perfect fit being a value of 1.0.

If the curve fit value does not meet criteria, check that the calibration standards were prepared properly, reanalyze and generate a new initial calibration curve..

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The acceptance criteria for the ICV is the same as for the CCV (described below). If control criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated. See QC Summary Table for further details.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

The percent difference (%D) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when responses for all analytes are within ≤15%. If a CCV does not meet acceptance criteria, reanalyze the CCV. See QC Summary Table for further details and corrective action to be taken should the CCV still fail.

So long as CCV analyses yield compliant results, and other QC samples are analyzed as required, the series of ten sample analyses bracketed before and after by successful CCV analyses may continue as long as the reserve of solvents lasts.

8.6 RETENTION TIME WINDOWS

For chromatographic methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used to compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections) of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (σ) of the absolute retention time yielded for

each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time ±3σ, such that the Upper Limit = +3σ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time shifts). Sample matrices may cause RT differences that require further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system

8.7 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATION, REPORTING)

8.7.1 If ICAL, verification and method blank analyses have been successfully performed, analyses may proceed. If ICAL is not necessary, inject a CCV and determine compliance with acceptance criteria. Up to 10 samples (including QC samples) may be injected after calibration check criteria are met. End the analytical sequence with a CCV analysis.

8.7.2 A constant volume, generally 50µL, of each standard, standard verification, blank, field or QC sample extract (each containing the surrogate) is injected via the autosampler into the HPLC for analysis.

Sample extracts are diluted to maintain response within the linear range when necessary. Note that where sample concentrations are expected to be significant enough, filtered aqueous sample aliquots may be directly injected into the HPLC.

Allow the HPLC system to equilibrate after each injection/analysis.

8.7.3 Tentative identification occurs when a peak's response falls within the RTW of the C_{18} column. Confirmation occurs when the peak's response also falls within the RTW on the ELP confirmation column. Note that per LIMS program specification, diode array detection spectral confirmation may also be used.

8.7.4 Sample concentration may be calculated using the average calibration factor, or using the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

Average CF:

$$\text{Concentration}_{(ug/L,\ ug/kg)} = \frac{(A_x)(V_t)(DF)}{(\text{Average CF})(V_s \text{ or } W_s)}$$

where:

A_x = analyte response (area units)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Average CF = average calibration factor

V_s or W_s = volume or weight of sample extracted (mL or g)

Linear Curve Equation:

$$x = \frac{(y - b)(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte
in ng/mL, ng/g (equal to ug/L, ug/Kg)

y = analyte instrument response (area units)

b = calculated intercept (area units)

m = calculated slope of the line (area units/conc. units-ng/mL)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples of like matrix that is associated with one unique set of QC samples and processed together as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS) and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Check LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method blanks (MBs) are aliquots of matrix (i.e., HPLC water for liquid analyses; Ottawa sand for solid analyses) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is processed, or there is a change in reagents, an MB must be prepared. Concentrations of target analytes, if any, must be less than the analyte reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this requirement is not met, analyses must be halted and the source of the contamination found and corrected. See also QC

Table. As the analyst deems necessary, aliquots of solvent may be injected to clean the analytical system and demonstrate that it is free from contamination.

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below:

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

See QC Table for evaluation criteria.

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as follows:

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

See QC Table for evaluation criteria.

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an

analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

See QC Table for evaluation criteria.

9.6 SURROGATE RECOVERY AND ACCEPTANCE CRITERIA
Paragon uses the compound 1,4-dinitrobenzene as the surrogate for this method. Surrogates are selected for chemical structure and detection characteristics that are similar to the target analytes, but not so much so that it co-elutes with any of the single component targets. It should be noted, however, that because the surrogate is not a deuterated analog of a target analyte, as in GC/MS methods, it is not extracted with exactly the same efficiency as the target compounds. Therefore, surrogate recovery problems are not entirely representative of target analyte recoveries.

The %R of the surrogate is calculated (see equation shown for LCS recovery above) for all field and QC samples. If the recovery is outside QC limits, the sample is reanalyzed to verify that analytical error was not the problem. If after re-injection the recovery is still out-of-control, initiate an NCR (SOP 928) to consult with the Project Manager (and client as needed), and apply the decided upon action.

9.7 A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses for each target analyte at a concentration level near to the capabilities of the method. The MDL study should be performed as needed, at a minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM THE METHOD

This SOP meets the requirements of Method SW8332, with the following exceptions:

10.1 The C_{18} column is used as the primary column and the ELP column is used for confirmation. The C_{18} column provides resolution and identification performance that meet method criteria and it outperforms the ELP column and is therefore used as the primary quantitation column.

10.2 A detector wavelength setting of 215nm is used for analysis (Method SW8332 states a 214nm detector setting).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.2 ***These samples are to be handled as explosive material and extreme caution should be applied as well as knowledge of explosives. The procedure is not intended for operations involving pure product explosives or non-environmental levels of explosives.***

11.1.3 ***Samples containing explosive material may under no circumstances be heated in any fashion (e.g., boiling a solution; drying in an oven).***

11.1.4 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.5 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.6 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.7 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.8 All flammable compounds must be kept away from ignition sources.

11.1.9 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.10 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Any rinse waters used for rinsing syringes or other devices prior to sample contact may be disposed of in the Aqueous Lab Waste.

11.2.2 Any hexane or other nonhalogenated organic solvent that has not been potentially contaminated with PCBs (e.g., the ACN:Water HPLC waste), may be discarded into the Acetonitrile/Nonhalogenated Waste stream.

11.2.3 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.4 The extract vials, associated extracts, and any PCB-contaminated debris that may contain PCBs in excess of 50ppm, shall be disposed of intact in the PCB Debris Waste.

11.2.5 All empty solvent bottles are disposed of according to the appropriate

SOPs. ***Please note that all labels and markings must be defaced prior to disposal.***

12. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 8332, Revision 0, December 1996.

DOCUMENT REVISION HISTORY

8/24/06: LIMS program specification references strengthened; analytical columns used clarified; consumables list added; standards discussion revamped. DOCUMENT REVISION HISTORY Section added.

2/8/07: Minor format updates. Precedence of SOP 300 deleted. ICV added to standards table. Calculations expanded and units better defined.

8/12/07: Calibration discussion further clarified, Section 8.3.3 and QC Table.

Analytical Method: SW8332	**Parameter:** NG / PETN by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
Initial Calibration; minimum 5-point; all analytes	As needed (i.e., at on-set of analyses, or when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate If RSDs over calibrated range exceed 20%, first order linear regression (using a minimum of 5 ICAL points) may be applied; r≥0.995 Higher order regression fits may be applied if more than 6 ICAL points are used; r^2≥0.99	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve
Initial Calibration Verification (ICV); conc. not equal to midpoint of calibration curve; second source	After each ICAL	If ≤15%, analyses may proceed	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8330 allows bracketing of 20 field sample analyses)	If ≤15%, analyses may proceed	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed before and after a failed CCV must be reanalyzed. If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of	Whenever a new column is installed	Column and compound specific. Window is ±3x the standard deviation of the 3-injection average for the respective column Note that the ICV and CCV analyses are also used to	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms (refer also to RT Shift).

Analytical Method: SW8332	**Parameter:** NG / PETN by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
variation		analyses are also used to monitor RT drift	(refer also to RT Shift).
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per each preparation batch of ≤20 samples of like matrix	See laboratory or other applicable limits; recoveries for spiked compounds must be within these limits	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause.

Analytical Method: SW8332	**Parameter:** NG / PETN by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
			- if still non-compliant and the samples are within the extraction holding time, then initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per batch, not to exceed 20 samples of like matrix	See laboratory or other applicable limits; recoveries for spiked compounds should be within these advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per batch ~~of samples~~, not to exceed 20 samples of like matrix	See Matrix Spike information above for MSD recoveries. RPDs should not exceed value specified in LIMS program specification (typically 20%)	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers.
Surrogate Spike	All extractions including field and laboratory QC samples	See laboratory or other applicable limits; recoveries should be within these limits	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with surrogate recovery outside the QC limits with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if surrogate recovery in the

Analytical Method: SW8332	**Parameter:** NG / PETN by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
			associated MB and LCS is not within limits and the samples are within the holding time, then re-extract and reanalyze all associated samples - if samples are beyond the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study; run at analyte concentrations near to the minimum detection capability of the method	As needed, at minimum, annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

_____A

daily calibration standard preparation form 410r7a.xls (03/01/05)

date_____ preparer_____ method-SW-846 **8330** SOP **404** Rev____
primary source standard tracking #_____ expiration date_____

target compound conc._____µg/ml (5.0) surrogate conc._____µg/ml (5.0)

conc. µg/ml	dilution factor	acidified water µl required	acidified water µl actual	acetonitrile µl required	acetonitrile µl actual	standard µl required	standard µl actual
0.5	10	500		400		100	

10-fold dilution example calculation:
100µl = 0.1ml (0.1ml) X (5µg/ml) = 0.5µg
500µl + 400µl + 100µl = 1000µl = 1ml (0.5µg) / (1ml) = 0.5µg/ml

Instrument Name _____ **Paragon Analytics** Logbook No./Page _____ **B**

Date Analyzed _____ Operator _____ Method _____ SOP _____ Rev. _____ **Reviewed by / date** _____

Sequence File: C:\HPCHEM_____\SEQUENCE_____ ICAL Date _____ Processing Method _____

Data Path:
C:\HPCHEM_____\DATA_____ Date Archived _____

CH_3OH Lot # _____ H_2O Lot # _____ H_2O w H_2SO_4 Lot # _____ CH_3CN Lot # _____ Col. Type & Serial No. _____

Vial	Inst. Method	Data File	Sample Name	Rerun?	Comments

Comments: _____ Form 410r7b.xls (03/01/05)

STANDARD OPERATING PROCEDURE 409 REVISION 6

TITLE: ANALYSIS OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY -- METHODS SW8082 and EPA 608

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 4.7.09

QUALITY ASSURANCE MANAGER _____ DATE 4/7/09

LABORATORY MANAGER _____ DATE 4-7-09

HISTORY: Rev0, 2/15/99, Rev1, 10/7/01; Rev2, 3/14/03; Rev3, 4/16/04; Rev4, 3/13/06; Rev5, 7/5/06; Rev6, 3/19/09.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references - SW846 Method 8082 and EPA 608, are used to determine the concentration of Aroclors 1016 through 1268 in various matrices. The following Aroclors may be analyzed:

Aroclor 1016	Aroclor 1242	Aroclor 1260
Aroclor 1221	Aroclor 1248	Aroclor 1262*
Aroclor 1232	Aroclor 1254	Aroclor 1268*

* Aroclors 1262 and 1268 are not routinely analyzed by the laboratory, but may be determined upon request. Decachlorobiphenyl (DCB) is normally added as a surrogate standard. However it can be reported as an analyte.

Aroclors are multi-component mixtures. Qualitative and quantitative determination may be more difficult if a sample contains more than one Aroclor, has been subjected to environmental degradation (weathering), or has been degraded by treatment technologies. Weathered and degraded samples exhibit patterns that differ from Aroclor standards.

The body of this SOP specifies the procedures to be used for Method SW8082 analysis. Any additional or contradictory requirements for Method EPA 608 are addressed in Section 10.

2. SUMMARY

Samples are extracted and the extracts concentrated and solvent exchanged using appropriate ALSLG-FC SOPs (i.e., 617 [CLLE]; 626 [Separatory Funnel]; 625 [Soxhlet]; 622 [Waste Extraction]; 607 [Kuderna-Danish Reduction]; and 637 [Concentration and Solvent Exchange]).

NOTE: With prior arrangement with the laboratory, solid samples may also be extracted using pulse sonication techniques.

The extracts are injected into a gas chromatograph (GC) containing a sample splitter and

two columns of varying selectivity (i.e., dissimilar elution and retention time properties). The target analytes are separated in the columns and detected by two electron capture detectors (ECDs). This chromatography system allows tentative identification by one column and confirmation by the other column to be performed simultaneously.

Quantitation is performed using the best column response yielded for each analyte. The Analyst considers performance data such as separation of interferences, calibration performance and matrix spike results in selecting the primary quantitation column for each analyte detected and reported. The particular value that is selected for reporting is often marked (designated) in the raw data (e.g., quantitation report, run log). If results from both columns are comparable, the highest result is reported. Second column confirmation is not required if the primary column does not detect an Aroclor pattern, and may not be necessary if the sample matrix is well characterized by previous analyses.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 ALSLG-FC's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALSLG-FC's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Interference from phthalate esters can be minimized by using plastic-free solvent

containers and scrupulously cleaned glassware (SOP 334) that has been kiln-baked or solvent-rinsed prior to use. Use of low phthalate gloves, such as nitrile, may also important. These practices are important both in the field and in the laboratory.

4.2 Sulfuric acid clean up techniques may be used to remove interferences caused by the presence of organochlorine and/or organophosphorous pesticides. See SOP 651 for instructions regarding Method SW3665A sulfuric acid clean up.

4.3 Elemental sulfur (particularly in sediment samples) may interfere with PCB pattern identification and can be removed by using appropriate clean up techniques prior to sample analysis. See SOP 634 for instructions regarding Method SW3660B sulfur cleanup.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH (GC), AUTOSAMPLER AND DETECTORS - Hewlett Packard (HP) 5890 Series II GC equipped with HP 7673A autosampler, dual on-column injection, and electron capture detectors (ECDs) or equivalents

5.2 CHROMATOGRAPHIC DATA ACQUISITION AND PROCESSING SYSTEM - Hewlett Packard ChemStation (Enviroquant™) or equivalent

5.3 COLUMNS –
The following specified columns or equivalent columns are used with this analytical method.

RTx-CLPesticides or equivalent (30m, 0.25 or 0.32mm ID, 0.5µm film), RTx-CLPesticides II or equivalent (30m, 0.25 or 0.32mm ID, 0.25µm film), guard column

Restek Pesticide Column:	RTX-CLPesticides	#11123	(0.25mm)
Restek Pesticide Column:	RTX-CLPesticides2	#11323	(0.25mm)
Restek Pesticide Column:	RTX-CLPesticides	#11139	(0.32mm)
Restek Pesticide Column:	RTX-CLPesticides2	#11324	(0.32mm)

5.4 GASES - ultra high purity (99.999%)
Helium - carrier gas
Nitrogen - make-up gas

5.5 MEASURING DEVICES
Syringes - 1.0µL-1000µL precision Hamilton™, or equivalent
Volumetric flasks, Class A with ground glass stoppers, 10mL and 25mL

5.6 GC CONSUMABLES

- Vials - National Scientific C4011-1, or equivalent
- Caps - National Scientific C4000-51B, or equivalent
- Inlet Seals, dual vespel ring - Restek 0.8mm #21243, or equivalent

- Septa, 11mm - Restek #20365 or equivalent
- O-ring, graphite, 6.5mm - Restek #20299, or equivalent
- O-ring, Viton - Restek #20377, or equivalent
- Liner, splitless, 4mm ID - Restek #20799-214.5, or equivalent
- Glass Wool, deactivated - Restek #20789, or equivalent
- Gold Seal - Restek #21306, or equivalent
- Universal Presstight Y - Restek #20469, or equivalent
- Vespel/Graphite Ferrule (detector) - Restek #20221, or equivalent
- Compact Vespel/Graphite Ferrule - Restek #20249, or equivalent
- Graphite Ferrules - various sizes
- Split Vent Trap (SW8081) - Agilent RDT-1023, or equivalent

6. REAGENTS

6.1 SOLVENTS - **Only pesticide residue grade or equivalent may be used.**
Hexane - Burdick and Jackson 216-4, or equivalent
Methanol - Burdick and Jackson 230-4, or equivalent

6.2 STANDARDS
All standards are stored following ALSLG-FC SOP 300 guidance, which is superseded by any guidance in this SOP. Generally after opening vials, the standards for this procedure are stored in the freezer (-10°C and -20°C), in PTFE-capped, or equivalent vials. Unopened stock standards in flame-sealed ampules are valid until the manufacturer's expiration date and may be stored at room temperature, if recommended by the manufacturer. Opened stock standards and intermediate standards expire six months from opening (preparation) or the manufacturer's expiration date, whichever is sooner. Standards may be replaced sooner if laboratory QC analyses or other factors indicate deterioration.

All stock and intermediate standards are documented in ALSLG-FC's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

6.2.1 Stock Standards: An approximately 1000mg/L (per component) stock solution is purchased from a suitable vendor or prepared in-house gravimetrically by accurately weighing 0.0100g of pure material into a 10mL Class A volumetric flask and diluting to volume with n-hexane. If purity of the compound is 96% or greater, no weight correction is necessary; if compound purity is less than 96%, the concentration must be corrected mathematically based on weight used.

A combination standard containing Aroclor 1016 and 1260 will generate peaks covering the range of all Aroclors of interest. Individual standards for all Aroclors must be created to assist in pattern recognition. The primary stock standards are subsequently diluted to create the intermediate stock standards. Undiluted, opened primary stock standards may be retained for up to six months.

6.2.2 Intermediate Standards: Generally prepared by diluting 1mL of stock standard to 25mL using a Class A volumetric flask and n-hexane. The intermediate stock standard is further diluted to create the calibration standards. Intermediate stock standards may be retained for up to six months.

6.2.3 Calibration Standards: Calibration standards are made daily from intermediate stock standards. Typically, ALSLG-FC prepares a mixture of Aroclor 1016/1260 at a minimum of 5 different concentrations that define the working linear range of the detector. The initial calibration must have a standard at or below the analyte reporting limit. A single point standard for the remaining requested Aroclors should be prepared at the analyte reporting limit. The single point standard will be used for pattern recognition, and to verify the sensitivity of the instrument for each Aroclor.

If the presence of an Aroclor other that 1016/1260 is suspected, a calibration curve containing a minimum of five concentration levels should be prepared for that Aroclor. Create calibration standards by preparing serial dilutions of the intermediate stock standard in n-hexane. A calibration standard at a concentration near the midpoint of the calibration curve will be used as a continuing calibration verification (CCV) standard. See SOP 300 for additional information about standard expiration dates.

6.2.4 Independent Calibration Verification Standard (ICV): Certified and purchased from a vendor or made gravimetrically in-house. Uses a source different from that of the calibration standard so that the accuracy of the calibration standard may be independently verified. Created and analyzed at a concentration level that is near the midpoint of the calibration range. The ICV should be prepared at a level different from the concentration used for the CCV, in order to verify a wider range of the calibration.

6.2.5 Surrogate Spike Solution - Certified and purchased from a vendor or made in-house. Typically, this standard contains 500ng/mL each tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) in methanol. During preparation, 1.0mL of this standard is spiked into each

sample, standard, and quality control (QC) sample. Other concentrations or solvents may be used as needed (i.e., as defined in the applicable LIMS Program Specification).

6.2.6 Spike Solution - A commercial (i.e., purchased from a vendor) primary standard containing 1,000ppm Aroclor 1016/1260 is used to prepare a 5ppm in methanol solution to be used by the Organics Extractions Group in preparing laboratory control samples (LCS/LCSD) or matrix spiked samples (MS/MSD); typically 1mL of spike solution is added. Other concentrations and/or solvents may be used as appropriate (i.e., as indicated in the applicable LIMS program specification).

NOTE: An internal standard is not currently used for Aroclor analysis. Qualitative identification is determined by pattern recognition and quantitation is accomplished using the external standard method. Dual column confirmation is also routinely performed.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are not chemically preserved and must be collected in amber glass containers (generally 1L) with Teflon-lined lids. Samples should be maintained at 4±2°C and extracted within 7 days of collection. Extracts should also be maintained at 4±2°C and analyzed within 40 days of preparation.

7.3 Solid samples are collected in 250mL widemouth glass containers with Teflon-lined lids. Solid samples are not chemically preserved and should be maintained at 4±2°C. Solid samples should be extracted within 14 days of collection, extracts maintained at 4±2°C, and analyzed within 40 days of extraction.

8. PROCEDURE

8.1 TYPICAL GAS CHROMATOGRAPHIC CONDITIONS

Carrier Gas (He):	1-6mL/min
Make-up Gas (N_2):	20-40mL/min
Purge:	on, 0.75min
Injector Temperature:	205°C
Detector Temperature:	325°C

Oven Temperature Program:

Initial Temperature:	110°C
Oven Ramp:	15°C/min. to 250°C

Oven Ramp A:	20°C/min. to 300°C
Oven Ramp B:	5°C/min. to 270°C
Hold:	5 min

8.2 CHROMATOGRAPHIC MAINTENANCE

8.2.1 Aliquots of solvent may be injected and analyzed to show that the analytical system is free from contamination. They may be injected following samples of unusually high concentration to check the status of the analytical system and to facilitate re-equilibration of the system. Solvent injections may be used to prime the system if it has sat idle for awhile.

8.2.2 Peak tailing for all components will be exacerbated by a dirty injector. Clean per manufacturer's instructions as needed.

8.2.3 ECD detector leak checks are performed semi-annually per the procedures outlined in SOP 016.

8.3 INITIAL CALIBRATION

Prepare calibration standards as discussed above (including addition of surrogate). Typically, a 5-point curve of Aroclor 1016/1260 is prepared and a single-point reporting-limit standard of the remaining Aroclors is prepared. Inject 1-2µL of each standard directly into the GC and analyze. Quantitation is accomplished using 3 to 8 peaks for each Aroclor via the external standard method of quantitation. Where possible, peaks should be chosen that are at least 25% of the height of the largest Aroclor peak. Analyte calibration factors (CFs) are calculated for each peak as follows:

$$CF = \frac{\text{Selected Peak Areas}}{\text{Mass of Aroclor Injected On-Column (ng)}}$$

NOTE: SW-846 8000C also allows for use of concentration instead of mass injected.

If the CFs over the working range of the detector are constant (i.e., ≤20% RSD), then response can be assumed to be invariant and the average (mean) CF may be used to quantitate sample content. Relative Standard Deviation (RSD) is calculated as:

$$RSD\ (\%) = \frac{\text{Standard Deviation (SD)}}{\text{Average (mean) CF}} \times 100$$

When RSD over the calibration range is ≥20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The type of curve fit applied should be chosen to best represent the data. The

regression calculation will yield a coefficient of determination (r^2 value) that must be >0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit" with perfect fit being a value of 1.0. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000C. A quadratic regression should not be used to compensate for detector saturation.

The type of curve fit applied should be chosen to best represent the data.

If the comparison of a sample to a one-point standard suggests that Aroclor 1221, 1232, 1242, 1248, 1262, or 1268 may be present, then a 5-point curve of the appropriate Aroclor standard is prepared. The sample is re-analyzed and quantified using the appropriate 5-point curve.

NOTE: If an initial calibration point is not used for any reason, the analyst must clearly notate why the data point was not used for instrument calibration. "Picking and choosing" among calibration points in order to meet criteria is NOT acceptable. Generally, calibration points are only discarded due to easily demonstratable causes.

The mathematics used in least squares regression have a tendency to favor numbers of larger value over numbers of smaller value. The regression curves that are generated will therefore tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels. To compensate for this, a "weighting" factor which reduces this tendency can be used. The Analyst may weight the curve to either the inverse of the concentration or to the inverse of the square of the concentration.

If regression criteria cannot be met, a new initial calibration must be performed.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

Though not required to be a second source by SW-846 Method 8082, a second source standard (ICV) is run after calibration. The concentration of the ICV should be varied over time and should not be equal to that of the continuing calibration verification (CCV). The acceptance criteria for the ICV are identical to those of the CCV described below. If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The concentration of the CCV is at or near the midpoint of the initial calibration. A CCV check is performed at the beginning (when initial calibration is not performed) and end, of each 12-hour analytical sequence (or batch of 20 samples). While QC samples are counted as part of the number of samples, solvent blanks are not.

NOTE: The CCV frequency given above should be considered a bare minimum, and some clients' LIMS program specifications may require more frequent CCV analysis. Even if this is not the case, a higher CCV frequency is strongly recommended. ALSLG-FC typically analyzes a CCV every 10 samples in order to reduce the amount of repeat injections necessary in the event of CCV failure.

Calculate the percent difference or drift (%D) between the initial and continuing calibration using the equations below:

$$\% \text{ Difference} = \frac{\overline{CF}_I - CF_c}{\overline{CF}_I} x100$$

where:

CF_I = The average calibration factor in the initial calibration

CF_c = Calibration factor for the continuing calibration

$$\%\text{Drift} = \frac{CC - TC}{TC} \times 100$$

where:

CC = Calculated concentration

TC = Theoretical concentration

Note that if a least squares regression is used, the CCV must be evaluated using a percent drift calculation.

If the %D is ≤20%, the CCV is acceptable, and sample analysis may begin. If a compound shows elevated response (> 20%D) and is not present in any samples associated with the CCV, re-analyses of those samples are not necessary.

If any CCV does not meet acceptance criteria, analyses must be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

8.6 RETENTION TIME WINDOWS

Retention Time Windows (RTWs) are established according to the criteria prescribed by Method SW8000C, Section 11.6. Analyze a mid-level standard in triplicate for each Aroclor, non-consecutively, during a 72-hour period. Calculate the mean and standard deviation (σ) of the three absolute retention times for three to five major peaks in each Aroclor. Each Aroclor's RTW is defined as three times the calculated standard deviation (±3σ) of each major peak, such that the Upper Limit = +3σ and the Lower Limit = -3σ.

8.7 SAMPLE ANALYSIS, CALCULATION AND REPORTING

A constant volume, generally 1µL, of each standard, blank, QC or field sample extract is directly injected into the GC via the automated injector. Sample extracts are diluted to maintain response within the linear range when necessary. All prepared extracts contain the surrogate (see Section 9).

8.7.1 Note that ALSLG-FC employs a sample splitter that facilitates simultaneous dual column injections; therefore, both columns are calibrated in the same manner and either column may serve as the column for quantitation.

8.7.2 Aroclors are identified through pattern recognition. Tentative identification occurs when selected peaks fall within the RTW of one column. If selected peaks also fall within their RTW on the second column, the analyte's presence has been confirmed. Quantitation is calculated from both column responses and the result with the least interference is reported. If both results are of equal quality, the higher result is reported. For the multi-response Aroclors, three to eight peaks are used for identification/quantitation. The same selected peaks must be consistently used for quantitation between the standard and sample set.

8.7.3 Analyst expertise is crucial in identifying and quantitating samples containing multiple Aroclors or Aroclors that are heavily weathered. Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to such an extent that a specific Aroclor pattern is no longer recognizable. Consult the Department Manager for assistance in interpreting complex chromatograms.

8.7.4 Sample analyte concentration is calculated using the equation of the linear curve (i.e., y = mx + b) or average calibration factor generated, which can be represented as:

linear: $A = mC + b$, or $C = (A - b) / m$

average calibration factor: $C = A/R_f$

where:

A = analyte response (area counts)
m = slope of the linear equation
C = concentration present at the instrument
b = the y-intercept of the linear equation
R_f = the average calibration factor from the initial calibration

A concentration is determined for each peak, and the total Aroclor concentration is then determined by averaging the concentrations of the 3 to 8 individual peaks.

8.7.5 Identification of Aroclors may be simplified by comparing standard peak patterns to sample patterns (i.e., RTW of the group of peaks, comparison of peak heights and ratios; software overlays may also be used as desired/possible). Assessment observations may be confirmed using the calculated RTWs. If a minor shift of the entire pattern is observed, the Aroclor may still be positively identified provided that the confirming column result also supports the decision.

8.7.6 Integration between the reference standard and the sample must be consistent. For example, the baseline may be drawn from the start of the first peak in the group to the baseline following the last peak, and lines dropped from peak valleys to baseline for calibration standards and the samples alike.

9. QUALITY CONTROL

9.3 DEFINITION OF ANALYSIS BATCH

For this method, an analysis batch is defined as a group of samples that are associated with one unique set of batch QC samples and analyzed together. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS) and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specification for additional or alternative requirements.

9.4 METHOD BLANKS

Method blanks are aliquots of matrix (i.e., organic-free water for liquids analyses; Ottawa Sand for solids analyses), which have been prepared and analyzed in the same manner as the associated field samples. To be acceptable, concentrations of analytes of interest detected (if any) in the MB must be below the analyte reporting limit, or as otherwise specified in the LIMS program specification. If this criterion is not achieved, analyses should be halted and the source of the contamination found and corrected.

A reagent or instrument blank is an injection of solvent analyzed to demonstrate that the analytical system is free from contamination. These blanks are typically analyzed following extremely contaminated samples.

9.5 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method and analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.6 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this analysis, either a field sample containing target compound contamination may be analyzed in duplicate, or the laboratory control sample (LCSD) or matrix spike (MSD) analysis can be performed in duplicate. The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD) as shown below. See QC Table for evaluation criteria.

$$\text{RPD} = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.7 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. See QC Table for evaluation criteria. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

Also note that for projects in which the client is to designate MS/MSD samples, an analysis batch may not contain an MS/MSD pair. Where this occurs, a notation will be made in the data package narrative.

9.8 SURROGATE RECOVERY AND ACCEPTANCE CRITERIA

The two surrogates (SUR) used for this procedure are those suggested in SW8081A. Both surrogates are added to all field and quality control samples prior to extraction; recovery is calculated per the recovery formula shown previously for the LCS. The two surrogates used were selected because they respond in a similar manner as the target compounds respond at the detector. Additionally these surrogates are not similar enough chemically to the target compounds to co-elute with the single component targets, nor do they suffer interferences from the multiple component targets. Tetrachloro-m-xylene (TCMX) elutes before any of the target compounds, and decachloro-biphenyl (DCB) elutes after all of the target compounds. However, because the surrogates are not deuterated analogs of targets as in GC/MS methods,

they are not extracted with exactly the same efficiencies as the target compounds. Therefore, surrogate recovery problems are not representative of target analyte recoveries.

Heavy co-extractive non-target compounds generally do not interfere with TCMX; light co-extractive non-target compounds generally do not interfere with DCB. However, some samples may produce matrix effects that cause surrogate recovery to be high or low; because of high concentrations of target and/or non-target compounds, quantification of the surrogates may even be precluded in some samples. Muddy aqueous samples, for example, generally adsorb DCB after spiking and limit recovery to a few percent. High concentrations of heavy hydrocarbons in soils oftentimes have a similar matrix effect on DCB recovery.

The extraction process itself can have an effect on surrogate recovery. An example of this process-caused effect is use of Method SW3520 for extraction of aqueous samples and associated "low" recoveries of DCB. DCB is a heavy molecule and very hydrophobic. When spiked into water, this compound tends to rapidly adsorb to particulates at the liquid-liquid interface and exhibits a low recovery.

For the reasons listed above, ALSLG-FC does not view the evaluation of surrogate recovery in this procedure to be a straightforward process. Therefore, ALSLG-FC observes the following guidance for evaluating surrogate recovery:

- ALSLG-FC's practice is to evaluate and report the recovery of both surrogates. When one or both surrogates are within laboratory control limits, the process is considered to be in control and no further action is taken (unless additional measures are stipulated in the LIMS program specification.

- When, due to elevated target concentrations, an extract requires a dilution of greater than 5X, ALSLG-FC does not consider the surrogate recoveries to have meaning; no further action is required.

- When both surrogates are outside of laboratory control limits (or other limits specified in the LIMS program specification), the extract is re-injected to assure that instrument error was not the cause. If after re-injection the recoveries of both surrogates remain out of control, then re-extraction and re-analysis may be performed as directed by the client. A non-conformance report (NCR; SOP 928) to document the problems is required.

This process of evaluating surrogate recovery is based on several methods and guidance documents and has evolved in particular from Method SW8080 guidance as well as from the National Functional Guidelines for Data Review.

9.9 METHOD DETECTION LIMITS

The MDL study should be performed as needed and at a minimum, annually. See SOP 329 for further guidance.

10. DEVIATIONS FROM METHOD

10.1 This SOP meets the requirements of Method SW8082. The following is the only known deviation from the method: The method allows for single point calibration of Aroclors 1221, 1232, 1242, 1254, 1262 and 1268 using a point near the midpoint concentration of the 1016/1260 curve. ALSLG-FC analyzes a single point for these Aroclors at the reporting limit to assist in pattern recognition as well as to show instrument sensitivity for all the targets. If Aroclor 1221, 1232, 1242, 1254, 1262 or 1268 is detected in the sample, then a calibration curve with at least 5 points is prepared and the sample re-analyzed for that Aroclor following the procedures discussed in this SOP. This more stringent approach is intended to provide more accurate quantitaton for these Aroclors.

Note that ALSLG-FC defines analytical shift (8000C) as per 24hrs, not 12hrs.

10.2 EPA 608: The items discussed in this Section list differences between Methods EPA 608 and SW8082:

10.2.1 EPA 608 states specific extraction methods, chromatographic conditions, etc. to be used in the execution of the method. Some of these materials, apparatus, and conditions have been eclipsed by the more modern technology listed in this SOP. Section 8.1.2. of EPA 608 also states that technological advances are recognized and allowed for use provided that the precision and accuracy requirements put forth by the method can be achieved.

10.2.2 EPA 608 specifies extraction of samples by separatory funnel. ALSLG-FC uses continuous liquid-liquid extractors (CLLEs) or separatory funnels to extract aqueous samples.

10.2.3 EPA 608 specifies that calibration standards be kept in isooctane. ALSLG-FC uses hexane as a solvent for calibration standards.

10.2.4 EPA 608 states that if the RF value over the range demonstrated by the initial calibration is $\leq$10%, the average response factor can be used for calculations. otherwise construct a linear regression curve. ALSLG-FC typically quantifies Aroclors from a linear regression curve.

10.2.5 EPA 608 specifies that a continuing calibration standard be analyzed every 24 hours. ALSLG-FC follows Method SW8082 that specifies a continuing calibration verification be analyzed every 12 hours and every 20 samples thereafter (although ALSLG-FC observes 10 samples between CCVs rather than 20).

10.2.6 The use of surrogate standards is not addressed in EPA 608. ALSLG-FC uses the two surrogates discussed in this SOP.

10.2.7 Because samples from several sites are usually batched together, only one spiking level is used for each compound. Per EPA 608, it is impractical to match each compound's spike amount with the amount of the compound in the samples chosen for spiking, and to match the spike amount to the appropriate regulatory level for each compound. This difference must be stated in the data package narrative for EPA 608 sample analyses.

10.2.8 Section 7.5 of EPA 608 prescribes the use of Florisil columns to remove co-extractives; a sulfuric acid clean up procedure is not discussed in EPA 608. ALSLG-FC routinely performs a Method SW3665A sulfuric acid clean up on all samples analyzed for PCBs only (see SOP 651).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 All flammable compounds must be kept away from ignition sources.

11.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.6 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport. The cylinder must be stored capped and secured at all times.

11.2 WASTE DISPOSAL

11.2.1 Any hexane or other nonhalogenated organic solvents that has not been potentially contaminated with PCBs may be disposed of in the

Acetonitrile/Nonhalogenated Waste.

11.2.2 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.3 The extract vials, associated extracts, and any PCB contaminated debris that may contain PCBs in excess of 50ppm shall be disposed of intact in the PCB Debris Waste.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 8082, Revision 0, December 1996.

12.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, Final Update IV, "Method 8000C", Revision 3, March 2003.

12.3 40 CFR, Part 136, Appendix A, 7-1-99 edition; Method 608.

DOCUMENT REVISION HISTORY

7/5/06: Strengthened LIMS program specification references, analytical columns and consumables used, and chromatographic interpretation. Changed standards storage temperature to -10°C to -20°C from 4±2°C to match practice. Added DOCUMENT REVISION HISTORY. Replacements issued for pages 12 and 16 (corrected RPD formula and updated matrix spike %R formula, updated DOCUMENT REVISION HISTORY).

3/19/09: Revised SUMMARY Section to make it consistent with other similar SOPs. Added Maintenance Section 8.2. Updated CCV discussion in Section 8.5. Updated references to 8000C. Included laboratory's definition of shift in DEVIATIONS Section 10.1.

Analytical Method: SW8082, EPA 608	**Parameter:** Polychlorinated Biphenyls (PCBs)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point; all analytes	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20% (Method SW8082) or ≤10% (EPA 608), use mean CFs to quantitate. If RSD >20% , calculate linear regression (not forced through origin); use for quantitation if coefficient of determination (r^2) is ≥ 0.99.	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Initial Calibration Verification (ICV); run near midpoint of calibration, but at a different concentration than CCV	With each initial calibration	If ≤20% D analyses may proceed.	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV); run at or near midpoint of calibration	Daily prior to sample analyses; brackets each set of 20 field sample analyses (10 sample analyses recommended)	If ≤20% D analyses may proceed.	Evaluate/correct instrument malfunction as needed (e.g., remove 1 meter from the guard column of the GC, prepare a new standard); reanalyze. - If CCV still non-compliant, recalibrate using a new curve. Samples analyzed after a failed CCV will be reanalyzed. - If target(s) in CCV fails high (>20%) and target is not present in samples, re-analyses of samples are not necessary. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW)	Whenever a new column is installed, based on 3 injections throughout a 72-hour period to be more representative of daily operations	Column and compound specific. Window is ±3x the standard deviation of the 3-injection average for the respective column. Note that the ICV and	If SD=zero, then either do additional injections or use a default SD of 0.01 minutes. Experience of analyst weighs heavily in interpretation of chromatograms (refer also to RT Shift).

Analytical Method: SW8082, EPA 608	**Parameter:** Polychlorinated Biphenyls (PCBs)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
		CCV analyses are also used to monitor RTW shift.	
Retention Time (RT) Shift	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate. Evaluate data based on a comparison with other standards run during the analytical sequence; consider the RTs for the surrogates and spiked compounds analyzed before and after the sample in question:
Method Blank (MB)	1 per each preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are outside the extraction holding time, then complete an NCR and contact PM for sample disposition.
Laboratory Control Sample (LCS)	1 per batch of ≤20 samples of like matrix	See laboratory limits; recoveries for the spiked compounds must be within the laboratory limits or other limits as specified in the LIMS program specification.	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions or analytical preparation was the cause. - if still non-compliant and the samples are within the extraction holding time, then request re-extraction using an NCR, and reanalyze all associated samples for the analyte that does not meet criteria. - if the samples are outside the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Matrix Spike (MS)	1 per batch of samples, not to exceed 20 samples of a given matrix	See laboratory limits; recoveries for the spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.

Analytical Method: SW8082, EPA 608	**Parameter:** Polychlorinated Biphenyls (PCBs)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Matrix Spike Duplicate (MSD) or Duplicate	1 per batch of samples, not to exceed 20 samples of a given matrix.	See laboratory limits; see Matrix Spike information above for MSD recoveries. RPDs should be within advisory limits.	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). If no errors are found and, if analyzed, LCSD RPD is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Surrogate Spike	All extractions including field and laboratory QC samples.	See laboratory limits; recoveries should be within current limits for one or both surrogates; alternative criteria as defined in the LIMS program specifications may apply.	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with both surrogate recoveries outside the recovery limits, with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if both surrogate recoveries in the associated MB are not within limits, and the samples are within the holding time, then re-extract and reanalyze all associated samples. - if samples are outside the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study	As needed and at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If `criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Must Discard 30 Days from _____ (date printed)

Amendment 7/21/08. Note (and in update) that methanol-extracted QC must be performed where methanol-extracted samples are processed. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 424 REVISION 12

TITLE: **DETERMINATION OF AROMATIC VOLATILE ORGANICS BY GAS CHROMATOGRAPHY – METHOD SW8021B**

FORMS: 412

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8-11-06

QUALITY ASSURANCE MANAGER _____ DATE 8/11/06

LABORATORY MANAGER _____ DATE 8-11-06

HISTORY: Rev0, 6/23/92; Rev1, 2/5/93; Rev2, PCN #216, 4/12/94; Rev3, PCN #433, 6/27/95; Rev4, 3/22/96; Rev5, 6/10/96; Rev6, 2/12/99, Rev7, 1/24/01; Rev8, 12/9/02; Rev9, 3/6/04; Rev10, 7/26/05; Rev11, 3/13/06; Rev12, 8/11/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references -- SW-846 Method 8021B -- is used to determine the concentration of aromatic volatile hydrocarbons in sludge, solids (tar, asphalt), petroleum products, water and all other aqueous and solid matrices.

The following compounds may be analyzed by this method:

benzene	toluene
chlorobenzene	ethyl benzene
1,2-dichlorobenzene	m- and p-xylene
1,3-dichlorobenzene	o-xylene
1,4-dichlorobenzene	methyl-t-butyl ether (MtBE)

Other compounds may be analyzed if successful method detection limit (MDL) and demonstration of capability (DOC) studies are performed.

2. SUMMARY

Prepared samples are loaded onto a purge and trap device and are subsequently heated and desorbed to a gas chromatograph (GC) containing a sample splitter and two capillary columns of varying selectivity (i.e., dissimilar elution and retention time properties). The target analytes are separated in the columns by temperature programming and detected by two photoionization detectors (PIDs). The PID responses are processed by an electronic integrator and the result is determined using an internal standard quantitation calculation. This chromatography system facilitates tentative identification by one column and confirmation by the other column to be performed simultaneously. Quantified values are reported from the best column for each analyte. The analyst considers performance data

such as separation of interferences, calibration performance and matrix spike results in selecting the quantitation column used for each analyte detected and reported. If results from both columns are comparable, the highest value is reported.

Preparation procedures are based on those described in Method SW5030C. Low/medium concentration samples may be purged and trapped either in neat or diluted form. Full (5mL or 5g) or reduced aliquots of low/medium concentration water or solid samples are heated while sparging (though heated purging of aqueous samples is not required by the method). High concentration aqueous samples may be further diluted using serial dilution techniques. High concentration solid samples are first subjected to methanolic extraction, with an aliquot of extract subsequently analyzed by its addition to 5mLs of reagent water and thus processed as an aqueous sample.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon’s standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Impurities in purge gas and outgassing from organic compounds in the plumbing ahead of the trap account for the majority of potential contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing laboratory blanks with every batch. Within the purging device, the use of non-PTFE (Teflon) plastic coated sealants or flow controllers with rubber components should be avoided.

4.2 Samples may be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling, handling and storage protocols can serve as a check on such contamination.

4.3 In this method, syringes are used to introduce the samples, quality control samples (method blank, LCS, MS, etc), and calibration standards into the purge and trap device. The laboratory uses dedicated disposable syringes to prevent cross-contamination. However, contamination by carryover from the trap and lines can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of organic-free reagent water to clean the system and ensure that it is contaminant-free. Frequent bake-out of trap and column is also helpful.

4.4 The laboratory where volatile analyses are performed should be completely free of solvents and the atmosphere must be adequately free of volatile organic compound vapors. The laboratory is sufficiently free of volatile organic interferences if acceptable method blank analyses are routinely accomplished.

4.5 Interferences are also minimized by the use of only high purity reagents.

5. APPARATUS AND MATERIALS

5.1 PURGE AND TRAP AUTOSAMPLER DEVICE
O-I Analytical, Arcon™, Model 4552 automated purge and trap device, or equivalent. Equipped with Supelco™ Trap K #21066-U or equivalent

5.2 GAS CHROMATOGRAPH (GC) / DETECTORS
Hewlett Packard™, Model 5890 Series II GC or equivalent, equipped with dual photoionization detectors (PIDs)

5.3 DATA ACQUISITION AND PROCESSING SYSTEM
Any data acquisition system capable of acquiring, storing and processing chromatographic data (e.g., Hewlett Packard Chem Station™ or equivalent)

5.4 COLUMNS - Equivalent columns/guard columns may also be used

J&W Capillary Column:	DB-624 #200-0113* (30m x 0.53mm ID, 3.0µm film thickness)
J&W Capillary Column:	DB-VRX #200-0015* (30m x 0.45mm ID, 3.0µm film thickness)

* J&W columns are available through Agilent, part numbers are Agilent numbers.

5.5 GASES - only high purity or higher grade gases may be used
Helium - carrier gas

5.6 MEASURING DEVICES
Luer-lock syringes, Becton & Dickinson or equivalent, disposable, 5mL or 25mL (used for sample introduction)

microsyringes, gas-tight, Precision Hamilton or equivalent, 5µL - 1.0mL sizes) (used for spiking)

volumetric flasks, Class A with ground glass stoppers, various sizes

balance (capable of weighing ±0.01g); used for weighing solid samples

5.7 CONSUMEABLES

- Photoionization Lamp - Restek #23020 Model 108 BTEX, or equivalent
- Compact Vespel/Graphite Ferrule - Restek #20264, or equivalent
- Graphite Ferrules - various sizes

6. REAGENTS

6.1 organic-free reagent water, purged with nitrogen per SOP 511

6.2 methanol (CH_3OH, MeOH), JT Baker, #9077-02 or equivalent, purge & trap grade

6.3 Ottawa sand, EMD, #SX0075-3 or equivalent

6.4 STANDARDS

6.4.1 All standards are maintained per PAR SOP 300, which supercedes any guidance in this SOP. Stock standards, in methanol, may either be prepared from pure standard materials (per SW8000B and SW8021B, Section 5.0) or purchased as certified solutions from suitable vendors. Unopened stock standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules, if recommended by the manufacturer. Standards for this procedure must be equilibrated to -10-20°C (stored in freezer) before opening. After opening/initial use, transfer remaining stock standard to a suitable vial (preferably Mininert™) with minimal headspace, and store in freezer (-10-20°C). All opened stock standards must be replaced after 3 months, or sooner, if comparisons with laboratory control samples indicate a problem.

6.4.2 At minimum, two independent sources of target analytes are required. Typically, certified stock standards are purchased from suitable vendors as single analyte solutions (which are later combined in-house) or as mixes. First source materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards. Second source materials are used to create the initial calibration verification (ICV) solution (used to independently verify the accuracy of the initial calibration, ICAL). Non-target analyte surrogate and internal standard stock standards are also prepared or purchased. The surrogate used for this method is 2,3,4-trifluorotoluene. The internal standard used for this procedure is ααα-trifluorotoluene. Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

6.4.3 An appropriate volume of stock standard (target analyte or mix, surrogate, internal standard) is diluted (with methanol) to a specific volume to create an intermediate standard. All dilutions should be performed using microsyringes, Class A volumetric flasks, and purge & trap grade (or higher) MeOH. The surrogate and internal standard are made together as a combined intermediate standard, containing 100µg/mL each of both 2,3,4-trifluorotoluene and α,α,α-trifluorotoluene.

NOTE: BFB (bromofluorobenzene) may also be included in the surrogate/internal standard solution as an additional surrogate, however, this second surrogate is not routinely reported.

The internal standard (IS) component is used to quantitate target analytes detected in samples. The surrogate standard (SS) component is used to monitor system performance and method effectiveness in dealing with each sample matrix. A 1µL nominal aliquot of the 500µg/mL IS/SS spiking solution is added to every sample to yield a final concentration of 100µg/L.

NOTE: If using a system with automated introduction of standards, such as the O-I Arcon™ autosampler, an equipment validation study must be performed to determine the actual volume delivered. The concentration of standard may be adjusted accordingly for the actual volume delivered by the autosampler at the 1µL setting. For example: (1.135µL actual delivery)(441µg/mL IS/SS spiking solution)/5mL = 100µg/L.

6.4.4 The intermediate calibration standards are injected into syringes containing reagent water to create working standards. Working standards (ICAL, ICV, CCV) are prepared on the day of use and documented in the analytical run log (Form 412). These working calibration standards must contain all target analytes, and the surrogate and internal standard. A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.4.5 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Aqueous samples are collected in 40mL glass VOA vials with screw tops and Teflon™-lined septa. Aqueous samples should be headspace-free.

7.3 Where applicable, aqueous samples should be dechlorinated with sodium thiosulfate at time of collection, then acidified with hydrochloric acid (HCl). Typically the addition of 4 drops of concentrated HCl to each 40mL VOA vial is sufficient to bring the pH of the sample to <2.

7.4 If untreated in the field, the Paragon Project Manager may direct that each aqueous sample is tested for residual chlorine upon receipt at the laboratory. Notify the Project Manager immediately if residual chlorine is detected. If the water sample remains unpreserved, the maximum holding time to analysis is 7 days from the date of collection.

7.5 The maximum holding time to analysis for acid-preserved aqueous samples is 14 days from the date of collection.

7.6 All samples are to be kept chilled (4±2°C)

7.7 Solid samples are collected in wide-mouth glass containers with Teflon™-lined lids. Solid samples are not chemically preserved and must be analyzed within 14 days of collection.

8. PROCEDURES

8.1 TYPICAL SYSTEM OPERATING CONDITIONS

Purge & Trap Device

Purge Gas Flow Rate:	45 - 50mL/min
Preheat:	0.01min to 40°C
Purge:	8min
Dry Purge:	2min
Desorb Preheat:	180°C
Desorb:	3min at 250°C
Bake:	4min at 260°C

Gas Chromatograph

Carrier Gas (Helium) Flow Rate:	2 - 6mL/min
Make up Gas (Helium) Flow Rate:	30mL/min
Transfer Line:	120°C
Injector Temperature:	240°C
Initial Oven Temperature:	3min at 40°C
Initial Oven Ramp:	12°C/min to 80°C
Oven Ramp A:	8°C/min to 130°C
Oven Ramp B:	35°C/min to 225°C
Hold:	225°C for 2.5 min
PID Temperature:	260°C

8.2 CHROMATOGRAPHIC MAINTENANCE

8.2.1 Dual columns are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector. Reattach the columns after cleanly cutting off at least two loops from the injection port side of the column using a capillary cutting tool or scribe. The accumulation of high boiling residues may change split ratios between dual columns and thereby change calibration factors. Clip a loop from the guard column or replace as necessary.

8.2.2 Columns may be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Oxidized columns will exhibit baselines that rise rapidly during temperature programming.

8.2.3 PID windows may be cleaned if the signal has weakened or annually. Lamps are replaced if signal is unstable or cleaning is ineffective. Replace both lamps at the same time and use equivalent lamps.

8.2.4 Replace trap if consistent MtBE recovery can not be achieved or if other trap performance problems are demonstrated and not alleviated by routine maintenance.

8.3 INITIAL CALIBRATION

8.3.1 Aqueous initial calibration standards are prepared at a minimum of five concentrations by spiking amounts of the prepared analyte (intermediate) standard into syringes containing organic-free reagent water. The range of concentrations of the initial calibration is intended to define the working range of the analytical system. One of the concentrations must be at or below the analyte reporting limit. The O-I Arcon adds the SS/IS mixture is to all non-ICAL samples. However, to facilitate the required multiple concentration levels, the SS is added manually for each ICAL standard, while the IS is added by the O-I Arcon. Typical calibration preparation is depicted below in Table 1.

TABLE 1
CALIBRATION STANDARDS

Level	µL Stock Standard (50µg/mL)	µL Surrogate (100µg/mL)	IS Standard (441µg/mL)	Analyte Concentration (µg/L)
ICAL 8	10	8µL	Added by Arcon	100
ICAL 7	6µL	7µL	Added by Arcon	60
ICAL 6	5µL	6µL	Added by Arcon	50
ICAL 5	4µL	5µL	Added by Arcon	40
ICAL 4	2µL	4µL	Added by Arcon	20
ICAL 3	1µL	3µL	Added by Arcon	10
ICAL 2	(10µL)(@50x)	2µL	Added by Arcon	2
ICAL 1	(2.5µL)(@50x)	1µL	Added by Arcon	1
ICV	Varied	*	*	Varied
CCV	5µL	*	*	50

*Added as mix by O-I Arcon

8.3.2 Solid initial calibration standards are similarly prepared by spiking appropriate amounts of prepared analyte (intermediate) standard onto a 5g aliquot of Ottawa sand that has been measured into a 40mL VOA vial. Then, 5mL of organic-free water (into which the surrogate has

been spiked, see 8.3.1) is added to the 40mL vial, to facilitate purging. The IS is added using the Arcon automated addition feature.

8.3.3 Electronically integrated peak area responses are tabulated and quantitated using internal standard quantitation. Response Factors (RFs) for each compound are calculated as follows:

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = response for the analyte to be measured

A_{is} = response for the internal standard

C_{is} = concentration of the internal standard (µg/L, µ/Kg)

C_s = concentration of the analyte to be measured (µg/L, µg/Kg)

8.3.4 If RF over the working range is constant (i.e., < 20% RSD), then the response is assumed to be invariant and the average (mean) RF may be used to quantitate sample content. Relative Standard Deviation (RSD) is calculated as:

$$RSD\ (\%) = \frac{\text{Standard Deviation (SD)}}{\text{Average (mean) CF}} \times 100$$

If more than five calibration concentration levels were acquired and the %RSD (of the RFs) exceeds 20% because one of the calibration injections is seen to have been ineffective, that one data point may be deleted from the initial calibration and the %RSD recalculated. The recalculated %RSD must meet acceptance criteria.

NOTE: A minimum of five (5) points must be used for the initial calibration. If more than one calibration point must be discarded to meet the % RSD criteria, the initial calibration is judged to be invalid and a new initial calibration must be generated.

If an initial calibration point is not used for any reason, the analyst must clearly notate why the data point was not used for instrument calibration.

When RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be $\geq$0.99 to be used for sample quantitation. Note that

the coefficient of determination (COD) is an expression of "goodness of fit", with perfect fit being a value of 1.0. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000. A quadratic regression should not be used to compensate for detector saturation.

Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

If regression criteria cannot be met, a new initial calibration must be performed.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source (ICV) standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV are identical to those of CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or around the midpoint of the initial calibration. Acquire a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

NOTE: Method SW8000B Section 7.7 allows up to 12 hours of analysis (approximately 20 injections) between CCVs. Paragon commonly analyzes 10 samples between CCVs to reduce the amount of repeat injections.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when all compounds are within 15%D or when the average of the %Ds for all compounds is $\leq$15% (individual compounds that exceeded 15% are noted in the data package narrative). If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the

CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

8.6 RETENTION TIME WINDOWS

For GC methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (σ) of the absolute retention time yielded for each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time $\pm 3\sigma$, such that the Upper Limit = $+3\sigma$ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time drift). Sample matrices may cause drift that requires further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system.

8.7 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATIONS, REPORTING)

Samples are introduced to the GC via purge and trap. Sample introduction techniques (i.e., choice of sample size or dilution) are chosen to maintain response within the linear quantitation range. QC samples (LCS, MS, etc.) are prepared in a manner similar to that of standards described above. A discussion of quantitation follows.

8.7.1 Note that Paragon employs a sample splitter that facilitates simultaneous dual column injections; therefore, both columns are calibrated in the same manner and either column may serve as the column for quantitation.

8.7.2 Tentative identification occurs when a sample peak falls within the RTW of one column. If the peak also falls within the RTW of the second column, then the analyte's presence has been confirmed. Quantitation is calculated from both column responses and the best result is reported. The analyst considers performance data such as separation of interferences, calibration performance and matrix spike results in selecting the quantitation column for each analyte detected and reported. If there are interferences present on one column, these need to be documented by printouts of that region of the chromatogram; the lower (i.e., other column's) results may be reported

in this case. If results from both columns are of comparable quality, the higher concentration is reported (per SW8000B).

8.7.3 The following equation is used to quantify sample concentration when RF (or mean RF) is employed:

$$\text{Concentration } (\mu g/L \text{ or } Kg) = \frac{[(A_x)(C_{is})(DF)]}{(A_{is})(\text{mean RF})(V_s \text{ or } W_s)}$$

where:

A_x	=	analyte response (area units)
C_{is}	=	amount of internal standard added (ng)
DF	=	Dilution Factor (if applicable); if no dilution was made, DF = 1 (dimensionless)
A_{is}	=	internal standard response (area units)
RF or mean RF	=	standard response (area units)
Vs or Ws	=	(volume or weight) of sample analyzed (mL or g)

Where linear regression is employed, quantitation of sample concentration is based on the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)\,(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte

y = analyte instrument response (area units)

b = calculated intercept

m = calculated slope of the line

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried

through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method Blanks (MBs) are aliquots of matrix (i.e., organic-free water for liquids, Ottawa sand for solids) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this criterion is not achieved, then analyses must be halted and the source of the contamination found and corrected.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. Percent Recovery (%R) for spiked analytes is calculated as follows (See QC Table for evaluation criteria:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right) (100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.6 SURROGATE RECOVERY

The %R of the surrogate is calculated (see equation shown for LCS recovery above) for all field and QC samples. If the recovery is outside QC limits, the sample is reanalyzed to verify that analytical error was not the problem. If after re-injection the recovery is still out-of-control, initiate an NCR (SOP 928) and apply the decided upon action. Typically, matrix effect is cited as the cause and the occurrence is narrated. However, the client may direct that the sample be re-extracted and reanalyzed (holding time is a consideration).

9.7 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW8021B and the preparatory procedures described in SW5030C. It should be noted, however, that Paragon may use a heated purge for aqueous samples, which rigorous but not required by SW5030C. SW5030C(mod) is the cited reference for solid sample preparation. Solid samples are prepared and analyzed taking guidance from SW5030C (Purge & Trap for Aqueous Samples) and SW5035A (Closed System Purge & Trap and Extraction of Solid Samples). Currently Paragon's analysis is not conducted on a closed system, hence the SW5035A method citation is not used. There are no other known deviations from the methods.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.1.8 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Solvent wastes must be disposed of in the appropriate waste containers.

11.2.2 Any rinse waters used for rinsing syringes or other devices prior to sample contact may be disposed of in the Aqueous Lab Waste.

11.2.3 Any methanol, hexane or other nonhalogenated organic solvents that has not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

EPA SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, 3rd edition, Final Update III, Method 8021B, Revision 2, December 1996.

DOCUMENT REVISION HISTORY

8/11/06: EPA 602 removed from SOP (Paragon is no longer supporting this method). LIMS program specification language strengthened. Dual column identification and interpretation of results clarified. List of consumables added. Use of Arcon device added. DOCUMENT REVISION HISTORY Section added.

Analytical Method: SW8021B	**Parameter:** Aromatic Volatile Organics (AVOs)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum 5-point, all analytes	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate Calculate linear regression (not forced through origin); use for quantitation if correlation coefficient (r) ≥0.995 or Calculate quadratic regression (minimum of six points required); use for quantitation if COD (r^2) ≥0.99	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Initial Calibration Verification (ICV); conc. not equal conc. to midpoint of calibration curve; second source	After each ICAL	≤15%D of each compound or mean %D ≤15% or as otherwise specified in applicable LIMS program specification	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8121B allows bracketing of 20 field sample analyses)	≤15%D of each compound or mean %D ≤15% or as otherwise specified in applicable LIMS program specification	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of	Whenever a new column is installed	Column and compound specific Window is ±3x the standard deviation of the 3-injection average for the respective column	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms

Analytical Method: SW8021B	**Parameter:** Aromatic Volatile Organics (AVOs)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
variation		Note that the ICV and CCV analyses are also used to monitor RT drift	(refer also to RT Shift).
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition.
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the

Analytical Method: SW8021B	**Parameter:** Aromatic Volatile Organics (AVOs)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; see Matrix Spike information above for MSD recoveries RPDs should be within advisory limits	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. Note in narrative. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers.
Surrogate Spike	All field and laboratory QC samples	See laboratory limits; recoveries should be within current limits alternative criteria as defined in the LIMS program specifications may apply	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if surrogate recovery in the associated MB is not within limits and the samples are within the

Analytical Method: SW8021B	**Parameter:** Aromatic Volatile Organics (AVOs)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			holding time, then re-extract and reanalyze all associated samples - if samples are beyond the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Paragon Analytics

Instrument ID ______________ Date _____________ Operator ____________ Method _______________ SOP _____ / Rev ____ Matrix _____________ Date Data Archived ______

Sequence Name: C:\HPCHEM____\SEQUENCE_________________ Processing Method ________________ Method Saved As ________________ Data Path: C:\HPCHEM____\DATA_________

Reagent Lots: **1. Primary Standard** # ________________; exp. date __________ **2. 2nd Source** # ________________; exp. date ___________ **3. IS + SS** # _______________; exp. date _________

4. IS only # ________________; exp. date ____________ **5. Surr only** # ________________; exp. date ____________ **P&T MeOH** # ________________; exp. date ___________

ICV or CCV *(circle 1)* 1 IS Det.#1 area _________________ ICV or CCV (circle 1) 1 IS Det.#2 area _________________ Balance ID ___________

Vial	Data File	Method	Sample Name	Sample pH	Sample wt / Vol	Std **1** Added (µL)	Std **2** Added (µL)	Std **3** Added (µL)	Std **4** Added (µL)	Std **5** Added (µL)	IS Check	Sur Check	Rerun?	Comments

Reviewed by / date ____ **Form 412r1.xls (7/5/2000)**

Must Discard 30 Days from _____ (date printed)

Amendment 7/21/08. Note (and in update) that methanol-extracted QC must be performed where methanol-extracted samples are processed. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 425 REVISION 12

TITLE: **ANALYSIS OF TOTAL VOLATILE PETROLEUM HYDROCARBON (TVPH) GASOLINE RANGE ORGANICS (GRO) BY GAS CHROMATOGRAPHY -- METHODS SW 8015B and CAL-LUFT**

FORMS: **412 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8.31.06

QUALITY ASSURANCE MANAGER _____ DATE 8/31/06

LABORATORY MANAGER _____ DATE 8-31-06

HISTORY: NEW, Rev 0, 11/8/92; Rev1, 2/5/93; Rev2, PCN #214, 4/11/94; Rev3, PCN #434, 6/27/95; Rev4, 4/23/98; Rev5, 2/15/99; Rev6, 2/17/00; Rev7, 1/15/02; Rev8, 3/01/02; Rev9, 3/14/03; Rev10, 4/16/04; Rev11, 3/13/06; Rev12, 8/24/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- SW8015B and CAL-LUFT -- are used to determine the concentration of Gasoline Range Organic (GRO) compounds in aqueous and solid/sludge samples.

Method SW8015B defines the alkane range corresponding to GRO as approximately C_6 through C_{10} boiling point, with the approximate boiling points ranging from 60°C to 170°C. State-specific or client-specific fuels analysis protocols may require analysis of a modified carbon range.

Gasoline is identified by pattern recognition; however, certain volatile aromatic compounds (e.g., benzene, xylenes, MtBE) are detectable as target analyte indicators. Analyst expertise is crucial to this method as multiple patterns may be present in a sample. Also, pattern responses in environmental samples may differ from textbook characterizations because of weathering. Any peak(s) present in the current GRO retention time window will be integrated and reported as GRO.

2. SUMMARY

Sample aliquots are introduced onto a purge and trap device and are subsequently desorbed onto a gas chromatograph (GC). The GC is temperature programmed to facilitate separation of surrogate standards, to produce a good GRO pattern and to resolve the early diesel elution pattern. Analytes of interest are detected using a photoionization detector (PID) in series with a flame ionization detector (FID). The PID output is used to monitor the internal standard and surrogate standard retention times and areas. Standard areas are subtracted from the FID/GRO area to achieve a valid total GRO response. Detector responses are recorded by an electronic data system. The sample response is

compared to the GRO response, of reference standards, using the internal standard method of quantitation to quantitatively determine GRO.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 High levels of heavier petroleum products (e.g., diesel fuels) may contain some volatile compounds that elute within the retention time range of GRO. Other organic compounds including halogenated solvents, ketones, and ethers are also measurable. As defined in the methods, GRO quantitation includes these compounds.

4.2 Samples may become contaminated by diffusion of volatile organic compounds (VOCs) through the sample container septum during shipment and storage. A trip blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination. Weekly checks

for possible sample storage refrigerator contamination are performed per SOP 512.

4.3 In this method, syringes are used to introduce aqueous samples, soil extracts, or an additional aliquot of organic-free water into the purge and trap device. The laboratory uses dedicated disposable syringes to prevent cross-contamination. However, contamination by carryover within the analytical system can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Samples analyzed in an autosampler run after high concentration samples may need to be re-analyzed if carryover contamination is suspected. Autosampler cleaning is addressed in Section 8.

4.4 Glassware must be scrupulously cleaned, details are provided in SOP 334. Purge tubes are scrubbed with a brush and hot water, rinsed with hot tap water and baked dry at 125°C (±25°C).

5. APPARATUS AND MATERIALS

5.1 PURGE AND TRAP AUTOSAMPLER DEVICE

OI MPM-16 autosampler equipped with pocket heaters and OI Model 4560 concentrator and Supelco Trap J #24939, or equivalents

or

OI Model 4552 Archon automated sampler with concentrator (i.e. Tekmar 3000) device equipped with Supelco Trap K #21066-U, or equivalent

5.2 GAS CHROMATOGRAPH (GC) AND DETECTORS
Hewlett Packard 5890 Series II GC or equivalent equipped with a photoionization (PID) and flame ionization detector (FID) in series

NOTE: An FID must be used for GRO quantitation because its response is similar for all hydrocarbons; other detectors will not produce accurately quantitated total GRO results.

5.3 GC COLUMNS - Equivalent columns/guard columns may also be used

J&W Capillary Column:	DB-624 # 21512-304 *	(30m x 0.53mm ID, 3.0µm film thickness)
J&W Capillary Column:	DB-VRX # 21512-270 *	(30m x 0.45mm ID, 2.55µm film thickness)

*J&W columns are available through VWR, part numbers listed are VWR numbers.

NOTE: The minimum acceptable column resolution should provide separation of MtBE from the methanol solvent front and ethylbenzene from m/p-xylenes in standards.

5.4 CHROMATOGRAPHIC DATA SYSTEM
Hewlett Packard ChemStation (Enviroquant™) or equivalent

5.5 GASES - use only ultra high purity (99.999%)
Helium (purge and carrier gas)
Hydrogen (flame FID detector gas)
Compressed Air (flame FID detector gas)

5.6 MEASURING DEVICES
5.6.1 Luer-lock syringes, Becton & Dickinson or equivalent, disposable, 5mL or 25mL (used for sample introduction)

5.6.2 microsyringes, gas-tight, Precision Hamilton or equivalent, 5µL - 1.0mL sizes (used for spiking)

5.6.3 balance, capable of weighing ±0.01g (used for weighing solid samples)

5.6.4 volumetric flasks, Class A with ground glass stoppers, various sizes

5.7 CONSUMEABLES
5.7.1 Photoionization Lamps, Restek Model 108 #23020 BTEX or equivalent (GRO 8015B or BTEX 8021B); also, Restek Model 108 #20675 or equivalent (GRO 8015B-only)

5.7.2 Compact Vespel/Graphite Ferrules, Restek #20264 or equivalent

5.7.3 Graphite Ferrules, various sizes

5.7.4 Purge Tube (19x150mm), Fisher Scientific Kimbal #14-925K or equivalent

5.7.5 VOA vials, unpreserved, 40mL

6. REAGENTS

6.1 organic-free water, carbon-filtered, heated and purged with helium prior to use (SOP 511)

6.2 Ottawa sand, EMD #SX0075-3 or equivalent

6.3 Methanol (CH_3OH, MeOH), purge and trap grade or higher, Burdick and Jackson #230-4 or JT Baker #9077-02 or equivalent

6.4 STANDARDS
6.4.1 All standards are maintained per PAR SOP 300, which supercedes any guidance in this SOP. Two independent sources of commercial stock standards, in methanol, are required for GRO. The stock standards are purchased as certified solutions from suitable vendors. Unopened stock standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules, if recommended

by the manufacturer. Standards for this procedure must be equilibrated to -10--20°C (stored in freezer) before opening. After opening/initial use, transfer remaining stock standard to a suitable vial (preferably Certan™) with minimal headspace, and store in a freezer (-10--20°C). All opened stock standards must be replaced after 3 months from date opened, or sooner, if comparisons with laboratory control samples indicate a problem.

6.4.2 First source materials are used to create calibration and continuing calibration verification (CCV) standards. Second source materials are used to create the initial calibration verification (ICV) solution. Spike standards may be from either source (the second source is most commonly used for spiking).

Paragon typically uses a commercial gasoline component standard, labeled as Wisconsin GRO mix, as the GRO target stock standard. This Wisconsin GRO mix is typically 10,000-20,000µg/mL total concentration, encompassing a carbon range from C_6 to C_{10}. It typically contains 1,000 to 2,000µg/mL each of benzene, ethylbenzene, methyl-t-butyl ether (MtBE), toluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, o-xylene, m-xylene, p-xylene and naphthalene (the GRO retention time window is set from this mix using MtBE and naphthalene elution times). Specific commercial gasolines or neat blended gasolines are not typically used.

Non-target analyte internal standard (IS) and surrogate (SS) stock standards are also purchased. The IS is used to quantitate GRO detected in samples. The SS is used to monitor system performance and method effectiveness in dealing with each sample matrix. The IS used for this procedure is α,α,α-trifluorotoluene; the SS used for this procedure is 2,3,4-trifluorotoluene. Each of the standards is purchased typically at a concentration of 2,000µg/mL. Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

NOTE: BFB (bromofluorobenzene) may also be included as an additional surrogate, however, this second surrogate is not routinely reported.

6.4.3 An appropriate volume of stock standard is diluted, with methanol, to a specific volume to create intermediate standards. All dilutions should be performed using microsyringes, Class A volumetric flasks, and purge & trap grade (or higher) MeOH.

A 500µL aliquot of the GRO 10,000µg/mL stock standard is spiked into a 10mL Class A volumetric flask and diluted to the mark using methanol, to create a 500µg/mL total (50µg/mL each component) intermediate calibration standard. The second source GRO stock standard is likewise diluted to create a 500µg/mL ICV intermediate standard.

Because the IS and SS may be added manually or automatically, also separately or together, several intermediate standards are made:

- Use of separate IS and SS standards facilitates surrogate addition at the varied concentration levels required for the ICAL (see Table 1).
- Manual addition is used when the OI MPM-16 purge & trap autosampler device is employed; automated addition is used when the OI Model 4552 Archon purge & trap autosampler device is employed.
- For manual addition, a larger volume (e.g. 5µL) of a 100µg/mL intermediate standard is spiked; for automated addition, a smaller volume (e.g. 1µL) of a 500µg/mL intermediate standard is spiked.
- The separate IS and SS 100µg/mL intermediate standards are prepared by diluting the 2,000µg/mL stock standards 20X using methanol (i.e., a 250µL aliquot of the stock standard is placed into a 5mL Class A volumetric flask and diluted to the mark using methanol).
- The combined IS/SS 500µg/mL intermediate standard is prepared by placing a 50µL aliquot of each of the IS and SS stock standards into a 5mL Class A volumetric flask and diluting to the mark using methanol.

All intermediate standards must be prepared monthly. Standards may be replaced sooner if laboratory quality control analyses or other factors indicate deterioration.

6.4.4 The intermediate GRO calibration standard is injected into syringes containing reagent water to create calibration working standards. Working standards (ICAL, ICV, CCV) are prepared on the day of use and documented in the analytical run log (Form 412). A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.4.5 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Aqueous samples are collected in 40mL glass VOA vials with screw tops and Teflon™-lined septa. Aqueous samples should be headspace-free. It is recommended that a minimum of three vials should be collected for each field sample. For a designated MS/MSD, the client may need to provide as many as six vials.

7.3 Where applicable, aqueous samples should be dechlorinated with sodium thiosulfate at time of collection. Aqueous samples are acidified to pH<2 with hydrochloric acid (HCl). Typically the addition of 4 drops of concentrated HCl to each 40mL VOA vial is sufficient to bring the pH of the sample to <2.

The Paragon Project Manager may direct that each aqueous sample is tested for residual chlorine upon receipt at the laboratory. Notify the Project Manager immediately if residual chlorine is detected.

The pH of an aqueous aliquot for each sample is measured and recorded immediately before analysis. Notify the Project Manager if the pH of the sample is greater than 2.

7.4 All samples are to be kept chilled (4±2°C).

7.5 The maximum holding time to analysis for acid-preserved aqueous samples is 14 days from the date of collection. If the water sample is unpreserved, the maximum holding time to analysis is 7 days from date of collection.

7.6 Closed vessel purging by SW5035 is not required. If SW5035 direct purge is requested, solid samples must be collected in Encore™ tubes, however, Paragon is not presently performing low-level SW5035 analysis. Otherwise, for SW5035 methanolic extractions or SW5030 direct purge preparation, solid samples may be collected in 125mL wide-mouth glass containers with Teflon™-lined lids. Solid samples are not chemically preserved and must be analyzed within 14 days of collection.

8. PROCEDURE

8.1 TYPICAL PURGE & TRAP DEVICE SETTINGS (OI Model 4560 concentrator)

Purge Gas Flow (He)Rate:	approximately 40mL/min
Preheat to 40°C:	1-2min
Purge:	8min
Dry Purge:	1min
Desorb Preheat:	none
Desorb:	2min at 255°C
Bake:	13min at 255°C
Valve:	120°C
Transfer Line:	120°C
Sample Heaters:	40°C

NOTE: It is recommended to use the trap manufacturer's temperature parameters. Also note that the dry purge time will remove water vapor and methanol from the injection; however, if the dry purge is overextended, it may cause breakthrough and limited recovery of lighter molecular weight target compounds.

Though not required by any of the referenced methods, Paragon typically applies a heated purge to both aqueous and solid samples. The heated purge will increase purge efficiency or have no effect given complete purge efficiency.

8.2 TYPICAL GC OPERATING CONDITIONS - Conditions may be altered to improve resolution of GRO compounds.

Purge and Carrier gas (He) Flow Rate:	30-50mL/min
FID H_2 Flow Rate:	30mL/min
FID Air Flow Rate:	350mL/min
FID Temperature	260°C
PID Temperature:	300°C
Injector Temperature:	180°C
Initial Oven Temperature:	3min at 35°C
Initial Oven Ramp:	10°C/min to 120°C
Oven Ramp A:	25°C/min to 220°C
Hold:	220°C for 2min

8.3 AUTOSAMPLER CLEANING

After use, each purge tube is removed from the autosampler, washed and regenerated per SOP 334. Additionally, each purge needle is flushed with organic-free DI water (note that the purge tube is rinsed in place, as part of the system program, if using the OI Archon autosampler), then the exterior is wiped with a KimWipe™ and MeOH.

8.4 CHROMATOGRAPHIC MAINTENANCE

8.4.1 Bake out the trap and column. Extra blanks may be necessary to achieve an adequate baseline if carryover is observed. Replace trap if performance problems are demonstrated and cannot be alleviated by routine maintenance.

8.4.2 If trap and front end are clean and functioning properly, clip a loop from the column or replace as necessary.

8.4.3 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Oxidized columns will exhibit baselines that rise rapidly during temperature programming. If a column is oxidized, replacement may be necessary.

8.4.4 The PID window may be cleaned if the signal has weakened or annually. Lamps are replaced if signal is unstable or cleaning is ineffective.

8.4.5 Standards may be purged and analyzed to ensure that the system is stable prior to acquisition of an ICAL or CCV (i.e., priming may be performed).

8.5 INITIAL CALIBRATION

8.5.1 The GRO initial calibration (ICAL) includes a minimum of 5 concentrations of calibration standards (typically 8 are used), defining the linear range of the detector, typically 50-6000 µg/L. The lowest concentration standard shall be at a level at or below the reporting limit (RL) of each analyte (GRO or component); not all compounds can be detected at the lowest levels of the calibration. Each ICAL standard must include the surrogate, at a level similar to the target analytes; each ICAL must also include the internal standard.

8.5.2 The calibration standards are prepared on the day of use by spiking amounts of intermediate calibration standard into a syringe containing

5mL of organic-free reagent water. Calibration standards are typically prepared as follows:

TABLE 1
GRO INITIAL CALIBRATION STANDARDS

Level	µL GRO Standard (500 µg/mL)	µL Surrogate (100µg/mL)	µL Internal Standard *	Final Volume (5mL)	Final GRO Conc. (µg/L)
ICAL 1	0.5	20	5 (manual), 1 (automated)		50
ICAL 2	1	40	5 (manual), 1 (automated)		100
ICAL 3	2	60	5 (manual), 1 (automated)		200
ICAL 4	5	80	5 (manual), 1 (automated)		500
ICAL 5 (CCV)	10	100	5 (manual), 1 (automated)		1000
ICAL 6	20	120	5 (manual), 1 (automated)		2000
ICAL 7	40	140	5 (manual), 1 (automated)		4000
ICAL 8	60	160	5 (manual), 1 (automated)		6000
ICV (varied)	15	120	5 (manual), 1 (automated)		1500

NOTES: Lower concentration standards may be analyzed, particularly if 8021B analysis is performed simultaneously.

* Concentration of intermediate standard for manual injection is 100 µg/mL, concentration of intermediate standard for automated injection is 500 µg/mL

Where automated injection is accomplished, an equipment validation study must be performed to determine the actual volume delivered. The concentration of standard may be adjusted accordingly for the actual volume delivered by the autosampler at the 1µL setting. For example: (1.135µL actual delivery)(441µg/mL IS/SS spiking solution)/5mL = 100µg/L.

8.5.3 Solid initial calibration standards are similarly prepared by spiking appropriate amounts of intermediate standard onto a 5g aliquot of Ottawa sand that has been measured into a purge tube that contains a small amount of glass wool at the bottom. Then, 5mL of organic-free water is added to facilitate purging.

8.5.4 Electronically integrated peak area responses are tabulated and quantitated using internal standard quantitation. Response Factors (RFs) for individual compounds are calculated as shown below. For

GRO, a 'fingerprint' of peaks within an established retention time range is used for quantitation of analyte concentration (Cs), calculated as shown below:

$RF = (A_x C_{is}) / (A_{is} C_s)$ when using average response factor

$C_s = [(As/Ais - b] [C_{is}/m]$ when using linear curve fit

where:

A_s = response for the analyte to be measured

A_{is} = response for the internal standard

C_{is} = concentration of the internal standard (µg/L, µ/Kg)

C_s = concentration of the analyte to be measured (µg/L, µg/Kg)

b = The intercept of the linear equation

m = The slope of the linear equation

8.5.5 If RF over the working range is constant (i.e., < 20% RSD), then the response is assumed to be invariant and the average (mean) RF may be used to quantitate sample content. Relative Standard Deviation (RSD) is calculated as:

$$RSD\ (\%) = \frac{\text{Standard Deviation (SD)}}{\text{Average (mean) RF}} \times 100$$

If more than five calibration concentration levels were acquired and the %RSD (of the RFs) exceeds 20% because one of the calibration injections is seen to have been ineffective, that one data point may be deleted from the initial calibration and the %RSD recalculated. The recalculated %RSD must meet acceptance criteria. If an initial calibration point is not used for any reason, the analyst must clearly notate why the data point was not used for instrument calibration.

When RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be $\geq$0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit", with perfect fit being a value of 1.0. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000. A quadratic regression should not be used to compensate for detector saturation.

Linear (most often) and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

8.6 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV are identical to those of the CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

8.7 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or around the midpoint of the initial calibration. A CCV must be analyzed and reviewed daily prior to the analysis of samples (unless the sequence starts with an ICAL/ICV), after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

NOTE: Method SW8015B allows for up to 12 hours of analysis between CCVs. Paragon commonly analyzes 10 samples between CCVs (less than 12 hours) to reduce the amount of repeat injections.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculate d concentrat ion}) - (\text{expected concentrat ion})}{\text{expected concentrat ion}} \right] (100)$$

Calibration is verified when all compounds are within 15%D or when the average of the %Ds for all compounds is $\leq$15% (individual compounds that exceeded 15% are noted in the data package narrative). If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

8.8 RETENTION TIME WINDOWS

The GRO retention time window (RTW) is set to include the C_6-C_{10} range (MtBE through naphthalene). The RTW is checked to ensure that it is sufficiently wide to include these compounds throughout each analytical batch (i.e., MtBE and naphthalene must be within the RTW for each CCV in the batch).

8.9 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATIONS, REPORTING)
Samples are introduced to the GC via purge and trap. Sample introduction techniques (i.e., choice of sample size or dilution) are chosen to maintain response within the linear quantitation range. QC samples (LCS, MS, etc.) are prepared in a manner similar to that of standards described above. A discussion of sample preparations and quantitation follows:

8.9.1 LOW/MEDIUM-LEVEL ANALYSIS

8.9.1.1 Per SW5030B, the nominal sample size is 5mL or 5g. Smaller soil aliquots (i.e., down to 1g) may be used to achieve dilutions up to 5X. Do not use soil sample sizes less than 1g, as smaller soil sample aliquots are likely to yield poor representativeness.

NOTE: See Subsampling for Soil and Sediments (workorder review\QA Info\Guidance Documents) for a discussion of representative soil sampling.

8.9.1.2 Add an appropriate aliquot of aqueous sample to a clean 5mL Luer-lock injection syringe.

When performing an in-syringe dilution (aqueous samples, dilutions >5X), allow enough headspace in the syringe for addition of the sample. Document the dilution on the run log (Form 412).

If the Archon automated injector is not used, spike the sample syringe with 5µL of 100 µg/mL internal standard/surrogate solution. Inject the prepared sample syringe into a purge tube.

8.9.1.3 For solid matrix samples, weigh 1g (nominal) of sample into a 25mL purge tube containing a small amount of glass wool at the bottom. Use a balance that has been verified per SOP 305. Record the exact weight of sample in the preparations logbook.

Attach the purge tube to the autosampler.

Measure 5mL organic-free water into a syringe. If the Archon automated injector is not used, spike the sample syringe with 5µL of 100 µg/mL of internal standard/surrogate solution. Inject the prepared water into the 25mL purge tube containing the measured sample.

8.9.1.4 Make sure the sample valves are placed on the 'purge' position. Analyze.

8.9.1.5 Samples with responses that exceed the calibration range require dilution. In instances where a sample response is out of range, investigation must be performed to ensure that ensuing sample results are not biased by carryover. Investigation includes reanalysis of the contaminated sample and the subsequent samples until confirmation of results demonstrates the lack of bias from carryover.

When high levels analytes are observed on a multi-position autosampler, a dry tube is installed on that position and purged on the next pass to demonstrate fitness of use for that position. In the case of autosampler runs, re-analyze a sample with positive results that follows an over-range sample.

8.9.2 METHANOL-EXTRACTED SAMPLES

8.9.2.1 Obtain solid sample to be extracted from refrigerator and allow it to warm to room temperature. Return sample to refrigerator once a suitable aliquot has been obtained.

8.9.2.2 A 5g to 5mL of methanol extraction is performed in accordance with SW5035. Weigh a minimum of 5.0g of sample into a 20mL VOA vial. Record the weight to 2 decimal places. Add 5.0mL of methanol, cap shake and centrifuge for two minutes at 1400RPM or allow the extract to settle until the methanol solution appears to be free of particles.

8.9.2.3 A maximum of 100µL of methanol extract may be injected so as to not overload the trap. Inject an aliquot of methanol extract into a syringe containing approximately 5mL of organic-free reagent water. If the Archon automated injector is not used, also spike the syringe with 5µL of internal standard/surrogate solution. Inject the prepared water into a purge tube and analyze.

The remaining methanol extract may be transferred to a suitable vial with a Teflon™-lined cap and stored with other extracts in the refrigerator.

8.9.2.4 A methanolic reagent blank (100µL methanol to 5mL organic free water) must also be analyzed.

8.9.2.5 Methanolic extracts must be analyzed within 14 days of sample collection, regardless of when the extraction was performed.

8.9.3 GRO IDENTIFICATION

Concentration of GRO in the sample is calculated using the sum of all peak responses (excluding internal standard and surrogates) from within the C_6 to C_{10} RTW.

8.9.4 LOW/MEDIUM-LEVEL QUANTITATION

The following internal standard quantitation formula is employed where RFs or CFs were used for calibration:

$$\text{Sample GRO}_{\mu g/L \text{ or } \mu g/ Kg} = \frac{(A_x)(DF)}{(\text{mean RF})(V_s \text{ or } W_s)}$$

where:

A_x = Summed GRO peak response in sample, in area units

DF = Dilution factor (if applicable); if no dilution was made, D=1 (dimensionless)

mean RF = Average (mean) RF from latest initial calibration, mg/area

V_s or W_s = Volume or Weight of sample purged, L or Kg

8.9.5 METHANOL-EXTRACTED SAMPLE QUANTITATION

The following internal standard quantitation formula is employed where RFs or CFs were used for calibration:

$$\text{Sample GRO}_{\mu g/L \text{ or } \mu g/Kg} = \frac{(A_x)(V_t)(DF)}{(\text{mean RF})(V_s \text{ or } W_s)(V_i)}$$

where:

A_x = Summed GRO peak response in sample, in area units

DF = Dilution factor (if applicable); if no dilution was made, D=1 (dimensionless)

mean RF = Average (mean) RF from latest initial calibration, mg/area

V_s or W_s = Volume or Weight of sample purged, L or KG

V_t = Total volume of methanol extract, mL

V_i = Volume of extract used for purging, mL

8.9.6 QUANTITATION WHERE CALIBRATED BY LINEAR REGRESSION

Where linear regression is employed, quantitation of sample concentration is based on the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte

y = analyte instrument response (area units)

b = calculated intercept

m = calculated slope of the line

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method Blanks (MBs) are aliquots of matrix (i.e., organic-free water for liquids, Ottawa sand for solids) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this criterion is not achieved, then analyses must be halted and the source of the contamination found and corrected.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results

of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$\text{RPD} = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. Percent Recovery (%R) for spiked analytes is calculated as follows (see QC Table for evaluation criteria):

$$\%\text{R} = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.6 SURROGATE RECOVERY

The %R of the surrogate is calculated (see equation shown for LCS recovery above) for all field and QC samples. If the recovery is outside QC limits, the sample is reanalyzed to verify that analytical error was not the problem. If after re-injection the recovery is still out-of-control, initiate an NCR (SOP 928) and apply the decided upon action. Typically, matrix effect is cited as the cause and the occurrence is narrated. However, the client may direct that the sample be re-extracted and reanalyzed (holding time is a consideration).

9.7 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the sensitivity limit of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM THE METHOD

10.1 This SOP meets the requirements of SW-846 Method 8015B and CAL-LUFT. Paragon notes that the suggested carbon range for gasoline (C_6-C_{10}) in SW-846 may be modified to meet our client's requirements. The spike mixture used in

this procedure contains a mixture of pure compounds whose straight-chain carbon equivalent numbers range from C_6 to C_{12}. These pure compounds (in their mixture) define the chromatographic retention time region used to identify and quantitate the gasoline components in the samples and allow for the application of an extended range analysis to C_{12} upon client request.

10.2 Heated purge of aqueous samples is not required by SW5030. Paragon may perform heated purging of aqueous samples. The heated purge of a water increases the purging efficiency or has no effect on a complete purge and will not adversely bias the results.

10.3 CAL-LUFT specifies a %D criterion of ±10% for daily calibration verification. Paragon defaults to the criteria listed in Method 8015B of ±15%D unless otherwise required by client or project specific needs (as indicated in the LIMS Project Specification).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.5 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.2 WASTE DISPOSAL

11.2.1 Any methanol, hexane, acetone, or other non-halogenated organic solvents that have not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste stream.

11.2.2 Any rinse waters used for rinsing syringes or other devices prior to contact with samples must be disposed of in the Aqueous Lab Waste.

11.2.3 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.4 The extract vials, associated extracts, and any PCB contaminated debris that may contain PCBs in excess of 50ppm shall be disposed of intact in the PCB Debris Waste stream.

11.2.5 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be removed or defaced prior to disposal.

12. REFERENCES

12.1 USEPA, SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, Volume 1B, Method 8015B, Revision 2, December 1996.

12.2 USEPA, SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, Volume 1B, Method 5035 Revision 0, December, 1996

12.3 California LUFT Field Manual, October 1989 update.

DOCUMENT REVISION HISTORY

8/24/06: LIMS program specification language strengthened. Standards and Analysis sections re-organized. Form attached. DOCUMENT REVISION HISTORY section added.

Analytical Method: SW8015B	**Parameter:** Total Volatile Petroleum Hydrocarbons		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum 5-points, all analytes	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate, If RSD ≥20%, calculate linear regression (not forced through origin); use for quantitation if correlation coefficient (r) ≥0.995 or calculate quadratic regression (minimum of six points required); use for quantitation if COD (r^2) ≥0.99	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Initial Calibration Verification (ICV); conc. not equal to midpoint of calibration curve; second source	After each ICAL	≤15%D of each compound or mean %D ≤15% or as otherwise specified in applicable LIMS program specification	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8015B requires minimum of once per 12 hour shift)	≤15%D of each compound or mean %D ≤15% or as otherwise specified in applicable LIMS program specification	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed before and after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV (bracketed by acceptable CCVs) will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.

Analytical Method: SW8015B	**Parameter:** Total Volatile Petroleum Hydrocarbons		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Retention Time Window (RTW); The retention time range for GRO includes MtBE through naphthalene, window is checked against CCV for each batch.	Whenever a new column is installed; and checked with each batch	Note that the ICV and CCV analyses are also used to monitor RT drift	Width of GRO window should include MtBE and naphthalene of bracketing CCVs.
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL	Each CCV	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix NOTE: Methanol extracts additionally require a methanol MB.	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze

Analytical Method: SW8015B	**Parameter:** Total Volatile Petroleum Hydrocarbons		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Sample (LCS)	matrix	limits as specified in the LIMS program specification	to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; see Matrix Spike information above for MSD recoveries. RPDs should be within advisory limits.	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. Note in narrative. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers. Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed)

Analytical Method: SW8015B	**Parameter:** Total Volatile Petroleum Hydrocarbons		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Surrogate Spike	All extractions including field and laboratory QC samples	See laboratory limits; recoveries should be within current limits alternative criteria as defined in the LIMS program specifications may apply	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the most likely cause. However, any samples with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if surrogate recovery in the associated MB is not within limits and the samples are within the holding time, then re-extract and reanalyze all associated samples - if samples are beyond the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Internal Standard	Each batch	50-200%	Investigate and correct standard or instrument
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

________________ *Paragon Analytics*

Instrument ID ______________ Date ____________ Operator ___________ Method ______________ SOP _____ / Rev ____ Matrix ____________ Date Data Archived ______

Sequence Name: C:\HPCHEM____\SEQUENCE________________ Processing Method _______________ Method Saved As _______________ Data Path: C:\HPCHEM____\DATA_________

Reagent Lots: **1. Primary Standard** # _______________; exp. date __________ **2. 2nd Source** # _______________; exp. date ___________ **3. IS + SS** # ______________; exp. date _________

4. IS only # ________________; exp. date ___________ **5. Surr only** # ________________; exp. date ___________ **P&T MeOH** # ________________; exp. date ___________

ICV or CCV *(circle 1)* 1 IS Det.#1 area ________________ ICV or CCV (circle 1) 1 IS Det.#2 area ________________ Balance ID ___________

Vial	Data File	Method	Sample Name	Sample pH	Sample wt / Vol	Std **1** Added (µL)	Std **2** Added (µL)	Std **3** Added (µL)	Std **4** Added (µL)	Std **5** Added (µL)	IS Check	Sur Check	Rerun?	Comments

Reviewed by / date ____ **Form 412r1.xls (7/5/2000)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 434 REVISION 8

TITLE: **ANALYSIS OF CHLORINATED HERBICIDES BY GAS CHROMATOGRAPHY -- METHODS SW8151A, EPA 615 AND EPA 515.1**

FORMS: **530 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER Dan Sherman DATE 7/24/06
QUALITY ASSURANCE MANAGER Deb Schaut DATE 7/21/06
LABORATORY MANAGER [signature] DATE 7-21-06

HISTORY: Rev0, PCN #254, 8/15/94; Rev1, 1/17/96; Rev2, 2/27/96; Rev3, 6/24/99; Rev4, 3/6/02; Rev5, 8/5/02; Rev6, 2/13/04; Rev7, 3/9/06; Rev8, 7/24/06. re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This Standard Operation Procedure (SOP) and the methods it references, SW8151A, EPA 615 and EPA 515.1, are used to determine the concentration of chlorinated herbicides in liquid (all) and solid matrices (SW8151A). The following compounds typically comprise Paragon's target analyte list:

Dalapon	Silvex
Dicamba	2,4,5-T
MCPP	2,4-DB
MCPA	Dinoseb
Dichloroprop	2,4-Dichlorophеylacetic acid
2, 4-D	

Other compounds may be analyzed if successful method detection limit (MDL) and demonstration of capability (DOC) studies are performed.

2. SUMMARY

The target herbicides are commonly applied as either an amine salt (usually trimethyl amine) or one of many esters of the base compound. These are easier to handle than the free acids. Hydrolysis, to covert any esters to free acids, is included in the sample preparation process. Samples are extracted, esterified and the extracts concentrated and solvent exchanged using appropriate Paragon Analytics (PAR) SOPs (i.e., 664, 607, 637). The extracts are injected into a gas chromatograph (GC) containing a sample splitter and two columns of varying selectivity (i.e., dissimilar RT elution properties). The target analytes are separated in the columns and detected by two electron capture

detectors (ECDs). This chromatography system allows tentative identification by one column and confirmation by the other column to be performed simultaneously. Quantitation is performed using the best column for each analyte. The analyst considers performance data such as separation of analytes and interferences, calibration performance and matrix spike results in selecting the quantitation column for each analyte detected and reported. If results from both columns are comparable, the highest result is reported.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, or other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. Only high purity solvents and reagents are used; prescriptive measures for cleaning glassware are detailed in SOP 334. All of these materials must be routinely demonstrated to be free from

interferences under the conditions of the analysis as evidenced by the analysis of interference-free reagent blanks.

4.2 The target herbicides are strong organic acids that react readily with alkaline substances and may be lost during sample preparation steps.

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being analyzed.

4.4 Organic acids, especially chlorinated acids, cause the most direct interference (due to reaction products formed in the methylation sample preparation step). Phenols, including chlorophenols, may also interfere.

4.5 Sample extracts must be free of water prior to methylation or poor recoveries will be obtained. The sodium sulfate drying agent must be acidified before use.

4.6 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might interfere with the electron capture analysis. However, hydrolysis might result in limited recovery of dinoseb (cleavage of alkyl group) and dalapon (hydrolysis to pyruvic acid).

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH, AUTOSAMPLER, DETECTORS
Hewlett Packard (HP) 5890 Series II GC equipped with HP7673A autosampler and dual electron capture detectors (ECDs), or equivalents

5.2 CHROMATOGRAPHIC DATA ACQUISITION/PROCESSING SYSTEM
Hewlett Packard ChemStation (Enviroquant™) or equivalent

5.3 COLUMNS - Equivalent columns may also be used

Restek Pesticide Column:	RTX-CLPesticides	#11123	(30m, 0.25mm ID, 0.5µm film)
Restek Pesticide (Guard) Column:	RTX-CLPesticides2	#11323	(30m, 0.25mm ID, 0.5µm film)
Restek Pesticide Column:	RTX-CLPesticides	#11139	(30m, 0.32mm ID, 0.25µm film)
Restek Pesticide (Guard) Column:	RTX-CLPesticides2	#11324	(30m, 0.32mm ID, 0.25µm film)

5.4 GASES - ultra high purity (99.999%)
Helium - carrier gas
Nitrogen - make-up gas

5.5 MEASURING DEVICES
Syringes - 10-1000µL
Volumetric flasks, Class A with stoppers, 10-100mL

5.6 GC CONSUMABLES

- Vials - National Scientific C4011-1, or equivalent
- Caps - National Scientific C4000-51B, or equivalent
- Inlet Seals - dual Vespel ring, 0.8mm, Restek #21243, or equivalent
- Septa - 11mm, Restek #20365, or equivalent
- O-ring - graphite, 6.5mm, Restek #20299, or equivalent
- O-ring - Viton™, Restek #20377, or equivalent
- Liner - splitless, 4mm ID, Restek #20799-214.5, or equivalent
- Glass Wool - deactivated, Restek #20789, or equivalent
- Gold Seal - Restek #21306, or equivalent
- Universal Presstight Y - Restek #20469, or equivalent
- Vespel/Graphite Ferrule (detector) - Restek #20221, or equivalent
- Compact Vespel/Graphite Ferrule - Restek #20249, or equivalent
- Graphite ferrules - various sizes
- Split Vent Trap (SW8081) - Agilent RDT-1023, or equivalent

6. REAGENTS

6.1 SOLVENTS - Only pesticide grade solvents may be used!

Methanol (CH_3OH, MeOH) - Burdick and Jackson #230-4, or equivalent

n-Hexane (C_6H_{14}) - Burdick and Jackson #216-4, or equivalent

Diethyl ether ($C_2H_5OC_2H_5$) - Burdick & Jackson #106-4, or equivalent. Must be peroxide-free. If preserved, stabilized with BHT (not ethanol), or unpreserved.

Methyl tert butyl ether $(CH_3)_3COCH_3$, MTBE - JT Baker #9043-02, or equivalent -- Method EPA 515.1 only

6.2 STANDARDS

6.2.1 Storage and Documentation - All standards are maintained per SOP 300, which supercedes any guidance in this SOP. Unopened stock standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules, if recommended by the manufacturer. Generally after opening ampules, the standards for this procedure are stored in the freezer (-10--20°C), in PTFE-capped, or equivalent, vials. Opened stock standards and intermediate standards expire six months from opening (preparation) or per the manufacturer's expiration date (whichever is sooner). Standards may be replaced sooner if laboratory quality control (QC) analyses or other factors indicate deterioration.

6.2.2 Calibration and Spike Standards - At minimum, two independent sources (first, second) of commercial stock standards are needed for target analytes. These certified stock standards are purchased from suitable vendors as free acid mixes (first source) and methyl esters

(second source). First source materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards. Second source materials are used to create the initial calibration verification (ICV) solution (used to independently verify the accuracy of the initial calibration, ICAL). Where commercially-derivatized methyl esters are used to prepare standards, the concentrations must be corrected back to the free acid form. A (non-target analyte) surrogate stock standard is also purchased. The surrogate used for this method is 2,4-dichlorophenylacetic acid (DCAA). Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

An appropriate volume of stock standard is diluted (in hexane) to a specific volume to create intermediate standards (the QC sample and surrogate spike standards, used by the Organics Extraction Group, are intermediate standards). The intermediate calibration standards are further diluted to volume using an appropriate solvent to create working standards. Working standards are prepared on the day of use and documented in the analytical run log (Form 530). A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.2.3 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory **D**epartment.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING, HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are generally not chemically preserved for SW8151A analysis and must be collected in amber glass containers (generally 1000mL) with Teflon™-lined lids. Samples must be maintained at 4±2°C and extracted within 7 days of collection (14 days for EPA 515.1). Sodium thiosulfate ($Na_2S_2O_3$) may be used to dechlorinate liquid samples such as drinking water or chlorinated wastewater. This should be accomplished by the client in the field. The Project Manager may designate the need for residual chlorine check of the sample upon receipt. Additionally, samples for EPA Method 608 may need to have pH adjusted upon receipt.

7.3 Solid samples are collected in wide-mouth glass containers with Teflon™-lined lids. Solid samples are not chemically preserved and must be maintained at 4±2°C. Solid samples must be extracted within 14 days of collection.

7.4 Extracts, from liquid or solid samples, must be maintained between ⁻10 and ⁻20°C and analyzed within 40 days of preparation.

8. PROCEDURE

8.1 TYPICAL GAS CHROMATOGRAPHIC CONDITIONS

Carrier gas (He):	2.2 mL/min
Make-up gas (N_2):	20-40 mL/min
Injection port temperature:	205°C
Injection volume:	1-2µL, splitless
Detector temperature:	325°C
Initial oven temperature:	50°C, hold 4min
Oven ramp A:	15°C/min to 130°C
Oven ramp B:	7°C/min to 190°C, hold 3.0min
Oven ramp C:	20°C/min to 320°C, hold 7.0min

The conditions used for sample analysis must be the same as the conditions used during initial calibration**.**

8.2 SYSTEM MAINTENENANCE AND PREPARATION

Because of the low concentrations injected on a GC/ECD, column adsorption (active sites) may be a problem when the GC has not been used for a day or more. Therefore, the GC column may need to be conditioned by injecting a suitable prime, such as mid to high concentrations of expired standards, prior to calibration. Solvent blanks are typically injected following the priming to demonstrate that the system is free from carryover.

8.3 INITIAL CALIBRATION

8.3.1 Prepare a minimum of 5 concentrations of calibration standards (generally six are used), defining the linear range of the detector (SW8151A). Fewer calibration levels are required by EPA 615 and 515.1, but the use of six calibration levels is recommended. The lowest concentration standard shall be at a level at or below the reporting limit (RL) of each analyte. Create calibration standards by diluting aliquots of the intermediate calibration standard using hexane. The mid-range calibration standard is used for continuing calibration verification (CCV). For herbicides analysis, the calibration range varies contingent upon the target analyte. Calibration standards are prepared with surrogate standards at similar levels to target analytes. A typical

calibration sequence and preparation steps are shown below in Table 1.

TABLE 1
CALIBRATION STANDARDS

Working Standard	Hexane (µL)	Intermediate Standard (µL)	Standard Concentration (ng/mL)
ICAL Level 6 (30%)	700	300	varies per analyte
ICAL Level 5 (25%)	750	250	varies per analyte
ICAL Level 4 (20%)	1000	250	varies per analyte
ICAL Level 3 (10%)	900	100	varies per analyte
ICAL Level 2 (5%)	950	50	varies per analyte
ICAL Level 1 (2.5%)	975	25	varies per analyte
2nd source ICV (10%)	900 varied over time	100 varied over time	varies per analyte
CCV (20%)	1000	250	varies per analyte

8.3.2 Inject and analyze 1µL of each calibration standard. Each data file quantitation is accomplished via the external standard method of quantitation. Analyte Response Factors (RFs) are calculated as follows:

$$RF = \frac{\text{integrated peak area of analyte}}{\text{analyte concentration}}$$

If the RFs over the working range of the detector are constant (i.e., $\leq$20% RSD), then response can be assumed to be invariant (linear through zero) and the average (mean) RF may be used to quantitate sample concentration.

8.3.3 Relative Standard Deviation (RSD) is calculated as:

$$RSD\ (\%) = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean response factor}} \right)(100)$$

When RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be $\geq$0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit", with perfect fit being a value of 1.0. Non-linear (quadratic)

regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000. A quadratic regression should not be used to compensate for detector saturation.

Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is injected after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV are identical to those of the CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated. Exception: Paragon has noted a consistent comparative elevated response for dinoseb and subdued response for dalapon between the first and second source vendor standards used. Paragon narrates this occurrence in the data package narrative.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or around the midpoint of the initial calibration. Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. After a valid CCV is achieved, up to 10 samples may be analyzed. After the 10th sample, a CCV must be analyzed and the percent difference (drift) calculated (see equation below). QC samples are counted as part of the number of injections, instrument blanks are not.

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

NOTE: Method SW8151A allows 20 samples to be analyzed between CCVs. Paragon commonly analyzes 10 samples between CCVs to reduce the amount of repeat injections.

Method 515.1 provides guidance that the concentration of calibration checks should be varied with one below the midpoint and one above the midpoint of the calibration range.

Calibration is verified when all compounds are within 15%D or when the average of the %Ds for all compounds is ≤15% (individual compounds that exceeded 15% are noted in the data package narrative). If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples

injected since the last compliant CCV must be reanalyzed. As long as CCV analyses are compliant (±15 %D), the run sequence may continue.

8.6 RETENTION TIME WINDOWS

For GC methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (equation given previously) of the absolute retention time yielded for each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time ±3σ, such that the Upper Limit = +3σ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time drift). Sample matrices may cause drift that requires further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system.

8.7 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATIONS, REPORTING)

A constant volume, generally 1µL of each standard, blank, QC or field sample extract is directly injected into the GC via the automated injector. Sample extracts are diluted to maintain response within the linear range when necessary. All prepared extracts contain the surrogate (see Section 9). Extract and sample concentration are determined as discussed below.

8.7.1 Note that Paragon employs a sample splitter that facilitates simultaneous dual column injections; therefore, both columns are calibrated in the same manner and either column may serve as the column for quantitation.

8.7.2 Tentative identification occurs when a peak from a sample extract falls within the RTW of one column. If the peak also falls within the RTW of the second column, then the analyte's presence has been confirmed. Quantitation is calculated from both column responses and the best result is reported. The analyst considers performance data such as separation of interferences, calibration performance and matrix spike results in selecting the quantitation column for each analyte detected and reported. If there are interferences present on one column, these need to be documented by printouts of that region of the

chromatogram; the lower (i.e., other column's) results may be reported in this case. If results from both columns are of comparable quality, the higher concentration is reported (per SW8000).

8.7.3 Sample concentration is calculated using the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)\,(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte

y = analyte instrument response (area units)

b = calculated intercept

m = calculated slope of the line

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (mL or g)

If the average CF is used for quantitation, the sample concentration is calculated using the following equation:

$$\text{Concentration}_{(ug/L,\ ug/kg)} = \frac{(A_x)(V_t)(DF)}{(\text{Average CF})(V_s \text{ or } W_s)}$$

where:

A_x = analyte response (area units)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Average CF = average calibration factor

V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition,

batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

MBs are aliquots of matrix (i.e., organic-free water for liquids and acidified boiling chips for solids) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this criterion is not achieved, then analyses must be halted and the source of the contamination found and corrected. As the analyst deems necessary, aliquots of solvent may be injected to clean the analytical system and demonstrate that it is free from contamination.

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix

on target analyte detection and recovery. See QC Table for evaluation criteria. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right) (100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.6 SURROGATE RECOVERY

The %R of the surrogate is calculated (see equation shown for LCS recovery above) for all field and QC samples. If the recovery is outside QC limits, the sample is reanalyzed to verify that analytical error was not the problem. If after re-injection the recovery is still out-of-control, initiate an NCR (SOP 928) and apply the decided upon action.

9.7 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at a minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Methods SW8151A, EPA 615 and EPA 515.1. Performance data substantiating the use of Soxhlet extraction as an appropriate preparative technique for solid samples is on file with Paragon's Quality Assurance Department.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.5 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.2 WASTE DISPOSAL

11.2.1 Any hexane, acetone, or other nonhalogenated organic solvents that have not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste stream.

11.2.2 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.3 The extract vials, associated extracts, and any PCB contaminated debris that may contain PCBs in excess of 50ppm shall be disposed of intact in the PCB Debris Waste stream.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be removed or defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods For Evaluating Solid Waste -- Physical/Chemical Methods, 3rd edition, Final Update III, “Method 8151A”, Revision 2, December 1996.

12.2 US EPA Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with Electron Capture Detector".

12.3 US EPA Method 615, "The Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater".

12.4 Paragon Technical Report: "Soxhlet Extraction of Herbicides in Soil", Steven Ignelzi, July 2006.

DOCUMENT REVISION HISTORY

7/14/06: LIMS program specification references strengthened; dual column use and results interpretation clarified; curve fit criteria discussion augmented; referenced Soxhlet Extraction of Herbicide in Soils technical report. DOCUMENT REVISION HISTORY added. Replacements for pages 11, 12, 14 issued 7/31/06 (corrected RPD and updated MS %R formulas, updated DOCUMENT REVISION HISTORY).

Analytical Method: SW8151A, EPA 615 & 515.1	**Parameter:** Analysis of Chlorinated Herbicides by Gas Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum 5-points, all analytes (SW 8151A); Methods EPA 615 & 515.1 do not require 5-points	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate Calculate linear regression (not forced through origin); use for quantitation if correlation coefficient (r) ≥0.995 or Calculate quadratic regression (minimum of six points required); use for quantitation if COD (r^2) ≥0.99	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Initial Calibration Verification (ICV); conc. not equal to midpoint of calibration curve; second source	~~Once~~ After each ICAL	≤15%D of each compound or mean %D ≤15% or as otherwise specified in applicable LIMS program specification	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8151A allows bracketing of 20 field sample analyses)	≤15%D of each compound or mean %D ≤15% or as otherwise specified in applicable LIMS program specification	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections	Whenever a new column is installed	Column and compound specific. Window is ±3x the standard deviation of the 3-injection average for the respective column	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound.

Analytical Method: SW8151A, EPA 615 & 515.1	**Parameter:** Analysis of Chlorinated Herbicides by Gas Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
throughout at least a 72-hour period to be representative of variation		Note that the ICV and CCV analyses are also used to monitor RT drift	Experience of analyst weighs heavily in interpretation of chromatograms (refer also to RT Shift).
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL		Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of $\leq$20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at $\geq$10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS);	1 per each preparation	See laboratory limits; recoveries	Check calculations and spike

Analytical Method: SW8151A, EPA 615 & 515.1	**Parameter:** Analysis of Chlorinated Herbicides by Gas Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCS)	batch of ≤20 samples of like matrix	for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions was the cause. - if still non-compliant and the samples are within the extraction holding time, then request re-extraction using an NCR, and reanalyze all associated samples for the analyte that do not meet criteria - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per batch, not to exceed 20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per batch ~~of samples~~, not to exceed 20 samples of like matrix	See laboratory limits; see Matrix Spike information above for MSD recoveries. RPDs should be within advisory limits.	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers.
Surrogate Spike	All extractions including field and laboratory QC samples	See laboratory limits; recoveries should be within current limits ~~for one or both surrogates~~; alternative criteria as defined in the LIMS program specifications may apply	Check calculations and spike preparation for documentable errors. - if no errors are found and the surrogate recoveries in the MB and LCS are within limits, then sample matrix effects are the

Analytical Method: SW8151A, EPA 615 & 515.1	**Parameter:** Analysis of Chlorinated Herbicides by Gas Chromatography		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			most likely cause. However, any samples with ~~both~~ surrogate recovery outside the QC limits with no visible chromatographic cause, should be re-injected to determine if an injection error was the cause for the low recovery. - if ~~both~~ surrogate recovery in the associated MB and LCS is not within limits and the samples are within the holding time, then re-extract and reanalyze all associated samples - if samples are beyond the holding time, then contact the PM via an NCR. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration.
Method Detection Limit (MDL) Study	As needed, ~~and~~ at minimum, annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Instrument Name **ECD#1** **Paragon Analytics** Logbook No./Page _____

Sequence File: C:\HPCHEM___\SEQUENCE_____ Date Analyzed _____ Operator _____ GC Method _____

Data Path: C:\HPCHEM___\DATA_____ Analytical Method _____ SOP _____ Rev. ____

Hexane Lot _____ **Reviewed by / date** _____ Form 530r5_d1.xls (12/10/2001)

Vial	Data File	Method	Sample Name	Comments	rr?

Comments: _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 438 REVISION 10

TITLE: **MICROEXTRACTION AND ANALYSIS OF EDB AND DBCP IN WATER BY GAS CHROMATOGRAPHY -- METHODS EPA 504.1 AND SW8011**

FORMS: **530, 532** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8-13-07
QUALITY ASSURANCE MANAGER _____ DATE 8/12/07
LABORATORY MANAGER _____ DATE 8-13-07

HISTORY: New, Rev0, 5/15/97; Rev1, 2/18/99; Rev2, 8/18/99; Rev3, 1/23/02; Rev4, 3/2/02; Rev5, 3/14/03; Rev6, 4/16/04; Rev7, 11/22/04; Rev8, 3/9/06; Rev9, 8/4//06; Rev10, 8/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- Methods EPA 504.1 and SW8011 -- are used to determine the concentration of 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in water. A third compound, 1,2,3-trichloropropane (1,2,3-TCP) may also be analyzed by this procedure, but this compound is not typically part of Paragon's target analyte list.

2. SUMMARY

A 6g portion of salt (NaCl) is added to a 40mL VOA vial containing approximately 35mLs of standard or sample (actual volume determined gravimetrically). Then, 2mLs of n-hexane (extraction solvent) is added to the vial, which is capped and shaken vigorously for 1min (manually micro-extracted). After the contents of the vial are allowed to settle (phase separation), 1µL of hexane extract is injected into a gas chromatograph (GC) that is equipped with a sample splitter, two dissimilar columns, and dual electron capture detectors (ECDs). Each column separates the target analytes, and an electronic integrator processes ECD peak response. Target compound concentration is calculated using an external standard method of quantitation. This dual column chromatography allows tentative identification by one column and confirmation by the other column to be performed simultaneously.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of

Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Trip blanks should be received with each sample submission for evaluation of possible contamination during shipment. Inform the Project Manager if no trip blank is received.

4.2 Contaminants in reagents such as the hexane extraction solvent, from glassware or carried over from within the analytical system, may cause the appearance of discrete artifacts or elevated baselines. Use of high purity reagents, scrupulously cleaned glassware and frequent maintenance of the analytical system minimizes these interferences. The absence of significant peak tailing is a good indication of proper system performance.

4.3 If present in very high concentrations, the common chlorination by-product, dibromochloromethane (synonym chlorodibromomethane), may mask low levels of EDB.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH (GC), AUTOSAMPLER AND DETECTORS
Hewlett Packard (HP) 5890 Series II GC equipped with dual on-column injection and electron capture detectors (ECDs), with Hewlett Packard 7673 Autosampler or equivalents

5.2 CHROMATOGRAPHIC DATA ACQUISITION AND PROCESSING SYSTEM
Hewlett Packard ChemStation (Enviroquant™), or equivalent

5.3 COLUMNS - Equivalent columns/guard columns may also be used

Restek Pesticide Column:	RTX-CLPesticides	#11123	(30m, 0.25mm ID, 0.5µm film)
Restek Pesticide Column:	RTX-CLPesticides2	#11323	(30m, 0.25mm ID, 0.5µm film)
Restek Pesticide Column:	RTX-CLPesticides	#11139	(30m, 0.32mm ID, 0.25µm film)
Restek Pesticide Column:	RTX-CLPesticides2	#11324	(30m, 0.32mm ID, 0.25µm film)

5.4 GASES - **Only high or ultra-high purity gases shall be used**
Helium (carrier/detector gas)
Nitrogen (makeup gas)

5.5 MEASURING DEVICES
Precision Hamilton™ microsyringes, or equivalent, in 10, 25, 100µL and 2.0mL sizes
Volumetric flasks, Class A with ground glass or PTFE stoppers, 10mL and 25mL sizes
Top-loading laboratory balance, with ±0.01g sensitivity

5.6 GC CONSUMABLES

- Vials - National Scientific C4011-1, or equivalent
- Caps - National Scientific C4000-51B, or equivalent
- Inlet Seals, dual Vespel ring - Restek 0.8mm #21243, or equivalent
- Septa, 11mm - Restek #20365 or equivalent
- O-ring, graphite, 6.5mm - Restek #20299, or equivalent
- O-ring, Viton - Restek #20377, or equivalent
- Liner, splitless, 4mm ID - Restek #20799-214.5, or equivalent
- Glass Wool, deactivated - Restek #20789, or equivalent
- Gold Seal - Restek #21306, or equivalent
- Universal Presstight Y - Restek #20469, or equivalent
- Vespel/Graphite Ferrule (detector) - Restek #20221, or equivalent
- Compact Vespel/Graphite Ferrule - Restek #20249, or equivalent
- Graphite Ferrules - various sizes
- Split Vent Trap (SW8081) - Agilent RDT-1023, or equivalent

5.7 Autosampler vials, with caps

5.8 Transfer pipets, disposable

6. REAGENTS - Only chemicals that are reagent grade or higher shall be used

6.1 Sodium chloride (NaCl), VWR, Cat. #VW6430-7 or equivalent: Prepare by pulverizing a batch of NaCl and placing it in a muffle furnace at room

temperature. Increase the temperature of the muffle furnace to 400°C for 0.5 to 6 hours. Remove the NaCl, allow to cool, place in a storage bottle and cap.

6.2 Deionized (DI) reagent water; obtained from Paragon's DI water system

6.3 SOLVENTS - **Only pesticide residue grade or equivalent may be used!**
Hexane (C_6H_{14}), Burdick and Jackson #216-4, or equivalent
Methanol (CH_3OH, MeOH), Burdick and Jackson #230-4, or equivalent

6.4 STANDARDS

6.4.1 All standards are maintained per PAR SOP 300, which supercedes any guidance in this SOP. Unopened stock standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules, if recommended by the manufacturer. Generally after opening ampules, the standards for this procedure are stored in the freezer (-10--20°C), in PTFE-capped, or equivalent, vials.

Opened stock standards and intermediate standards expire six months from opening (preparation) or per the manufacturer's expiration date (whichever is sooner). Standards may be replaced sooner if laboratory quality control (QC) analyses or other factors indicate deterioration.

6.4.2 Two independent sources of commercial stock standards are required for target analytes. These certified stock standards are purchased from suitable vendors. First source materials are used to create calibration and continuing calibration verification (CCV) standards. Second source materials are used to create the initial calibration verification (ICV) solution and the QC sample (i.e., LCS/LCSD, MS/MSD) spike standard. Section 9 of this SOP gives definitions and uses of batch QC samples. Per SW8011, Paragon does not utilize a surrogate for this procedure.

For this procedure, aliquots of primary stock standard are spiked directly into an approximate volume of 35mLs of DI water (actual volume determined gravimetrically) to create the uppermost three instrument calibration standards. The stock standard is also diluted 10-fold (with methanol) to create an intermediate standard, from which aliquots are spiked directly into approximate volumes of 35mLs of DI water to create the lower three instrument calibration standards, as well as the CCV. Second source materials are diluted with methanol to create an intermediate ICV (used by the analyst) and QC sample (used by the Organics Extraction Group) spike standard.

All working standards (i.e., those prepared in DI water) are made on the day of use. Microextractions are documented on Form 532; analyses are documented on run log Form 530. A detailed description regarding calibration standards can be found in Section 8 of this SOP.

6.4.3 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Samples must be collected in analyte-free 40mL screw-cap vials with Teflon™ septa. Note that samples are micro-extracted in their original containers.

7.3 Sodium thiosulfate ($Na_2S_2O_3$) may be used to dechlorinate liquid samples that contain residual chlorine. This should be accomplished by the client in the field. One of two preservation procedures may be used: Either sample containers may be prepared by adding 3.0mg of $Na_2S_2O_3$ crystals, or, samples may be preserved in the field via the addition of 75µL of freshly prepared $Na_2S_2O_3$ solution (40mg/mL concentration). The Paragon Project Manager may designate the need for residual chlorine check of the sample upon receipt.

7.4 Samples must be maintained at 4±2°C and extracted within 14 days of collection. Analysis must occur within 24hrs of extraction (EPA 504.1).

8. PROCEDURE

8.1 TYPICAL GC OPERATING CONDITIONS

Carrier gas:	1.5mL/min (constant flow mode 9.3psi)
Make-up gas:	20-40mL/min
Injector Temperature:	200°C
Initial Oven Temperature:	60°C
Initial Hold:	0.5min
Oven Ramp A:	10°C/min to 120°C
Oven Ramp B:	30°C/min to 210°C
Hold:	0.5 min
Detector Temperature:	325°C

8.2 CHROMATOGRAPHIC MAINTENANCE

8.2.1 Dual columns are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector. Reattach the columns after cleanly cutting off at least two loops from the injection port side of the column using a capillary cutting tool or scribe. The accumulation of high boiling residues may change split ratios between dual columns and thereby change calibration factors. Clip a loop from the guard column or replace as necessary.

8.2.2 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Oxidized columns will exhibit baselines that rise rapidly during temperature programming.

8.2.3 Peak tailing for all components is exacerbated by dirty injectors, dirty guard columns, and dirty glass Y's.

8.2.4 Prime is needed to fill the GC system's active sites and to stabilize instrument response. A standard, at a level approximately twice that of the CCV, is injected repeatedly until reproducible peak areas are observed (usually three injections). If the system remains unstable, additional maintenance must be performed to correct the problem prior to continuing with the analysis.

8.3 INITIAL CALIBRATION

8.3.1 Prepare a minimum of 5 concentrations of calibration standards to define the linear range of the detector. For this procedure, the working calibration standards are created by adding aliquots of a 200µg/mL stock standard to a VOA vial of reagent water, for a total volume of 35mLs (actual volume is determined gravimetrically and recorded). A 6g portion of salt is then added to each VOA vial followed by the addition of 2mLs of hexane. After manually shaking (micro-extraction) and allowing the vial's contents to settle, a 1µL volume of hexane extract is directly injected into the GC for analysis.

NOTE: For EPA 504.1 analysis, if the samples were treated with sodium thiosulfate ($Na_2S_2O_3$) to remove residual chlorine, the calibration and calibration check standards must also be prepared with an amount of $Na_2S_2O_3$ equal to that used to treat the samples.

Each ICAL standard must include all target analytes. The lowest concentration standard shall be at a level at or below the analyte

reporting limit (RL). A typical calibration sequence and preparations are shown below in Table 1.

Table 1
CALIBRATION STANDARDS

Calibration Level	Amount of Standard (µL)	Final Volume H_20 (mL)	Final Concentration (µg/L)
ICAL 6	70 (primary)	35	0.4
ICAL 5	35 (primary)	35	0.2
ICAL 4	17.5 (primary)	35	0.1
ICAL 3	70 (intermediate)	35	0.04
ICAL 2	35 (intermediate)	35	0.02
ICAL 1	17.5 (intermediate)	35	0.01
CCV	17.5 (primary)	35	0.1
ICV	17.5 (primary, 2nd source)	35	0.1

8.3.2 Inject and analyze 1µL of each calibration standard. Each data file quantitation is accomplished via the external standard method of quantitation. Calibration Factors (CFs) are calculated as follows:

$$CF = \frac{\text{Peak Area}}{\text{Amount of analyte injected}}$$

If the CFs over the working range of the detector are constant (i.e., ≤20% RSD), then response can be assumed to be invariant (linear through zero) and the average (mean) CF may be used to quantitate sample content.

8.3.3 Relative Standard Deviation (RSD) is calculated as:

$$\text{RSD (\%)} = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean response factor}} \right)(100)$$

When RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first (minimum of 5 ICAL points used, r) or second (minimum of 6 ICAL points used, r^2) order regression curve fit that does not pass through zero (e.g., least squares method) may be constructed. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000B. A quadratic regression should

not be used to compensate for detector saturation. Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

If a first order regression fit is applied, the correlation coefficient (r) value yielded must be $\geq$0.995. If a second order regression fit is applied, the coefficient of determination (COD, r^2 value) yielded must be $\geq$0.99. Note that the curve fit value expresses "goodness of fit", with perfect fit being a value of 1.0.

If the curve fit value does not meet criteria, check that the calibration standards were prepared properly, reanalyze and generate a new initial calibration curve.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The acceptance criteria for the ICV is the same as for the CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated. See QC Summary Table for further details.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or around the midpoint of the initial calibration (0.1µg/L). Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

NOTE: Method SW8011 allows 20 samples to be analyzed between CCVs. Paragon commonly analyzes 10 samples between CCVs to reduce the amount of repeat injections.

The percent difference (%D) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when responses for all analytes are within $\leq$30%D for EPA 504.1 and $\leq$40%D for SW8011. If a CCV does not meet acceptance criteria, reanalyze the CCV. See QC Summary Table for further details and corrective action to be taken should the CCV still fail.

8.6 RETENTION TIME WINDOWS

For GC methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used to compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (σ) of the absolute retention time yielded for each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time $\pm 3\sigma$, such that the Upper Limit = $+3\sigma$ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time shifts). Sample matrices may cause RT differences that require further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system.

8.7 SAMPLE MICROEXTRACTION, ANALYSIS, CALCULATIONS, REPORTING

8.7.1 Remove samples from storage and allow them to come to room temperature before starting preparation.

8.7.2 Uncap a 40mL sample vial and pour off approximately 5mL.

8.7.3 Recap the sample vial, weigh to the nearest 0.01g, record on benchsheet (Form 532).

8.7.4 Remove cap and add 6g prepared NaCl. Recap and shake container until dissolved.

8.7.5 Remove cap. If sample is to be used as a QC sample, spike with appropriate amount of QC spike solution. Use a syringe to add 2mLs n-hexane. Recap and shake vigorously for 1min.

8.7.6 Set vial aside and allow phases to separate.

NOTE: If stored at this stage, *keep container upside down initially*. Turn bottles upright after several hours.

8.7.7 Remove cap. Using a clean transfer pipette, carefully transfer an aliquot of the n-hexane layer to a clean autosampler vial and cap the vial. Place in automated sampler for subsequent analysis.

NOTE: The remaining hexane phase (being careful not to include any of the water phase) may be transferred into a second autoinjector vial, capped, and stored at 4±2°C as a reserve for reanalysis if needed. However, the extract holding time is only 24 hour.

8.7.8 Discard the remaining contents of the 40mL container into the appropriate waste stream for mixed aqueous/non-halogenated solvent. Rinse with water and shake empty vial briskly to remove any liquid that is still clinging. Recap and weigh to the nearest 0.01g and record on benchsheet. The net weight (g) is equivalent to the sample volume (mL) extracted.

8.7.9 A constant volume, generally 1µL of each standard, blank, QC or field sample extract is directly injected into the GC via the automated injector. When necessary, sample extracts are diluted (with hexane) to maintain response within the linear range.

8.7.10 Note that Paragon employs a sample splitter that facilitates simultaneous dual column injections. Both columns are calibrated in the same manner and either column may serve as the column for quantitation.

Tentative identification occurs when a peak falls within the RTW of one column. If the peak also falls within the RTW of the second column, then the analyte's presence has been confirmed. Quantitation is calculated from both column responses, and the best result is reported. The analyst considers performance data such as separation of interferences, calibration performance and matrix spike results in selecting the quantitation column for each analyte detected and reported. If there are interferences present on one column, these need to be documented by printouts of that region of the chromatogram; the lower column's results may be reported in this case. If results from both columns are of comparable quality, the higher concentration is reported (per SW8000).

8.7.11 Sample concentration is calculated using the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)\,(V_t)(DF)}{m(W_s)}$$

where:

x = concentration of the analyte

y = analyte instrument response (area units)

b = calculated intercept

m = calculated slope of the line

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

W_s = volume or weight of sample extracted (g)

If the average CF is used for quantitation, the sample concentration is calculated using the following equation:

$$\text{Concentration}_{(ug/L,\ ug/kg)} = \frac{(A_x)(V_t)(DF)}{(\text{Average CF})(W_s)}$$

where:

A_x = analyte response (area units)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Average CF = average calibration factor

W_s = weight of sample extracted (g)

Linear regression is the preferred method of quantification for this procedure.

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method Blanks (MBs) are aliquots of DI water that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the reagents, glassware and the analytical system are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this criterion is not achieved, then analyses must be halted and the source of the contamination found and corrected. See QC Summary Table for further information. As the analyst deems necessary, aliquots of solvent may be

injected to clean the analytical system and demonstrate that it is free from contamination.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below:

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

See QC Summary Table for evaluation criteria.

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below:

$$RPD = \left[\frac{(concentration\ sample - concentration\ duplicate)}{1/2(concentration\ sample + concentration\ duplicate)} \right](100)$$

See QC Summary Table for evaluation criteria.

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

See QC Summary Table for evaluation criteria.

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement is to perform these analyses is waived, and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.6 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM THE METHOD

Section 7.19 of EPA 504.1 discusses the use of dichlorophenylacetic acid (DCAA) as a surrogate. Per SW8011, Paragon does not utilize a surrogate for this procedure.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.5 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.2 WASTE DISPOSAL

11.2.1 Any rinse waters used for rinsing syringes or other devices prior to sample contact may be disposed of in the Aqueous Lab Waste.

11.2.2 Any hexane, acetone, or other nonhalogenated organic solvents that have not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste stream.

11.2.3 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be removed or defaced prior to disposal.

12. REFERENCES

12.1 EPA/600/R-95/131, Methods for the Determination of Organic Compounds in Drinking Water, EMSL-Cincinnati, October 1994. "Method 504.1", Revision 1.1 Edited by J. W. Munch (1995).

12.2 US EPA SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, "Method 8011", Update III, Revision 0, July 1992.

DOCUMENT REVISION HISTORY

8/4/06: LIMS program specification language augmented. Dual column identification and interpretation of results clarified. List of consumables added. DOCUMENT REVISION HISTORY section added.

8/12/07: Calibration discussion further clarified, Section 8.3.3 and QC Table.

Analytical Method: SW8011, EPA504.1	**Parameter:** EDB & DBCP		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum 5-points, all analytes	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean CF to quantitate Calculate linear regression (not forced through origin); use for quantitation if COD (r^2) ≥0.99 or Calculate quadratic regression (minimum of six points required); use for quantitation if COD ≥0.99	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Initial Calibration Verification (ICV); second source	After each ICAL	70-130% (EPA 504.1) 60-140% (EPA SW8011) Other client-specific criteria may apply, consult applicable LIMS program specification	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses	70-130% (EPA 504.1) 60-140% (EPA SW8011) Other client-specific criteria may apply, consult applicable LIMS program specification	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of	Whenever a new column is installed	Column and compound specific Window is ±3x the standard deviation of the 3-injection average for the respective column	Wider windows can be used to screen for compounds; If zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms

Analytical Method: SW8011, EPA504.1	**Parameter:** EDB & DBCP		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
representative of variation		Note that the ICV and CCV analyses are also used to monitor RT drift	in interpretation of chromatograms (refer also to RT Shift).
Retention Time Shift	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	one per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	one per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions was the cause.

Analytical Method: SW8011, EPA504.1	**Parameter:** EDB & DBCP		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			- if still non-compliant and the samples are within the extraction holding time, then request re-extraction using an NCR, and reanalyze all associated samples for the analyte that do not meet criteria - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	one per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits, as prescribed in the applicable LIMS program specification	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	one per preparation batch of ≤20 samples of like matrix	See laboratory limits; see Matrix Spike information above for MSD recoveries. RPDs should be within advisory limits, as prescribed in the applicable LIMS program specification	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. Note in narrative. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers.
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Paragon Analytics

Microextraction Benchsheet

WO #s _____ **Matrix:** Water **Method:** 504.1 8011 **Batch #** _____ **Prep. Date/Time** _____

SOP _____ **Rev** _____ **Standard (A) Code** _____ **Standard (B) Code** _____ **Balance ID** _____ **Initials** _____

Sample Number	Initial Weight (g) (vial + sample)	Final Weight (g) (vial)	Sample Amount (g)	Spike Amount (µL) & Standard	Solvent Amount (mL)	Comments

Reagent Lots: Hexane _____ NaCl _____ Reviewed by / Date _____

Form 532r0.frm (5/23/2002)

Instrument Name **ECD#3** | **Paragon Analytics** | Logbook No./Page ________________

Sequence File: C:\HPCHEM___\SEQUENCE___________________ Date Analyzed ___________ Operator _______ GC Method ___________

Data Path: C:\HPCHEM___\DATA______________ Analytical Method __________ SOP _______ Rev. ____

Hexane Lot ________ **Reviewed by / date** ______________________ Form 530r5_d1.xls (12/10/2001)

Vial	Data File	Method	Sample Name	Comments	rr?

Comments: ____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 439 REVISION 5

TITLE: **ANALYSIS OF NITROGUANIDINE BY HPLC -- METHODS CRREL 89-35 AND SW8000B**

FORMS: **410** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/6/07

QUALITY ASSURANCE MANAGER _____ DATE 2/6/07

LABORATORY MANAGER _____ DATE 2-9-07

HISTORY: DRAFT, Rev0, 4/27/00, Rev1, 12/31/01; Was retired then reinstated, Rev2, 3/15/04; Rev3, 3/9/06; Rev4, 9/1/06; Rev5, 2/8/07.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- CRREL 89-35 and SW-846 Method 8000B -- are used to determine the concentration of nitroguanidine and related compounds such as guanidine nitrate in aqueous and solid matrices. **All procedures must be conducted with care as the analytes of interest may present an explosion hazard. Nitroguanidine is a primary component of U.S. Army triple-base propellants, which also contain nitrocellulose and nitroglycerin.**

2. SUMMARY OF METHOD

Aqueous samples are analyzed by direct injection. Turbid aqueous samples may be filtered with 0.45µm nylon filters. Solid matrix samples are extracted with water, allowed to settle, and filtered. An aliquot of prepared sample extract is then injected into a high performance liquid chromatograph (HPLC) containing an Ultra IBD chromatography column (or equivalent). An isocratic flow condition is used to elute the target compound from the column. The target analytes are then detected by an ultraviolet (UV) detector at two wavelengths (263nm, 215nm). Responses of the analyte are recorded and calculated by a data acquisition system, using an external standard method of quantitation. Identification is confirmed by the presence of a peak at both wavelengths within the appropriate retention time. No surrogate standard is utilized due to the lack of an established representative surrogate compound and because water samples are directly injected (essentially no preparation variables).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of

Supervisory/training review, by the results of precision and accuracy tests performed, or by other suitable means.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the analytical review sheet and the case narrative indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action by the reviewer or analyst. Corrective actions may include re-analysis or correcting errors in logbooks or on chromatograms or in associated electronic records.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Contaminants in reagents, from glassware or within the analytical system may cause the appearance of discrete artifacts or elevated baselines. Use of high purity reagents, scrupulously cleaned glassware (SOP 334) and frequent maintenance of the analytical system minimizes these interferences.

4.2 Interferences introduced from the sample matrix will vary considerably from source to source.

4.3 Degradation of nitroguanidine is accelerated by exposure to light. Light exposure should be limited during sample storage, extraction and analysis.

5. APPARATUS AND MATERIALS

5.1. HPLC SYSTEM

A Hewlett-Packard (HP) 1090 or equivalent HPLC equipped with a system controller, column oven, autosampler, diode array uv-vis detector or other multi-wavelength uv-vis detector.

5.2. DATA SYSTEM

Data acquisition system capable of acquiring, storing and processing HPLC data

(e.g., LC ChemStation™ or equivalent).

5.3. MEASURING DEVICES
microsyringes, glass, various µL sizes
volumetric flasks, Class A with ground glass or Teflon™ stoppers, 10-100mL sizes

5.4 COLUMN - equivalent column may be used

Restek Ultra IBD (intrinsically base deactivated) # 9175565 150 x 4.6mm, 5µm

5.5. CONSUMABLE SUPPLIES

- PTFE syringe filters, 0.45µm
- extraction vials
- autosampler vials
- glass pipettes, 5mL
- centrifuge tubes, plastic
- Ottawa sand (if solid matrix samples are to be analyzed)

5.6. sonicator

5.7. vortex mixer

6. REAGENTS - Only UV, HPLC grade solvents may be used!

6.1 SOLVENTS
acetonitrile (ACN; CH_3CN), Burdick & Jackson #015-4 or equivalent
methanol (MeOH, CH_3OH), Burdick and Jackson 230-4 or equivalent
HPLC (reagent water), Burdick and Jackson 365-4 or equivalent

6.2 STANDARDS

6.2.1 All standards are maintained per PAR SOP 300. Target analyte stock standards, typically 1,000µg/mL, are generally purchased as a certified solution, but may be prepared from pure standard material dissolved in MeOH or ACN. Two independent sources (first, second) of target analyte stock standards are needed.

Intermediate standards are made by diluting an appropriate aliquot of stock standard to a specific volume using acetonitrile, and are stored in Teflon™-sealed vials. Typically, a 100-fold dilution is made, thus creating intermediate standards at a concentration of 10µg/mL. First source target analyte materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards (used by the Organics Extraction Group). Second source target analyte materials are used to create the initial calibration verification (ICV)

solution. Section 9 of this SOP gives definitions and uses of QC (i.e., LCS/LCSD, MS/MSD) samples.

Unopened stock standards are valid until the manufacturer's expiration date and are stored in accord with manufacturer's guidelines. Transfer remainders of opened stock standards to Teflon™-sealed vials for storage. Stock standards are stored in the freezer (i.e., dark, -10 to -20°C). Opened stock or prepared intermediate standards expire 30 days from opening (preparation), or per the manufacturer's expiration date (whichever is sooner). All intermediate standards must be stored in the dark (i.e., refrigerator, 4±2°C) and may be retained for 30 days. Standards may be replaced sooner if laboratory QC analyses or other factors indicate deterioration.

6.2.2 The intermediate target analyte standards are further diluted with reagent water to create working standards. These working standards (ICAL, ICV, CCV) are prepared on the day of use. Calibration standards are documented in the analytical run log (Form 410). A detailed description of the concentration of the calibration standards and how they are used can be found in Section 8 of this SOP.

6.2.3 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are not chemically preserved and must be collected in amber glass containers (generally 40mL VOA vials) with Teflon™-lined lids. Samples must be maintained in the dark, and chilled (i.e., 4±2°C).

7.3 Solid samples are collected in wide-mouth glass containers, preferably amber, with Teflon™-lined lids. Solid samples are not chemically preserved and must be maintained in the dark, chilled (i.e., 4±2°C).

7.4 Aqueous samples must be analyzed within 14 days of collection. Solid samples must be extracted within 14 days of collection, extracts must be maintained in the dark at 4±2°C, and analyzed within 14 days of preparation.

8. PROCEDURE

8.1 TYPICAL ISOCRATIC HPLC CONDITIONS

Mobile Phase Flow Rate:	1.0mL/min
Mobile Phase Composition:	100% water (HPLC)
Column Temperature:	40°C (held constant throughout run)
UV Detector:	215 and 263nm
Injection Volume:	100µL

NOTE: If a diode array detector is used, data should be collected between 210 and 300nm for spectral identification.

8.2 ROUTINE MAINTENANCE AND PRE-RUN CHECK

Prior to analyzing samples or establishing calibration curve, the following suggested maintenance may be performed to aid in achieving more consistent results:

- Change the column frits as needed (i.e., if pressure increase is observed).
- Change the cartridge on the guard column as necessary (i.e., pressure increase or poor chromatography).
- Install fresh HPLC water for every run.
- Restart the computer and instrument before starting equilibration and analysis.
- Minimize air currents blowing on the instrument and vials loaded on the autosampler tray.
- Replace UV lamp at 2yr or upon observation of degraded signal.
- Major repairs on contract (by Full Spectrum or equivalent).
- Ensure that instrument is equilibrated, may be primed with one or more injections of the CCV solution prior to initiation of the CCV for the acquisition sequence.

8.3 INITIAL CALIBRATION

8.3.1 Prepare a minimum of 5 concentrations of calibration standards as shown below in Table 1 or as required for each sample set, to define the linear range of the detector. The lowest standard's concentration standard shall be at or below the reporting limit (RL).

TABLE 1
CALIBRATION STANDARDS

Volume of 10µg/mL Nitroguanidine Standard (µL)	Final Volume in Water (mL)	Working Standard Concentration (µg/mL)
500	1.0	5.0
250	1.0	2.5
125	1.0	1.25
100 (CCV, ICV-Level)	1.0	1.0
50	1.0	0.50
20	1.0	0.20

8.3.2 Inject 100µL of each calibration standard into the HPLC and acquire data. Quantitation is accomplished using the external standard method. Analyte Calibration Factors (CFs) are calculated as follows:

$$CF = \frac{\text{integrated peak area of analyte}}{\text{analyte concentration } (ng/mL)}$$

If the CFs over the working range of the detector are constant (i.e., ≤20% RSD), then response can be assumed to be invariant (linear through zero) and the average (mean) CF may be used to quantitate sample concentration.

8.3.3 Relative Standard Deviation (RSD) is calculated as:

$$RSD\ (\%) = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean calibration factor}} \right)(100)$$

When the RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be ≥0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit" with perfect fit being a value of 1.0.

Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000. A quadratic regression should not be used to compensate for detector saturation.

The type of curve fit applied should be chosen to best represent the data. Strong linearity is expected for this method. If other response is observed, check for poor peak shape or other system problems.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The acceptance criteria for the ICV is the same as for the CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated. See QC Summary Table for further details.

8.5 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

The percent difference (%D) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when responses for all analytes are within $\leq$15%. If a CCV does not meet acceptance criteria, reanalyze the CCV. See QC Summary Table for further details and corrective action to be taken should the CCV still fail.

So long as CCV analyses yield compliant results, and other QC samples are analyzed as required, the series of ten sample analyses bracketed before and after by successful CCV analyses may continue as long as the reserve of solvents lasts.

8.6 RETENTION TIME WINDOW

For chromatographic methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used to compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (σ) of the absolute retention time yielded for each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time $\pm 3\sigma$, such that the Upper Limit = $+3\sigma$ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time shifts). Sample matrices may cause RT differences that require further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target compounds are not missed by the data system

8.7 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATION, REPORTING)

8.7.1 Solid matrix samples are extracted by mixing 2g of air-dried sample with 40mL of water in centrifuge tube. The centrifuge tube is then vortex mixed for 30 seconds and sonicated in a ultrasonic bath for 2hrs. The solution is then allowed to settle for 0.5hr and/or filtered with 0.45µm nylon syringe filter. Filtering is helpful to maintain consistent HPLC performance.

8.7.2 Where necessary, reduced aliquots of aqueous sample are analyzed or diluted (HPLC water) sample extracts are analyzed to keep target analyte response within the detectors' linear range.

8.7.3 Tentative identification occurs when 263nm response falls within the RTW for the IBD column. Confirmation occurs when 215nm response for the analyte also falls within the RTW for the IBD column. Optionally, spectral matching can also be used to determine presence or absence of nitroguanidine.

8.7.4 If the average CF is used for quantitation, the sample concentration is calculated as follows:

$$\text{Concentration}_{(ug/L,\ ug/kg)} = \frac{(A_x)(V_t)(DF)}{(\text{Average CF})(V_s \text{ or } W_s)}$$

where:

A_x = analyte response (area units)

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Average CF = average calibration factor (area/concentration in mg/mL)

V_s or W_s = volume or weight of sample extracted (L or kg)

8.7.5 Sample concentration, in ppb (µg/L or µg /kg), may also be calculated using the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)\ (V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte (nitroguanidine, ppb)
y = intercept for analyte instrument response (area)
b = calculated intercept (area)
m = calculated slope of the line (area/concentration in ng/mL)
V_t = total volume of concentrated extract (mL)
DF = Dilution Factor (if applicable); if no dilution, then DF = 1
V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples of like matrix that is associated with one unique set of QC samples and processed together as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS) and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Check LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

MBs are aliquots of matrix (i.e., HPLC water for liquids analyses; Ottawa sand for solids) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is processed, or there is a change in reagents, an MB must be prepared. Concentrations of target analytes, if any, must be less than the analyte reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this requirement is not met, analyses must be halted and the source of the contamination found and corrected.

Carryover blanks are aliquots of contaminant-free matrix that are analyzed to clean the analytical system. There are no acceptance criteria associated with these blanks other than the qualitative observation that all significant carryover has been alleviated.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below:

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

See QC Table for evaluation criteria.

9.4 LABORATORY DUPLICATE

A duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this, the matrix spike analysis is typically performed in duplicate (MSD). Relative percent difference (RPD) for each analyte of the duplicate pair is calculated as follows:

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.4 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. See QC Table for evaluation criteria. Percent Recovery (%R) for spiked analytes is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right)(100)$$

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.5 METHOD DETECTION LIMIT (MDL) STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses for each target analyte at a concentration level near to the capabilities of the method. The MDL study should be performed as needed and at a minimum, annually (SOP 329).

10. DEVIATIONS FROM THE METHOD

The method is this SOP contains proprietary techniques developed by Paragon Analytics.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 **Samples containing explosive material may under no circumstances be heated in any fashion (e.g., boiling a solution;**

drying in an oven). Also, all operations in the sonic bath must be performed with the cooling coil in place and operational along with the cold water turned on.

11.1.2 **Solid samples with explosive residue content as high as 2% may be safely homogenized using a mortar and pestle. Visual observation of the sample is important. Lumps of material that have a chemical appearance should not be ground. Explosives are generally a very finely ground grayish-white material.**

11.1.3 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

11.1.4 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.5 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.6 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

11.1.7 Any non original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.8 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Any rinse waters used for rinsing syringes or other devices prior to sample contact may be disposed of in the Aqueous Lab Waste.

11.2.2 The ACN-Water HPLC waste may be discarded into the ACN Waste Stream (Nonhalogenated Waste) container.

11.2.3 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.4 The extract vials, associated extracts, and any PCB-contaminated

debris that may contain PCBs in excess of 50ppm, shall be disposed of intact in the PCB Debris Waste.

11.2.5 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 8000B, December 1996.

12.2 U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory Special Report 89-35, Analytical methods for determining nitroguanidine in soil and water.

DOCUMENT REVISION HISTORY

9/1/06: LIMS program specification language strengthened. Updated format. DOCUMENT REVISION HISTORY section added.

2/8/07: Minor format updates. Precedence of SOP 300 deleted. Standards section updated, ICV added to standards Table. Added Form.

Analytical Method: CRREL 89-35 & SW8000B	**Parameter:** Nitroguanidine by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
Initial Calibration; minimum 5-point; all analytes	As needed (i.e., at on-set of analyses, or when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate Correlation coefficient (r^2) for linear regression must be ≥0.99	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve
Initial Calibration Verification (ICV); conc. not equal to midpoint of calibration curve; second source	After each ICAL	If ≤15%, analyses may proceed	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses; (SW8330 allows bracketing of 20 field sample analyses)	If ≤15%, analyses may proceed	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed before and after a failed CCV must be reanalyzed. If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of variation	Whenever a new column is installed	Column and compound specific. Window is ±3x the standard deviation of the 3-injection average for the respective column Note that the ICV and CCV analyses are also used to monitor RT drift	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms (refer also to RT Shift).
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate

Analytical Method: CRREL 89-35 & SW8000B	**Parameter:** Nitroguanidine by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
ICAL			Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per each preparation batch of ≤20 samples of like matrix	See laboratory or other applicable limits; recoveries for spiked compounds must be within these limits	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the

Analytical Method: CRREL 89-35 & SW8000B	**Parameter:** Nitroguanidine by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
			samples are within the extraction holding time, then initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per batch, not to exceed 20 samples of like matrix	See laboratory or other applicable limits; recoveries for spiked compounds should be within these advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Duplicate	1 per batch, not to exceed 20 samples of like matrix	See laboratory or other applicable limits; recoveries for spiked compounds should be within these advisory limits RPDs for the spiked compounds should also be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Method Detection Limit (MDL) Study; run at analyte concentrations near to the minimum detection capability of the method	As needed, at minimum, annually	Positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

_____A

daily calibration standard preparation form 410r7a.xls (03/01/05)

date_____ preparer_____ method-SW-846_**8330**_ SOP__**404**_ Rev____
primary source standard tracking #_____ expiration date_____

target compound conc._____µg/ml (5.0) surrogate conc._____µg/ml (5.0)

conc. µg/ml	dilution factor	acidified water µl required	acidified water µl actual	acetonitrile µl required	acetonitrile µl actual	standard µl required	standard µl actual
0.5	10	500		400		100	

10-fold dilution example calculation:
100µl = 0.1ml (0.1ml) X (5µg/ml) = 0.5µg
500µl + 400µl + 100µl = 1000µl = 1ml (0.5µg) / (1ml) = 0.5µg/ml

Instrument Name _____ **Paragon Analytics** Logbook No./Page _____ **B**

Date Analyzed _____ Operator _____ Method _____ SOP _____ Rev. _____ **Reviewed by / date** _____

Sequence File: C:\HPCHEM_____\SEQUENCE_____ ICAL Date _____ Processing Method _____

Data Path:
C:\HPCHEM_____\DATA_____ Date Archived _____

CH_3OH Lot # _____ H_2O Lot # _____ H_2O w H_2SO_4 Lot # _____ CH_3CN Lot # _____ Col. Type & Serial No. _____

Vial	Inst. Method	Data File	Sample Name	Rerun?	Comments

Comments: _____ Form 410r7b.xls (03/01/05)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 444 REVISION 1

TITLE: **EXTRACTION AND DETERMINATION OF GLYCOLS BY GAS CHROMATOGRAPHY -- METHOD SW8015B**

FORMS: **531 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-21-06

QUALITY ASSURANCE MANAGER _____ DATE 11/21/06

LABORATORY MANAGER _____ DATE 11-21-06

HISTORY: Rev0, 11/11/02 and 7/8/05; Rev1, 11/20/06. re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references, SW-846 8015B, are used to extract and determine the concentration of glycols in aqueous and solid matrices. The following substances are currently analyzed at Paragon using this procedure:

ethylene glycol propylene glycol

Other compounds may be analyzed using this procedure, if successful MDL studies and initial demonstration of capability are performed. At present, no second column confirmation can be performed, as Paragon is unaware of an alternative column phase that is suitable for this test.

2. SUMMARY

Aqueous samples are analyzed by direct injection onto a gas chromatograph. Solid samples are extracted with deionized water and the aqueous extract is injected onto a gas chromatograph. Both water samples and the aqueous extracts from soils are mixed with acetone prior to injection to improve retention time stability and reproducibility of the injections. The GC is temperature programmed to facilitate separation and identification of target compounds. The analytes are detected by a flame ionization detector (FID). Detector responses are recorded by a data acquisition system to facilitate processing of data. Quantitation is accomplished using the external standard method. Reporting limits are at or above the low standard incorporated into the calibration curve.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of

Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Interferences from phthalate esters can be minimized by using plasticizer-free solvent containers and scrupulously cleaned glassware (SOP 334) that has been solvent rinsed prior to use.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH, AUTOSAMPLER AND DETECTOR SYSTEM
Hewlett Packard 5890 Series II GC, equipped with a Hewlett Packard 7673 Automated Injection System, and a flame ionization detector (FID) or equivalent system.

5.2 CAPILLARY COLUMN
Restek Stabilwax 30m, 0.32mm ID, 1µm film thickness or equivalent.

5.3 CHROMATOGRAPHIC DATA ACQUISITION AND PROCESSING SOFTWARE
Any data acquisition system capable of acquiring, storing and processing chromatographic data (e.g., Hewlett Packard ChemStation™ or equivalent).

5.4 GASES - **Use only high purity gases!**
Helium - carrier gas
Hydrogen - to supply FID

Compressed Air - to supply FID

5.5 MEASURING DEVICES

5.5.1 Microsyringes, Hamilton Precision™ or equivalent, various sizes (e.g., 5µL-1.0mL)

5.5.2 Top loading balance, capable of weighing to ±0.01g (sample preparation)

5.5.3 Top loading balance capable of weighing to ±0.0001g (standard preparation).

5.5.4 Volumetric flasks, Class A with ground glass or PTFE stoppers, 10mL and 25mL sizes, or other sizes as appropriate

5.6 CONSUMABLES

septa	preconditioned, 11mm, Agilent 5183-4759 or equivalent
inlet liner	open-top Uniliner, Restek 20843-205 or equivalent
gold seal	0.8mm ID, Restek 21317 or equivalent
ferrules	graphite, 0.8mm, Restek 20251 or equivalent
o-ring	6.5mm ID, Restek 20299 or equivalent
glass wool	Siltek deactivated, Restek 21100 or equivalent
filter	Whatman 6890-2507 0.7µm GD/X or equivalent

6. REAGENTS

6.1 SOLVENTS - **Only chromatography grade or higher quality solvents may be used**

acetone

organic-free reagent water, laboratory deionized (DI) water is suitable for use

6.2 STANDARDS

6.2.1 Details pertaining to standard preparation and storage procedures are documented in SOP 300.

6.2.2 Two independent sources (first, second) of target analyte standards are required. Pure compounds may be purchased and primary standards prepared gravimetrically from the neat compounds. Alternatively, solutions containing the compounds of interest may be purchased from commercial vendors and utilized as primary standards.

First source materials are used to create calibration and continuing calibration verification (CCV) standards. Second source materials are used to create the initial calibration verification (ICV) solution.

6.2.3 No surrogate or internal standards are used in this procedure.

6.2.4 Laboratory Control Sample (LCS) and Matrix Spike (MS) spike standards may be from either source (the second source is most commonly used).

6.2.5 Secondary standards are prepared by dilution of the primary standards using an appropriate solvent. These standards can generally be stored for six months when prepared in organic solvents.

6.2.6 Unopened stock (primary) standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules or other container as recommended by the manufacturer.

6.2.7 Working standards are prepared fresh daily. This category of standards includes those to be injected on the GC.

7. SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Aqueous samples are collected in 40mL glass VOA vials with screw tops and Teflon-lined septa; amber glass is preferred. Where applicable, aqueous samples should be dechlorinated with sodium thiosulfate at time of collection. The Paragon Project Manager may direct that each aqueous sample is checked for residual chlorine upon receipt at the laboratory. Notify the Project Manager immediately if residual chlorine is detected.

No acidification is required.

7.3 Soil samples are collected in wide-mouth glass (amber preferred) containers with Teflon-lined lids.

7.4 All samples (and extracts) must be maintained chilled (4±2°C).

7.5 Aqueous samples must be analyzed within 7 days from collection, or 14 days from preparation by mixing with acetone. Solid samples must be extracted within 14 days from collection, and must be analyzed within 14 days following mixing with acetone.

8. PROCEDURE

8.1 TYPICAL GC OPERATING CONDITIONS

Carrier Gas Flow Rate:	3-5mL/min
FID H_2 Flow Rate:	30mL/min
FID Air Flow Rate:	350mL/min

Injector Temperature:	210°C
Initial Oven Temperature:	100°C for 1.5min
Oven Ramp:	15°C/min to 200°C
Hold:	200°C for 2min
FID Temperature:	225°C

Purge Off for entire analytical time

8.2 CHROMATOGRAPHIC MAINTENANCE

8.2.1 Bake out the column. Extra blanks may be necessary to achieve an adequate baseline if carryover is observed. Clean injector, cut or replace column as necessary to maintain adequate peak shape and response.

8.2.2 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Oxidized columns will exhibit baselines that rise rapidly during temperature programming. If a column is oxidized, replacement may be necessary.

8.3 INITIAL CALIBRATION

8.3.1 Prepare calibration standards, in DI water, at suitable concentrations. A minimum of five levels must be used. Note that the aqueous calibration standards are mixed with an equal volume of acetone prior to analysis.

Concentration (µg/mL)	10	25	50	100	200

Typically 1µL of standard or field or QC sample extract is injected by automated injector for analysis. Analyze the initial calibration and process using the data processing software.

8.3.2 Peak area responses are tabulated by the data acquisition system. Quantitation is accomplished using an external standard approach, typically using linear regression (not forced through the origin).

If average response factor calibration is employed, then a calibration factor (CF) for each standard is calculated as follows:

$$Calibration\ factor\ (CF) = \frac{peak\ area}{analyte\ concentration}$$

8.3.3 If the CFs over the working range are constant (i.e., <20% RSD), then response can be assumed to be invariant and the average (mean) CF may be used to quantify sample concentrations.

Relative Standard Deviation (RSD) is calculated as follows:

$$RSD = \frac{\text{Standard deviation}}{\text{mean CF}}\ (100)$$

If the RSD is >20%, then a form of calibration other than average response factor must be employed. Linear regression is typically utilized even when the RSD is less than 20%. The regression calculation will yield a correlation coefficient (r^2) that must be $\geq$0.99 to be used for sample quantitation. Note that the correlation coefficient is an expression of "goodness of fit" with perfect fit being a value of 1.0. Non-linear curve fitting is allowed with minimum of 6 points following guidelines in SW-846 Method 8000B.

8.3.4 INITIAL CALIBRATION VERIFICATION (ICV)
Before samples may be analyzed, an ICV must be analyzed to verify the working calibration curve. The ICV should be analyzed at a concentration different from the continuing calibration verification standards to ensure the curve is valid over much of the range of the initial calibration. Refer to QC Table for acceptance criteria.

8.4 DAILY CALIBRATION VERIFICATION

8.4.1 Consistent detector response during a run sequence is verified by the analysis of a Continuing Calibration Verification (CCV) standard. The calibration verification standard does not need to always be performed at or near the midpoint of the initial calibration. Levels above and below the mid-range should be analyzed over time.

8.4.2 After an initial calibration and acceptable ICV are analyzed, up to ten samples, blanks or quality control (QC) samples may be analyzed. After the tenth injection, a CCV must be analyzed and the Percent Difference (%D) calculated:

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}}\right](100)$$

The analytical sequence of 10 injections, CCV, 10 injections, CCV, etc., may continue so long as the CCVs yielded are acceptable (±15%D). Refer to QC Table for appropriate corrective measures.

8.5 RETENTION TIME WINDOWS

8.5.1 RTWs are used to define the integration envelope for quantifying various compounds in samples. The retention time window (RTW) is determined by making a minimum of three injections of the appropriate standard throughout the course of at least a 72-hour period. Serial injections over less than a 72-hour period result in RTWs that are too tight. Guidelines are given in Method SW8000B.

8.5.2 Calculate the mean and standard deviation of the start time and end time of the RTW for the analyte. Multiply by three, add, and subtract from the means to generate windows.

8.5.3 Integration of peak areas is performed by the chromatographic data processing system, but can be manually performed by the analyst following the guidelines of SOP 939.

8.5.4 The experience of the analyst weighs heavily in interpretation of the chromatogram. Environmental samples may contain more than one type or class of compound.

8.6 SAMPLE PREPARATION, ANALYSIS, QUANTITATION, REPORTING

8.6.1 Aqueous samples are not extracted in preparation for analysis. All aqueous samples are mixed with an equal volume of acetone prior to injection (as are the calibration standards). The addition of acetone yields more reproducible injections and retention times than when direct aqueous injection is used.

8.6.2 Solid samples (soils, sediments, waste or other solids) are extracted with deionized water for two hours in an ultrasonic bath prior to analysis. Typically, extraction is accomplished in 40mL VOA vials or 4oz. glass jars, using 20g aliquots of sample with 30mL of DI water added.

The samples are removed from the ultrasonic bath after 2hrs and a portion of the aqueous extract is removed and centrifuged or filtered with an appropriate 0.7µm filter.

A portion of the filtered extract is then mixed with an equal volume of acetone before injection on the GC.

8.6.3 Standard and sample preparations are introduced onto the GC via an automated injector. Typically a 1µL aliquot of standard, prepared aqueous sample, extract, or QC sample is injected. The volume of the injection must be the same for standards and samples.

Once successful calibration has been achieved (Section 8.3), the automated injector is staged to continue in a CCV, 10 injections, CCV, etc. sequence (as described in Section 8.4), so long as samples require analysis and CCVs yield acceptable performance (refer to QC Table).

8.6.4 Make sure all gas and rinse solvents are adequate to last throughout the automated run.

8.6.5 Where necessary, dilute samples or extracts to keep response within the calibration range.

8.6.6 Concentration of targets in the sample is calculated using the integrated peak areas at the correct retention time.

If the average CF is used for quantitation, the extract concentration (µg/mL) is calculated as follows:

$$extract\ conc. = \frac{area}{mean\ CF}$$

where:

area = integrated peak response in sample

mean CF=average CF from the multipoint calibration

Where linear regression is employed, quantitation of sample concentration is based on the equation of the linear curve generated during initial calibration (i.e., y = mx + b):

$$x = \frac{(y - b)\,(V_t)(DF)}{m(V_s \text{ or } W_s)}$$

where:

x = concentration of the analyte

y = analyte instrument response (area units)

b = calculated intercept

m = calculated slope of the line

V_t = total volume of concentrated extract (mL)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

V_s or W_s = volume or weight of sample extracted (mL or g)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method Blanks (MBs) are aliquots of matrix (i.e., organic-free water for liquids, typically Ottawa sand for solids) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification. If this criterion is not achieved, then analyses must be halted and the source of the contamination found and corrected.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). A field sample may also be analyzed in duplicate. The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. Percent Recovery (%R) for spiked analytes is calculated as follows (see QC Table for evaluation criteria):

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right) (100)$$

NOTE: Typically, one MS and MSDuplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

9.6 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the sensitivity limit of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of SW-846 Method 8015B.

11. SAFETY HAZARDS AND WASTE

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.6 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.1.7 Food and drink are prohibited in all lab areas..

11.2 WASTE DISPOSAL

11.2.1 Solvent wastes must be disposed of in the appropriate waste containers.

11.2.2 Any rinse waters used for rinsing syringes or other devices prior to contact with samples must be disposed of in the Aqueous Lab Waste stream.

11.2.3 Any methanol or other nonhalogenated organic solvents that have not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/ Nonhalogenated Waste stream.

11.2.4 The extract vials and associated extracts that contain methanol or other organic solvent but not PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

11.2.5 The extract vials, associated extracts, and any PCB contaminated debris that may contain PCBs in excess of 50ppm shall be disposed of intact in the PCB Debris Waste.

11.2.6 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

12. REFERENCES

12.1 EPA SW-846, Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, 3rd edition, Final Update III, “Method 8015B”, Revision 2, December 1996.

12.2 EPA SW-846 Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, 3rd edition, Final Update III, "Method 8000B", Revision 2.

DOCUMENT REVISION HISTORY

7/8/05: Re-released without revision.

11/17/06: Format updated, minor clarifications where necessary. GC maintenance added to Section 8. DOCUMENT REVISION HISTORY section added.

Instrument Name _____ **Paragon Analytics** Logbook No./Page _____

Sequence File: C:\HPCHEM___\SEQUENCE_____ Date Analyzed _____ Operator _____ GC Method _____

Data Path: C:\HPCHEM___\DATA_____ Analytical Method _____ SOP _____ Rev. ___

Hexane Lot _____ Dichloromethane Lot _____ **Reviewed by / date** _____ Form 531r2.xls (9/14/2001)

Vial	Data File	Method	Sample Name	Comments	rr?

Analytical Method SW8015B	**Parameter:** Glycols		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum 5 points; all analytes	As needed (i.e., when the daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitated. If RSD ≥20%, calculate linear regression (not forced through origin); use for quantitation if coefficient of determination (r^2) ≥0.99 or calculate quadratic regression (minimum of six points required); use for quantitation if COD ≥0.99	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Initial Calibration Verification (ICV); all analytes	After each ICAL	≤15%D of each compound or mean %D ≤15%	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); all analytes	Run at start of sequence if ICAL not performed; brackets each set of 10 injections; (SW8015B requires minimum of once per 12 hour shift)	≤15%D of each compound or mean %D ≤15%	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed before and after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV (bracketed by acceptable CCVs) will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on 3 injections throughout a 72-hour period to be more representative of daily operations	Whenever a new column is installed,	Column and compound specific. Window is ± 3x the standard deviation of the 3-injection average for the column Note that the ICV and CCV analyses are also used to monitor RTW drift	If zero, substitute window of close-eluting similar compound. Wider windows can be used to screen for compounds; experience of analyst should weigh heavily in interpretation of chromatograms (refer to RT Shift).
Retention Time (RT) Shift; RT of analyte in CCV is evaluated against the midpoint of the ICAL or the preceding CCV	Each CCV	Column and compound specific, varies with each initial calibration	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate. Evaluate data based on a comparison with other standards run during the analytical sequence; consider the RTs for spiked compounds analyzed before and after the

Analytical Method SW8015B	**Parameter:** Glycols		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			sample in question: - expand RTW to encompass the shift in compound location - if no peaks are found in the expanded window, report the compound as non-detect
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD) or Laboratory Control Sample Duplicate (LCSD)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; see Matrix Spike information above for MSD recoveries. RPDs should be within advisory limits.	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and

Analytical Method SW8015B	**Parameter:** Glycols		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
			spike preparation). Check unspiked sample results and surrogate recoveries for indications of matrix effects. Note in narrative. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers. Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. If still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed)
Method Detection Limit (MDL) Study; run at analyte concentrations near to the minimum detection capabilities of the method	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

STANDARD OPERATING PROCEDURE 446 REVISION 2

TITLE: **ANALYSIS OF CRYSTAL VIOLET IN WATER BY HPLC**

FORMS: **410, 611** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3-26-09

QUALITY ASSURANCE MANAGER _____ DATE 3/20/09

LABORATORY MANAGER _____ DATE 4-8-09

HISTORY: Rev0, 1/28/05; Rev1, 7/24/06; Rev2, 3/19/09.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) is used to determine the concentration of crystal violet in aqueous samples. Crystal violet, also known as gentian violet or hexamethyl-pararosanilinen chloride, is used to control fungi and has various purposes in human and veterinary medicine. This compound belongs to the group of triphenylmethane dyes, which are linked to an increase in health risks. This procedure was developed at ALSLG-FC from literature references. The direct aqueous injection of waters is modified from SW-846 Method 8330. The HPLC conditions are adapted from available literature references.

Analyte (IUPAC Name)	**CAS #**
Methyl Violet 2B	8004-87-3

2. SUMMARY

Aqueous samples are prepared for analysis by dilution with solvent (acetonitrile with C18 column, or methanol with cyano column). The diluted sample is injected into a high performance liquid chromatograph (HPLC). The target analyte is separated under gradient or isocratic mobile phase flow conditions, as detailed in Section 9. The target analyte is then detected by an ultraviolet (UV/Vis) detector, using the absorption maxima of crystal violet at 588nm and 300nm. Responses of the analyte are recorded and calculated by a data acquisition system, using an external standard method of quantitation. Identification is confirmed by the presence of a peak at both wavelengths at the expected retention time. No surrogate is utilized because water samples are directly injected (essentially no preparation variables) and due to the lack of a representative surrogate compound.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review or results of precision and accuracy tests performed.

3.3 ALSLG-FC 's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALSLG-FC standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the appropriate review sheets and case narrative indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work, and documentation of measures taken to correct the problem.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Contaminants in reagents from glassware or within the analytical system may cause the appearance of discrete artifacts or elevated baselines. Use of high purity reagents, scrupulously cleaned glassware and frequent maintenance of the analytical system minimizes these interferences.

4.2 Interferences from the sample matrix may vary considerably from source to source. If significant interferences are observed, these are reported in the results narrative.

5. APPARATUS AND MATERIALS

5.1 HPLC SYSTEM

Hewlett-Packard (HP) 1050 or 1090 or equivalent HPLC equipped with a degassing system (helium sparge or vacuum degasser), system controller, column oven, autosampler, diode array UV-Vis or other adequate UV-Vis detector.

NOTE: If the HP 1050 is used, two separate acquisition methods are required, one using 588nm and another for 300 nm.

5.2 DATA SYSTEM

Any data acquisition system capable of acquiring, storing and processing HPLC data (e.g., LC ChemStation™ or equivalent).

5.3 MEASURING DEVICES

- Pipettes – air displacement/conical tip, or equivalent, various µL ranges
- Volumetric Flasks, Class A, various sizes

- Graduated cylinders, glass, 5 to 1000mL, or equivalent
- Analytical Balance, capable of reading +0.0001g.

5.4 HPLC COLUMNS - Equivalent columns may also be used

C_{18} column:	Zorbax Extend™ C18; 3.0x 100mm, 3.5µm 80Å
Cyano column:	Develosil™ CN-UG 5µm (250 X 4.6mm) or equivalent

NOTE: Either of these two columns may be used with dual wavelength confirmation.

5.5 CONSUMABLE SUPPLIES

- solvent inlet filter frit-1/4", 4.6mm, 2µm, Restek #25071 or equivalent
- HPLC pump maintenance kit, Restek #25270 or equivalent
- autosampler maintenance kit, Restek #25259 or equivalent
- PTFE syringe filter, 0.45µm (see note below)
- autosampler vials and caps
- glass pipets, disposable

NOTE: Do not filter water samples prior to addition of solvent. Loss to filters has been documented prior to solvent addition. Allowing the sample to settle or use of a centrifuge may be preferable. Also, glass contact surfaces (test tubes, autosampler vials, standards storage vials), are preferable to HDPE. Crystal violet is attracted to HDPE surfaces.

6. REAGENTS

6.1 SOLVENTS - **Only HPLC grade solvents with acceptable UV cutoffs may be used.**

methanol (CH_3OH), Burdick and Jackson 230-4 or equivalent

6.2 REAGENTS

- reagent water (H_2O), Burdick and Jackson 365-4 or Millipore filtered water or equivalent
- glacial acetic acid, VWR VW0125-3 or equivalent
- ammonium hydroxide, EM Science AX1303-3 or equivalent
- Cyano Column Buffer: approximately 0.02M acetate buffer - adjusted to pH 4 with ammonium hydroxide (2.87mL glacial acetic acid + 1mL ammonium hydroxide brought to 1000mL with reagent water)
- C18 Column Buffer: approximately 50mM ammonium acetate; 7.5g of ammonium acetate to 2.0 L of reagent water, pH to 4.00 with acetic acid.

6.3 STANDARDS

6.3.1 All standards are maintained per SOP 300. Target analyte stock standards, typically 100µg/mL, are prepared from pure standard reference materials dissolved in a small aliquot of MeOH and/or ACN and brought to final volume in reagent water. For neat standards or standard materials

of a purity <95%, adjust concentration for purity when calculating standard concentration. Two independent sources (first, second) of target analyte stock standards are required. No surrogate is required in association with this method because water samples are directly injected (essentially no preparation variables) and due to the lack of a representative surrogate compound.

Intermediate standards are made by diluting an appropriate aliquot of stock standard to a specific volume using reagent water, and are stored in Teflon™-sealed vials. Typically, a 10-fold dilution is made, thus creating intermediate standard at a concentration of 10µg/mL. A 500µg/L intermediate is also typically prepared to facilitate preparation of calibration standards. First source target analyte materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards (used by the Organics Extraction Group). Second source target analyte materials are used to create the initial calibration verification (ICV) solution.

All stock and intermediate standards are stored in the freezer (i.e., dark, -10 to -20°C). Stock standards expire 1 year from the date of preparation, or per the manufacturer's expiration date (whichever is sooner). Intermediate standards expire one week from preparation. Standards may be replaced sooner if laboratory QC analyses or other factors indicate deterioration.

NOTE: Standards must be equilibrated to room temperature, sonicated and vortex mixed prior to diluting to avoid low recovery from solution.

6.3.2 The intermediate target analyte standards are further diluted to create working standards. These working standards (ICAL, ICV, CCV) are prepared on the day of use, directly in analysis vials, using aliquots of intermediate and diluent to create sufficient standard volume for analysis. Calibration standards are documented in the analytical run log (Form 410). A detailed description of the concentration of the calibration standards and how they are used can be found in Section 9 of this SOP.

6.3.3 All stock and intermediate standards are documented in ALSLG-FC's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are not generally chemically preserved and must be collected in glass containers (generally 40mL) with Teflon-lined lids. Samples must be maintained at 4±2°C and prepared for analysis within 7 days of collection. Prepared aqueous samples must be maintained in the dark at 4±2°C and analyzed within 7 days of preparation. Preparation of aqueous samples consists of mixing with acetonitrile (C18 chromatography) or methanol (cyano chromatography).

8. SAMPLE PREPARATION

Aqueous samples are prepared by mixing 5mL of sample with 1mL of acetonitrile (if analyzed on the C18 column) or 1mL methanol (if analyzed on the cyano column). Samples are allowed to settle or a centrifuge may be used if sediments are present in the sample. If filters are used, solvent must be added first and recovery of crystal violet from the filer should be demonstrated.

9. ANALYTICAL PROCEDURE

9.1 TYPICAL HPLC ANALYSIS CONDITIONS FOR C18 COLUMN

Flow rate: 0.5mL/min

Gradient:

Time (min.s)	% A (Water)	%B (Acetonitrile)
0	60	40
9	10	90
10	10	90
11	60	40
14	60	40

Post Time (for further equilibration): 4 minutes

Oven temperature: 32°C

Injection volume (C18): 80µL (within an acquisition, injection-volume is held constant)

9.2 TYPICAL HPLC ANALYSIS CONDITIONS FOR CYANO COLUMN

Flow rate: 1.0mL/min

Solvent: isocratic 75% methanol, 25% acetic acid buffer

Oven temperature: 32°C

Injection volume (cyano): 100µL (within an acquisition, injection-volume is held constant)

9.3 Routine maintenance is performed prior to the initiation of each run. This includes ensuring that the mobile phase is within expiration and sufficiently degassed, that no

leaks are observed upon initiation of flow, and that system pressure and baseline are consistent prior to the start of the acquisition.

If the instrument has sat idle for a period of time, it may be necessary to condition the column with one or more injections of the CCV prior to analysis of the CCV for the acquisition sequence.

9.4 INITIAL CALIBRATION

9.4.1 Intermediate Standards for Preparation of Calibration Standards: A 5 parts reagent water plus 1 part solvent diluent solution is first prepared. For example aliquot 10mL of reagent water to a vial and then add 2.0mL of solvent (acetonitrile if C18 column is to be used; methanol if cyano column is to be used).

Conc. of Solution Diluted	**Volume of Solution Diluted** (µL)	**Volume of Diluent** (µL)	**Concentration of Intermediate Solution** (µg/L)
100 µg/mL	100	900	10,000
10,000 µg/L	50	950	500

9.4.2 The linear range of the analytical system is defined using a minimum of five different concentrations. The lowest concentration standard shall be at a level at or below the analyte reporting limit. A typical set of calibration standards is depicted below:

ICAL Dilutions for Use with C18 Column

Diluent (µL)	**µL of Intermediate Standard**	**Final Conc. (µg/L)**
850	150µL of 500µg/mL	75
900	100 µL of 500µg/mL	50
920	80µL of 500µg/mL	40
940	60µL of 500µg/mL	30*
960	40µL of 500µg/mL	20
970	30µL of 500µg/mL	15
980	20µL of 500µg/mL	10
990	10µL of 500µg/mL	5

*Recommended CCV and ICV level.

ICAL Dilutions for Use with Cyano Column

MeOH (µL)	Reagent Water (µL)	µL of Intermediate Standard	Final Conc. (µg/L)
1000	4750	250µL of 10µg/mL	416
1000	4900	100µL of 10µg/mL	167
1000	4950	50µL of 10µg/mL	83
1000	4875	125µL of 2µg/mL	42
1000	4950	50µL of 2µg/mL	16.7
1000	4975	25µL of 2µg/mL	8.3
1000 (ICV)	4875	125µL of 10µg/mL (2^{nd} source)	208
1000 CCV	4900	100µL of 10µg/mL	167

9.4.3 Inject and analyze 80µL (C18 column) or 100µL (cyano column) of each calibration standard and sample. Each data file quantitation is accomplished via the external standard method of quantitation. Analyte Response Factors (CFs) are calculated as follows:

$$CF = \frac{\text{integrated peak area of analyte}}{\text{analyte concentration}}$$

Relative Standard Deviation (RSD) is calculated as:

$$RSD\,(\%) = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean response factor}}\right)(100)$$

When RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r2 value) that must be >0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit", with perfect fit being a value of 1.0. Non-linear (quadratic) regression curve fitting is also allowed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000. A quadratic regression should not be used to compensate for detector saturation.

Linear and 2nd order regressions are used almost exclusively with this procedure. The type of curve fit applied should be chosen to best represent the data.

9.5 INDEPENDENT CALIBRATION VERIFICATION

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV are identical to those of the CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

9.6 CONTINUING CALIBRATION VERIFICATION

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or around the midpoint of the initial calibration. Inject a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when all compounds are within 15%D or when the average of the %Ds for all compounds is $\leq$15% (individual compounds that exceeded 15% are noted in the data package narrative). If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

9.7 RETENTION TIME WINDOWS

For chromatographic methods, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed, and are used compensate for minor RT shifts. It is important to establish valid RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures normal system variation). Calculate the standard deviation (equation given previously) of the absolute retention time yielded for each analyte for the set of analyses used for the RTW study. Define each analyte's RTW as the mean retention time $\pm 3\sigma$, such that the Upper Limit = $+3\sigma$ and the Lower Limit = -3σ.

Per SW-846 Method 8000B, RTWs may be centered on the midpoint standard if applied to samples run immediately after an initial calibration, or centered on the CCV for subsequent application (corrects for minor retention time drift). Sample matrices may cause drift that requires further analyst interpretation. RTWs and integration parameters should be set to err on the side of false positives, so target

compounds are not missed by the data system.

Tentative identification occurs when a peak response falls within the RTW at primary wavelength (588nm) on the cyano column. Confirmation occurs when the peak's response also falls within the RTW for the confirmation wavelength (300nm) on the cyano column. Diode array spectral confirmation may also be used on a project and client specific basis.

9.8 QUANTITATION

Sample analyte concentration is calculated using the equation of the linear curve generated (i.e., y = mx + b), which can be represented as:

$$A = mC + b$$

where:

A = analyte response (area counts)
m = slope of the linear equation
C = concentration present at the instrument
b = the y-intercept of the linear equation

10. QUALITY CONTROL

10.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or less field samples of like matrix that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS) and matrix spike and duplicate (MS/MSD). All quality control samples must be carried through all stages of the sample preparation and measurement steps.

10.2 BLANKS

MBs are aliquots of matrix (i.e., HPLC reagent water) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that Interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is prepared, analyzed, or there is a change in reagents, a MB must be processed.

To be acceptable, concentration of the analyte of interest detected (if any), in the MB must be below the analyte reporting limit or as otherwise prescribed in the LIMS program specification. If this criterion is not met, analyses must be halted and the source of the contamination found and corrected.

10.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. The LCS is similar to the matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS). Percent recovery is calculated as follows:

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right) (100)$$

See QC Table for evaluation criteria.

10.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this, the matrix spike analysis is performed in duplicate (MSD). Precision is evaluated as Relative Percent Difference (RPD) for each analyte of the duplicate pair, and is calculated as follows:

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right) (100)$$

See QC Table for evaluation criteria.

10.5 MATRIX SPIKE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection. Analyte recovery is calculated as shown below:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right) (100)$$

where:

$Conc_{found}$ = analyte concentration found in the MS or MSD sample

$Conc_{sample}$ = analyte concentration found in the field sample

$Conc_{target}$ = target (anticipated) analyte conc. based on amount spiked

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation is made in the data package narrative.

10.6 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

11. DEVIATIONS FROM THE METHOD

This SOP documents procedures developed at ALSLG-FC and as such, is **proprietary information**.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

12.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

12.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.5 All flammable compounds must be kept away from ignition sources.

12.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

12.1.7 Food and drink are prohibited in all lab areas.

12.2 WASTE DISPOSAL

12.2.1 Any rinse waters used for rinsing syringes or other devices prior to sample contact may be disposed of in the Aqueous Lab Waste.

12.2.2 The methanol-water HPLC waste may be discarded into the ACN Waste Stream container.

12.2.3 The extract vials and associated extracts that do not contain PCBs greater than 50ppm may be disposed of intact in the Discarded Extract Vial Waste.

12.2.4 The extract vials, associated extracts, and any PCB-contaminated debris that may contain PCBs in excess of 50ppm, shall be disposed of intact in the PCB Debris Waste.

12.2.5 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

13. REFERENCES

13.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 8330, "Nitroaromatics and Nitramines by High Performance Liquid Chromatography", Revision 2, December 1996.

13.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 8000B, "Determinative Chromatographic Separations", Revision 2, December 1996.

13.3 OSHA Draft Primary Sampling/Analytical Method (SLC1), "Gentian Violet", August 1992.

13.4 Samanidou, V.F., Nikolaidou, K.I. and Papadoyannis, I.N., "Development and Validation of a Gradient HPLC method for the Identification of Ballpoint Pen Ink Components: Study of Their Decomposition", Journal of Liquid Chromatography and Related Technologies, 2004, pp215-235.

13.5 Tarbin, J.A., Barrnes, K.A., Bygrave, J. and Farrington, W.H.H., "Screening and Confirmation of Triphenylamine Dyes and Their Leuco Metabolites using HPLC-VIS and ESP-LC-MS", The Analyst, 1998, pp2567-2571.

13.6 Wendy C. Anderson, Sherri B. Turnipseed, Christine M. Karbiwynk, Rebecca H. Lee, Susan B. Clarke, W. Douglas Rowe, Mark R. Madson, Kieth E. Miller. "Quantitative and Confirmation Analses of Crystal Violet (Gentian Violet) and Brilliant Green in Fish", FDA Center for Food Safety and Applied Nutrition Laboratory Information Bulletin No. 4395, May 2007; Updated May 2008.

DOCUMENT REVISION HISTORY

7/24/06: Augmented RESPONSIBILITIES, added FORMS and DOCUMENT REVISION HISTORY.

3/19/09: Added analyte Table to Scope and Section 9. Updated standard preparation and management practices. Added recent literature reference.

Analytical Method: In-house Procedure	**Parameter:** Crystal Violet by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point; all analytes	As needed (i.e., at on-set of analyses or when calibration verification does not meet criteria)	When RSD ≤20%, may use mean CF to quantitated Calculate linear regression (not forced through origin); use for quantitation if correlation coefficient (r^2) ≥0.99 or Calculate quadratic regression (minimum of six points required); use for quantitation if COD ≥0.99	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Independent Calibration Verification (ICV); run above or below midpoint of calibration	After each ICAL	≤20 %D	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); run at midpoint of calibration	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses	≤20 %D	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of variation	Whenever a new column is installed	Column and compound specific Window is ±3x the standard deviation of the 3-injection average for the respective column	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms (refer also to RT Shift).

Analytical Method: In-house Procedure	**Parameter:** Crystal Violet by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
		Note that the ICV and CCV analyses are also used to monitor RT drift	
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question.
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition
Blank Spike (BS); Laboratory Control Sample (LCS)	1 per preparation batch of ≤20 samples of like matrix	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions was the cause. - if still non-compliant and the samples are within the extraction holding time, then request re-extraction using an NCR, and reanalyze all associated samples for the analyte that do not meet criteria - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration

Analytical Method: In-house Procedure	**Parameter:** Crystal Violet by HPLC		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Matrix Spike (MS)	1 per batch, not to exceed 20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike (MS)	1 per batch, not to exceed 20 samples of like matrix	See laboratory limits; recoveries for spiked compounds should be within advisory limits	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated BS (LCS) is within limits, then sample matrix effects are the most likely cause. Note in narrative.
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

_____A

daily calibration standard preparation form 410r7a.xls (03/01/05)

date_____ preparer_____ method-SW-846_**8330**_ SOP_**404**_ Rev____
primary source standard tracking #_____ expiration date_____

target compound conc._____µg/ml (5.0) surrogate conc._____µg/ml (5.0)

conc. µg/ml	dilution factor	acidified water µl required	acidified water µl actual	acetonitrile µl required	acetonitrile µl actual	standard µl required	standard µl actual
0.5	10	500		400		100	

10-fold dilution example calculation:
100µl = 0.1ml (0.1ml) X (5µg/ml) = 0.5µg
500µl + 400µl + 100µl = 1000µl = 1ml (0.5µg) / (1ml) = 0.5µg/ml

Instrument Name _____ **Paragon Analytics** Logbook No./Page _____ **B**

Date Analyzed _____ Operator _____ Method _____ SOP _____ Rev. _____ **Reviewed by / date** _____

Sequence File: C:\HPCHEM_____\SEQUENCE_____ ICAL Date _____ Processing Method _____

Data Path:
C:\HPCHEM_____\DATA_____ Date Archived _____

CH_3OH Lot # _____ H_2O Lot # _____ H_2O w H_2SO_4 Lot # _____ CH_3CN Lot # _____ Col. Type & Serial No. _____

Vial	Inst. Method	Data File	Sample Name	Rerun?	Comments

Comments: _____ Form 410r7b.xls (03/01/05)

Paragon Analytics

MISCELLANEOUS EXTRACTIONS / CLEANUP WORKSHEET

WO #s ____________________ **Matrix** AQ Solid Other ______ **Batch ID** _____________ **Sur Code** ______________ **M Spike Code** _____________ **Balance ID** ____

Extraction: Method (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)W Dilute **SOP** ______ **Rev** ___ **Date** _____________ **Time** ________ **Initials** _____

Cleanup: Code (3620B) Florisil (3640A) GPC (see other forms) **SOP** ______ **Rev** ____ **Date** __________ **Time** __________ **Initials** ______

SAMPLE								EXTRACT / CLEANUP						
Sample No.	Amount (g / mL)	Initial pH	pH (≤ 2)	pH (11-13)	Surro-gate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	GPC Date	Florisil Date	Date KD (Final)	Final Volume (mL) / Solvent	Date Vialed	**Comments**
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Solvent Lots: $MeCl_2$ ____________________ **Hexane** ____________________ **Acetone** ____________________ **Florisil** ____________________ **(see other forms for GPC Information)**

Reviewed by / Date ____ **Form 611r4.frm (7/24/2002)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 447 REVISION 0

TITLE: **DETERMINATION OF HEXAVALENT CHROMIUM IN AIR BY ION CHROMATOGRAPHY**

FORMS: **413, 414** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 12/8/06

QUALITY ASSURANCE MANAGER _____ DATE 12/8/06

LABORATORY MANAGER _____ DATE 12-12-06

HISTORY: NEW, Rev0, 12/7/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- NIOSH 7605 and OSHA ID215 -- are used to determine exposure to hexavalent chromium, in the workplace, through determination of the concentration of hexavalent chromium [CrO_4^{-2}/diphenylcarbazide (DPC) complex; Cr(VI)] in airborne particulates collected on PVC air sampling filters. Filters are extracted and the extract is analyzed using HPLC/post-column derivatization and UV detection at 540nm.

2. SUMMARY

Sampling is performed, in the field, by pumping a controlled and measured volume of air from the source of interest through a 5.0µm PVC membrane filter. The filter is then sent to the laboratory (either in cassette or in a vial) where it is extracted and analyzed to determine the total hexavalent chromium content. Sample preparation procedures are based on those described in the NIOSH 7605 and OSHA ID215 methods. Hexavalent chromium is extracted from particulates collected on 5.0µm PVC membrane filters by transferring each sample filter to a 50mL disposable centrifuge tube, wetting with precipitation reagent (phosphate buffer and magnesium sulfate), and extracting with NaOH- Na_2CO_3 solution on a heated water bath set at 100°C for 45minutes to one hour with periodic mixing. The precipitate is removed through centrifugal separation and filtering and the final volume is taken to 10mL with ASTM Type II water. An aliquot is then analyzed by ion chromatography.

A 100uL sample is introduced to the ion chromatograph and anion exchange separation is performed prior to post column complexation with 1,5-diphenylcarbazide (DPC) and UV detection at 540nm. Detector responses are processed using an electronic integrator and the result is determined using an external standard quantitation calculation.

Dual column confirmation is not required because the anion exchange separation and relatively unique detection characteristics of the complex at 540nm provide sufficient selectivity to support quantitative determination of hexavalent chromium.

The concentration of hexavalent chromium in the air trapped by the filter is then calculated based on the field data. Both the weight of hexavalent chromium per filter and the concentration in the volume of air sampled are typically reported.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Reducing metal species, primarily Fe(II), may interfere with the determination of Cr(VI) by reducing the Cr(VI) to Cr(III).

4.2 Colored compounds, metals and organic compounds that react with 1,5-diphenyl carbazide such as copper, lipids and ketones are separated from hexavalent chromium. The anion exchange separation provides greater selectivity than the spectrophotometric method.

4.3 Method OSHA ID215 provides the procedure for use of magnesium sulfate/phosphate buffer (PBE) to precipitate potential metal interferences. The

basic extraction/digestion solution also serves to retard the rate of Cr(VI) reduction relative to a less basic solution.

4.4 Interferences are also minimized by the use of high purity reagents.

5. APPARATUS AND MATERIALS

5.1 HPLC, AUTOSAMPLER, DETECTORS

Hewlett-Packard (HP) 1050 (or equivalent) HPLC equipped with:

- gradient or isocratic pumping system
- autosampler
- system controller
- column oven (method runs at ambient temperature)
- post-column reagent pump
  (capable of pumping 0.7 mL/min at 400-1000 PSI)
- heated mixing loop: 2.2m PEEK at 30 ± 3 ºC or equivalent
- ultraviolet (UV) detector

5.2 DATA SYSTEM

Any data acquisition system capable of acquiring, storing and processing HPLC data (e.g., LC ChemStation™ or equivalent)

5.3 COLUMNS - Equivalent columns may also be used

Guard Column: Dionex NG1 4x35mm PN039567
Analytical Column: Dionex Ion Pak 4x250mm PN035393

5.4 MEASURING DEVICES

Pipettes – air displacement/conical tip, or equivalent, various µL ranges

Graduated cylinders – 5 to 1000mL glass or polymer (translucent plastic, PMP), or equivalent

Beaker (with stir bar and stir plate for reagent preparation)

Analytical balance, 0.0001g sensitivity (for preparation of standards)

Top-Loader Balance, 0.01g sensitivity

5.5 CONSUMABLES

- Filter for Mobile Phase and Derivatization Reagent: VWR Vacuum filtration system PES 0.45µm #87006-070 or equivalent.
- Filter (matrix) for Laboratory Blank and LCS/LCSD: 37mm, 5.0µm PVC; SKC Inc. #225-8-01-1 or equivalent
- See Guard Column (above 5.3)
- Solvent Inlet Filter Frit-1/4” 4.6mm, 2µm, Restek #25071

- Pump Maintenance Kit -Agilent 1050 HPLC, Restek #25270
- Autosampler Maintenance Kit -Agilent 1050 HPLC, Restek #25259
- Plastic test tubes (for mixing standards)
- Disposable plastic sample cups
- Disposable transfer pipettes-SAMCO #202 or equivalent
- 50 mL disposable centrifuge tubes-Falcon #35720 or equivalent
- Syringe Filter-Restek 25mm, 0.22µm PTFE #26146 or equivalent
- Autosampler vials and caps

6. REAGENTS

6.1 Mobile Phase: 250mM ammonium sulfate; 100mM ammonium hydroxide (Expiration-2 months)

6.1.1 ASTM Type II or Millipore water.

6.1.2 ammonium sulfate, Mallincrodt ACS or equivalent

6.1.3 ammonium hydroxide, EM Science AX1303-3 or equivalent

Dissolve 33g of ammonium sulfate in about 500mL of deionized water, add 6.5mL ammonium hydroxide, bring to a final volume of 1.0L with ASTM Type II water. Filter (0.45µm).

6.2 Post Column Derivatization Reagent: 2.0mM DPC; 10% methanol; 1N sulfuric acid (Expiration-4 days ambient, 1 week refrigerated)

6.2.1 1,5-diphenyl carbazide (DPC), Aldrich ACS or equivalent; avoid inhalation or exposure to skin, and eyes.

6.2.2 Methanol (CH_3OH; MeOH), Burdick & Jackson #230-4, or equivalent; TWA 200ppm, STEL 250ppm

6.2.3 Sulfuric acid (H_2SO_4), EM trace metals grade or equivalent; TWA 1mg/m^3 (0.25ppm); STEL 3mg/m^3 (0.75ppm); corrosive causes severe burns to skin and all body tissue.

Dissolve 500mg of DPC in 100mL methanol; stir and add 500 mL of water with 28mL of concentrated sulfuric acid bring to a final volume of 1.0L with ASTM Type II or Millipore water. Filter (0.45µm).

6.3 Water, ASTM Type II or Millipore water is used for **all** applicable reagents and system washes.

6.4 Magnesium Sulfate Solution (Expiration-2 months): Dissolve and bring 9.9g of ACS magnesium sulfate ($MgSO_4$) to a final volume of 100mL water.

6.5 Phosphate Buffer Solution (Expiration-2 months):

6.5.1 68g of potassium phosphate, monobasic (KH_2PO_4); ACS

6.5.2 87.1g of potassium phosphate, dibasic (K_2HPO_4); ACS

Dissolve and bring to final volume of 1.0L in ASTM Type II or Millipore water.

6.6 Precipitation Reagent (Expiration-4 hours): Combine 50mL of phosphate buffer solution with 25mL of magnesium sulfate solution.

6.7 Filter Extraction Solution: 2% Sodium hydroxide; 3% sodium carbonate (Expiration-2 months)

6.7.1 Sodium hydroxide VWR ACS or equivalent; TLV 2 mg/m, corrosive, may cause severe burns.

6.7.2 Sodium carbonate (Na_2CO_3) ACS

Dissolve 20g sodium hydroxide and 30g sodium carbonate in ASTM Type II water and bring to a final volume of 1.0L in ASTM Type II water.

6.7.3 For standards dilution, dilute 1:5 in ASTM Type II or Millipore water (Expiration-2 months).

6.8 Potassium dichromate ($K_2Cr_2O_7$) ≥99%; OSHA PEL (as CrO_3): C 0.1 mg/m^3 (0.01ppm) Chromium (VI) is a known carcinogen (cancer hazard), take precautions when handling including use of safety glasses, gloves and good ventilation. Treat as a carcinogen

6.9 STANDARDS

6.9.1 All standards are maintained and documented per PAR SOP 300. Certificates of Analysis are maintained by the applicable laboratory Department. Stock standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer.

6.9.2 At minimum, two independent sources of target analyte are required. First source materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards. Second source materials are used to create the initial calibration verification (ICV) solution (used to independently verify the accuracy of the initial calibration, ICAL)

6.9.3 A 500mg/L hexavalent chromium stock solution is prepared by dissolving 0.1414g of potassium dichromate ($K_2Cr_2O_7$) in ASTM II or Millipore

water. The solution is brought to a final volume of 100mL in ASTM II or Millipore water.

6.9.4 A 10mg/L intermediate standard solution is prepared by diluting 2.0mL of the 500mg/L hexavalent chromium stock solution to 100mL in ASTM II or Millipore water.

6.9.5 An appropriate volume of stock standard (10mg/L) is diluted in 1:5 filter extraction solution to a specific volume to create working standards. All dilutions should be performed using calibrated pipettes (SOP 321). A one-week expiration is assigned to standards diluted from stock.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected in accord with NIOSH or OSHA standards. Air sampling is performed by the client in the field. NIOSH 7605 specifies sampling flows from 1-4L/min. and sampling volumes from 1-400L.

7.2 Samples are collected on 37mm, 5.0µm PVC membrane filter cartridges and may be shipped at ambient or cooler temperatures.

7.3 Filter samples are shipped in the original cassettes or removed from the cassette and shipped in a vial. NIOSH 7605 recommends shipping with bagged refrigerant.

7.4 Samples may be held, prior to extraction, for 2 weeks at ambient temperature and for 4 weeks refrigerated (4±2°C).

7.5 Sample extracts may be held for up to 1 week.

7.6 All samples are to be to be kept chilled (4±2°C).

8. PROCEDURES

8.1 TYPICAL SYSTEM OPERATING CONDITIONS

HPLC DEVICE

Flow Rate (mobile phase):	1 mL/min
Injection Volume:	100µL
Column Temperature:	Ambient to 30°C
Post-Column Mixing Temperature:	32°C
Post Column Derivative Flow:	0.7 mL/min
Detector Wavelength	540nm

8.2 HPLC MAINTENANCE

Prior to analyzing samples or establishing calibration curves, the following suggested maintenance can be performed to aid in achieving more consistent results:

- Restart the instruments and computer prior to beginning equilibration and analysis.
- Ensure that mobile phase and derivatizing reagent have not expired prior to initiating each run.
- Run several primes (1:5 DI extraction solution) before each run until baseline has stabilized. Run curve from high to low to avoid minor effects from active sites on the analytical column.
- Test the total flow prior to each run. The total flow should be 1.6-1.9mL/minute. Also ensure that each pump's pressure is steady and that the solvent effluent rate is steady.
- Change the column frits as needed (i.e., if pressure increase is observed). At the time of method draft, the observed pressures are 180-195bar for mobile phase (1.0mL/min) and approximately 600PSI (0.7mL/min) for the post column derivative pump.
- Change the guard column as necessary (i.e., pressure increase or poor chromatography).
- Inject ASTM type II or Millipore water, at the end of each run to rinse the injector. Then flush the entire analytical system (including the columns) with DI water after each use (a water method may be used to inject water and to flush the system). Remove column after flushing with water.
- When pumps fail to produce acceptable flow, flush system with water, remove and cap column. Then isopropyl alcohol (IPA) may be pumped. Pumping IPA helps to seat the pump seals, clean and seat check valves and to clean the detector window (remove column prior to pumping IPA). IPA is then removed by pumping water. If the problem persists clean pump heads. Check inlet frits and in-line filter, and mobile phase filter.
- **IMPORTANT:** Ensure that system is effectively purged with water prior to allowing IPA to be pumped. It is crucial to prevent a precipitation event and serious damage to the system.

  Flush system with DI water prior to and after IPA use!

- Major repairs are contracted (see Manager regarding applicable service contacts).

8.3 INITIAL CALIBRATION

Initial calibration standards are prepared in 1:5 extraction solution (6.7.4), at a minimum of six concentrations. The range of concentrations of the initial calibration is intended to define the working range of the analytical system. One of the concentrations must be at or below the analyte-reporting limit. The working standards are assigned a 1-week expiration period.

TABLE 1
CALIBRATION STANDARDS

Level	Analyte Concentration (µg/L)	Standard Diluted	Standard Added (µL)	Final Volume (mL)
ICAL 7 (Optional)	2000	10mg/L Stock	2000	10
ICAL 6	1000	10mg/L Stock	1000	10
ICAL 5	250	ICAL 6 (1000)	250	1.0
ICAL 4	100 (CCV-level)	10mg/L Stock	1000	100
ICAL 3	50	ICAL 4 (100)	500	1.0
ICAL 2	25	ICAL 4 (100)	250	1.0
ICAL 1	5	ICAL 4 (100)	250	5.0
ICV	1000	10mg/L ICV Stock	1000	10
Dilution Blank	0.0	N/A	1:5 Standard Dilution Solution	N/A

8.3.1 Inject 100µL of each calibration standard into the HPLC and acquire data. Quantitation is accomplished using the external standard method. Analyte Calibration Factors (CFs) are calculated as follows:

$$CF = \frac{\text{integrated peak area of analyte}}{\text{analyte concentration (µg/L)}}$$

If the CFs over the working range of the detector are constant (i.e., $\leq$20% RSD), then response can be assumed to be invariant (linear through zero) and the average (mean) CF may be used to quantitate sample concentration.

8.3.2 Relative Standard Deviation (RSD) is calculated as:

$$\text{RSD (\%)} = \left(\frac{\text{standard deviation of the analyte's response factors}}{\text{mean calibration factor}} \right)(100)$$

8.3.3 When the RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points (e.g., least squares method) may be constructed. The curve is not to be forced through zero. A zero point may be included if using a quadratic fit provided that a zero point is acquired and that no interference is present. The regression calculation will yield a coefficient of determination (r^2 value) that must be >0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit" with perfect fit being a value of 1.0.

Non-linear (quadratic) regression curve fitting is allowed, with a minimum of 6 points. A quadratic regression should not be used to compensate for detector saturation.

The type of curve fit applied should be chosen to best represent the data.

NOTE: A minimum of five (5) points must be used for the initial calibration. A minimum of five calibration points must be used to meet the %RSD criteria, or the initial calibration is judged to be invalid and a new initial calibration must be generated.

If an initial calibration point is not used for any reason, the analyst must clearly notate why the data point was not used for instrument calibration.

If regression criteria are not met, a new initial calibration must be performed.

8.4 INITIAL CALIBRATION VERIFICATION (ICV)

A second source (ICV) standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV are identical to those of CCV (described below). If the below criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

8.5 PREPARATION OF SAMPLE EXTRACT

8.5.1 Prepare one blank sample with the same filter lot to be used for the LCS/LCSD.

8.5.2 Label two centrifuge tubes LCS and LCSD. Add one unused filter to each tube. Record the tare weight of the original tube plus sample filter.

8.5.1.1 Add 1.5mL of precipitation reagent to each tube. Add 100uL of 10mg/L Cr^6 standard to each LCS. Ensure that each filter is effectively wetted with the precipitation reagent to control possible interferences.

8.5.1.2 Add 5.0mL of filter extraction solution (Reagent 6.7) to each. The formation of a precipitate should be observed upon addition of the filter extraction solution.

8.5.3 Remove tape from outside of each sample cassette. Open each cassette.

8.5.4 Handle the filters carefully, loss of particulates will cause a low bias. Remove the filter (omitting/discarding the backup pad) from the cartridge and transfer it to the centrifuge tube for extraction.

8.5.5 A second filter is moistened with precipitation reagent and used to wipe the cassette casing associated with the filter surface (specified by OSHA for welding operation samples). Filters are placed in the centrifuge tube with the samples surfaces on the outside to facilitate contact with the extraction solution.

8.5.6 Record the tare weight of the tube and filters. Add 1.5mL of precipitation reagent and ensure that the filter surfaces are contacted.

8.5.7 Add 5.0mL of extraction solution to each centrifuge tube. The formation of a precipitate should be observed upon addition of the filter extraction solution.

8.5.8 Heat tubes, with regular agitation, for 55 to 65 minutes in a hot water bath (set to 95 ± 10°C).

8.5.9 Remove tubes from heat. Adjust the final volume to 10mL by adding ASTM II or Millipore water to achieve a final weight equal the tare weight plus 10.49 g. Note: 1.5mL of precipitation reagent plus 5.0mL of extraction solution brought to a final volume of 10.0mL with ASTM Type II or Millipore water weighs 10.49g.

8.5.10 Spin the samples, in a centrifuge, at 3200rpm for 20-30 minutes. Additional filtration of the supernatant using a syringe filter (Restek 25mm, 0.22µm PTFE #26146 or equivalent) is recommended. Note: The precipitate particles increase in size over time.

8.5.11 It is important to omit particulates during transfer to the autosampler vial (ASV). An aliquot of supernatant or filtered supernatant is transferred to an ASV, capped and analyzed. The extracts should be analyzed within one week of extraction.

8.5.12 *Ensure that no visible precipitate remains in each ASV prior to initiating HPLC injection.*

8.6 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is within the quantitation range of the method. Acquire a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when all compounds are within 15%D or when the average of the %Ds for all compounds is $\leq$15% (individual compounds that exceeded 15% are noted in the data package narrative). If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

8.7 RETENTION TIME WINDOWS

Evaluate bracketing standards and set the retention time window (RTW) to include the hexavalent chromium peak. Ensure that the RTW is sufficiently reproducible to support proper evaluation of samples.

RTWs are used to define the integration envelope for quantifying various products in samples. Peak area integration will begin immediately prior to elution of the hexavalent chromium peak and will stop after the peak has attained baseline response.

8.8 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATIONS, REPORTING)
Samples are extracted with warm extraction solution and brought to a final volume of 10mL. QC samples (LCS, MS, etc.) are prepared in a manner similar to that of standards described above. A discussion of quantitation follows.

8.8.1 Dual column confirmation is not required because the separation and detection of the method provides a high level of selectivity. The anion exchange separation together with the relatively unique detection characteristics of the DPC complex (detection at 540nm) provide highly selective method performance.

8.8.2 The following equation is used to quantify sample concentration when CF (or mean CF) is employed:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(DF)}{(\text{mean CF})(V_s \text{ or } W_s)}$$

where:

A_x	=	analyte response (area units)
DF	=	dilution factor (if applicable); if no dilution was made, DF = 1 (dimensionless)
CF or mean CF	=	standard response (area units/concentration)
Vs	=	volume of sample analyzed (L)

NOTE: The final volume is 10mL. The final volume in mL is entered into LIMS.

8.8.3 Where linear regression is employed, quantitation of sample concentration is based on the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)\,(V_t)(DF)}{m}$$

where:

x = concentration of the analyte (µg/filter)

y = analyte instrument response (area units)

b = calculated intercept (area units)

m = calculated slope of the line (area/conc. in µg/L)

V_t = total volume of concentrated extract (L)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

Calculation of $\mu g/m^3$: x/air volume sampled in m^3

Reporting Limit: LIMS default in µg/filter (based on MDL study)

Limit Associated with Volume Sampled: (µg/filter)/(Volume Sampled in m^3)

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS) and laboratory control sample duplicate (LCSD). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method Blanks (MBs) are aliquots of matrix (i.e., PVC air-sampling filters) that have been prepared and analyzed in the same manner as the associated field samples. Blank filter media should be submitted, by the client, with the samples. MBs are analyzed to demonstrate that interferences from the analytical system, media, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification. NIOSH 7605 specifies that blank correction be performed if interferences are observed. Report any observed blank positives to Supervisor.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. An LCS is similar to a matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE
Not required for air sampling since the LCS is a spike of the PVC filter (matrix spike).

9.6 SURROGATE RECOVERY
Not applicable, no surrogate standard is required in association with this method.

9.7 METHOD DETECTION LIMIT STUDY
A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

10.1 This SOP meets the requirements of NIOSH 7605. A minor modification of NIOSH 7605 is specified to facilitate improved sensitivity by using a final volume of 10.0mL. This step is validated in OSHA ID215.

10.2 Method NIOSH 7605 specifies that precipitation may be performed to remedy interferences. Since various sources of PVC filters are known to provide varying background levels of interference for hexavalent chromium, the precipitation step has been included. No blank interferences were observed during method validation.

10.3 Extraction solution is per NIOSH 7605 and varies from that specified in OSHA ID215.

10.4 Paragon policy does not call for the use of blank subtraction. If blank interference is observed, it is reported.

10.5 NIOSH 7605 specifies 1.0 mL/min mobile phase and 0.7mL/min. derivatization reagent. OSHA specifies 0.9 and 0.6 mL/min flows respectively. Both flow rates appear to function well. This method calls for 1.0mL/min mobile phase and 0.7mL/min derivatization -reagent flow.

10.6 Holding Times and sample storage, specified in this method, are in accord with NIOSH 7605, OSHA ID215 has additional specifications for samples from various sources. The LIMS Program Specification may be used to specify project-specific requirements.

10.7 Standards are diluted in a 1:5 dilution of sample extraction solution. The precipitation reagent is not included. Method development data demonstrates that accurate results are achieved with this matrix-matching strategy.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with safety showers, eye wash stations, fire extinguishers, fire blankets, and first aid kits. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time. Potassium dichromate, sulfuric acid, ammonium hydroxide, sodium hydroxide and diphenyl carbazide are utilized in this procedure, familiarity with the associated hazards is important.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area. Gloves and safety glasses are important at the HPLC due to the use of strong base and strong acid mobile phase and derivatization reagent.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Reagent preparation, for this method, should be performed in a hood.

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport (compressed gas is used for the Agilent 1050's pneumatic system).

11.1.8 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Mobile phase waste is collected and disposed of in accord with SOPs 003 and 015.

11.2.2 Hexavalent chromium standards and sample vials are emptied and added to the mobile phase waste (11.2.1).

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

NIOSH 7605
OSHA ID215

Analytical Method: NIOSH 7605; OSHA ID215	**Parameter:** Hexavalent Chromium		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL); minimum five-point	As needed (i.e., when daily calibration verification does not meet criteria)	When RSD ≤20%, may use mean RF to quantitate Calculate mean response, linear regression (not forced through origin); use for quantitation if coefficient of determination (r^2) ≥0.99 or quadratic curve fit to best characterize data and to meet acceptance requirements.	Evaluate/correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Initial Calibration Verification (ICV); conc. not equal conc. to midpoint of calibration curve; second source	After each ICAL	≤15%D	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at midpoint of calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 field sample analyses.	≤15%D	Evaluate/correct instrument malfunction as needed (e.g., rinse or change liner, remove some of the guard column); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed. - If holding times are an issue, complete a Non Conformance Report (NCR) and notify the PM for sample disposition.
Retention Time Window (RTW	Evaluated with each acquisition	RT must be stable within each run to support valid data interpretation.	If significant drift is observed, reject the associated data, perform maintenance on the system and re-inject/re-analyze the samples. Ensure that all extracts are free of visable particulates that may effect injection, low and RT.
Method Blank (MB)	1 per preparation batch of ≤20 samples of like	<RL: MB should not contain any target compounds at or	Reanalyze to determine if instrument contamination was the cause. If MB

Analytical Method: NIOSH 7605; OSHA ID215	**Parameter:** Hexavalent Chromium		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
	matrix Client should provide blank filters. Analyze all submitted blanks. One or more LCS-media blank(s) are also analyzed.	above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition.
Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD)	1 per preparation batch of ≤20 samples of like matrix. Filter is spiked after PBE addition and before BE addition.	See laboratory limits; recoveries for spiked compounds must be within laboratory limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level≤ to that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Paragon Analytics

HEXAVALENT CHROMIUM SOP 447 -- EXTRACTION BENCHSHEET **Reviewed by/Date** _____

WOs _____ **Batches** _____ **Method** NIOSH 7605-OSHA ID 215 **SOP** 447 **Rev** ___ **Dilution Reagent** Millipore Water **Date** _____ **Initials** ____

$MgSO_4$ ID _____ **Phosp. ID** _____ (PBM is 2:1 Phos. to $MgSO_4$) **Extn Soln (BE) ID** * _____ **Spike Soln ID** _____ **Witness** ____ **Balance ID** ____

SAMPLE EXTRACTION										
Sample Number	Tare Wt. Tube+Filt (s) (NA if 2nd tube used) (g)	PBM check (1.5mL) Complete (√)	LCS Spike check (100µL) Complete (√)	BE check (5mL) Complete (√)	Heated check (95±5 °C, 55±5 Min) Complete (√)	Desired Wt. (Tare+10.49g) adjust with Millipore H_2O	Actual Final Wt. (Tare+10.49g = 10.0mL Final Vol)	Centrifuge check (3200rpm-20 min) Complete (√)	Filter check (0.22µm) Complete (√)	Comments

* Note: Calibration standards are diluted with 1:5 Extn Soln : Millipore Water.

Form 413r0.doc (10/24/06)

Instrument Name _____ **Paragon Analytics** Logbook No./Page _____

Date Analyzed _____ Operator _____ Method _____ Col. Type & Serial No. _____ SOP 447 Rev ___

Sequence File: C:\HPCHEM_____\SEQUENCE_____ ICAL Date _____ Processing Method _____

Data Path: C:\HPCHEM_____\DATA_____ Date Archived _____ Mobile Phase ID _____ Deriv. Rgnt ID _____

Vial	Method	Data File	Sample Name	Rerun?	Comments

Reviewed by / date _____

Form 414r0.xls (10/24/06)

STANDARD OPERATING PROCEDURE 448 REVISION 1

TITLE: **DETERMINATION OF PERCHLORATE IN LIQUIDS AND SOLIDS USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY, ELECTROSPRAY IONIZATION TANDEM MASS SPECTROMETRY (LC/MS/MS)**

FORMS: **415** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1-5-09

QUALITY ASSURANCE MANAGER _____ DATE 1/5/09

LABORATORY MANAGER _____ DATE 1/5/09

HISTORY: NEW Rev0, 3/20/08; Rev1, 12/31/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references – EPA SW6850 (multi-matrix), DoD Perchlorate Handbook, and Method 331.0 (drinking water matrix), are used to determine the concentration of perchlorate in liquid and solid samples.

Analyte	CAS #
Perchlorate ClO_4^-	14797-73-0

2. SUMMARY

Water samples are filtered prior to analysis, soil samples are extracted with reagent water then filtered prior to analysis. An internal standard (IS) is added to the sample/extract, which is then well-mixed, before being filtered and analyzed. Samples/extracts may be subjected to a C_{18} or ion exchange cleanup prior to HPLC separation with subsequent multi-reaction monitoring (MRM) analysis by LC/MS/MS, with electrospray ionization and isotope dilution quantitation. Data is captured via an integrator, and instrument operation and data processing are assisted by a personal computer (PC).

NOTE: Cleanup removes high hydrocarbon level interferences and discoloration. The ion chromatography versions of this method use multiple cleanup procedures via filter technology, such as Hydronium (–H) for carbonate, silver (-Ag) for chloride, and barium (Ba^{2+}) for sulfate. Method validation showed that such cleanup is usually unnecessary when using the K' column and solvent diversion valve. Two barium cartridges with one hydronium cartridge in parallel or a combined bed cartridge may be used to remedy extreme matrix challenges.

A 100uL sample (including added acetonitrile and acetic acid) is introduced into the

HPLC. Perchlorate (ClO_4^-) is separated chromatographically from the sample/extract matrix. Early eluting interferences may be diverted to waste prior to introducing the HPLC stream to the ion source. The HPLC is connected to the ion source of the MS/MS, where electrospray ionization is performed. Perchlorate ions m/z 99 ($^{35}ClO_4$), 101($^{37}ClO_4$) and 107 ($^{35}Cl^{18}O_4$) are selectively filtered to the collision cell by the first quadrupole mass filter, where perchlorate is partially fragmented via collisionally induced dissociation. Multiple reaction monitoring (MRM) is performed and fragment ions m/z 83 ($^{35}Cl0_3^-$), 85 ($^{37}ClO_3^-$) and 89 ($^{35}Cl^{18}O_3^-$) are selectively detected. Detector responses are processed by an electronic integrator and the result is determined using an internal standard quantitation calculation. Since the internal standard used is an isotopically labeled version of the analyte and is added at the start of the sample preparation process, this is an isotope dilution method with recovery correction included.

This technique is highly sensitive and selective. Perchlorate presence, confirmed by MS/MS MRM products, has a high level of certainty.

Precursor Ion (m/z)	**Fragment Lost (m/z)**	**Product Ion (m/z)**
$^{35}ClO_4$ (99) quant. ion	^{16}O (16)	$^{35}Cl0_3^-$ (83)
$^{37}ClO_4$ (101) conf. ion	^{16}O (16)	$^{35}Cl0_3^-$ (85)
$^{35}Cl^{18}O_4$ (107) IS ion	^{18}O (18)	$^{35}Cl^{18}O_3^-$ (89)

Please note that as stated in Section 10, the requirements prescribed in this SOP meet or exceed the requirements set forth in EPA SW6850. A summary of QC parameters and associated corrective actions is provided as a Table at the end of the SOP. Note also (Section 3.2) that these requirements may be superceded by the requirements prescribed via a specific client program specification. Consult the individual program specification for client-specific criteria and corrective actions.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for

client-specific requirements prior to initiating handling of samples or data.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented as prescribed in SOP 928.

4. INTERFERENCES

4.1 Sulfate has essentially the same parent mass as perchlorate. However, sulfate cannot form the collision products that are monitored from perchlorate, and sulfate is well separated from perchlorate by the K' RP column.

4.2 Carbonate, chloride and other anions and eluting ions may also interfere if present at sufficiently high concentrations.

4.3 Co-eluting entities can cause ion suppression. Absence of ion suppression as a problem below 4500mg/mL challenge (31,200µS/cm) was demonstrated during validation of EPA Method 6850 and is documented as shown in Table 3 below:

Table 3
Matrix Challenge Study Results

Conc. Suppressors (mg/mL)	Conductivity (µS/cm)	Suppression Observed	RT Drift
500	5000	No	Within Divert
2000	16620	No	Within Divert
4000	28500	No	Exceeds Divert
4500	31200	No	Exceeds Divert
5000	34000	IS < 50%	Exceeds Divert
5500	36700	IS < 50%	Exceeds Divert

NOTE: $^{35}ClO_3^-$ (m/z83)/ $^{35}ClO_3^-$(m/z85) ratio acceptable throughout study range.

A study to determine the maximum tolerable concentration of known ion suppressors bicarbonate, carbonate, chloride and sulfate was performed. This study included no divert event. Diversion of the HPLC effluent prior to elution of perchlorate may be used to protect the instrument from contamination. However,

as sample conductivity increases, perchlorate retention decreases, and perchlorate will go to divert at conductivity beyond about 17000 µS/cm. For this reason, 16620uS/cm (2000 mg/mL) is the level selected for the matrix conductivity threshold (MCT).

In light of retention time drift, samples with sufficiently high conductivity to cause perchlorate to be diverted from the mass spectrometer must be diluted for analysis (assuming required reporting limit can be met), subjected to cleanup, or analyzed without divert. Dilution may be performed routinely, provided that the required sensitivity is achieved.

An Interference Check Sample (ICSL), may be analyzed to verify method performance for perchlorate, at the RL, in the MCT solution. Refer to QC Table at the end of this SOP or information given in the specific client program specification for ICSL acceptance criteria.

4.4 Additional cleanup procedures may be used. SPE C_{18} (for organic contamination) and/or cartridge cleanups such as Ba^{2+} (for sulfate), -H (for carbonate), and Ag (for chloride), may be used if removal of these interferences is appropriate. Two barium and one hydronium cartridge in series have been shown to be effective in removal of high sulfate and carbonate interferences. If cleanup columns are used, associated QC samples must be prepared in the same manner as the batch sample(s).

4.5 Interferences are also minimized by the use of high purity reagents.

5. APPARATUS AND MATERIALS

5.1 HPLC, AUTOSAMPLER, DETECTORS

Shimadzu Prominence (or equivalent) binary HPLC equipped with:

- gradient pumping system
- autosampler
- system controller – interface to MS data system
- column oven

Tandem mass spectrometer

- Applied Biosystems API 3200 MS/MS or equivalent

5.2 DATA ACQUISITION

Any data acquisition system capable of acquiring, storing and processing HPLC/ mass spectrometry data (e.g., Analyst™ or equivalent) to support qualitative and quantitative requirements may be used.

5.3 COLUMNS - Equivalent columns may also be used

Guard Column: Optional; guard must not undermine system performance
Analytical Column: K' Technologies, Inc. RP HPLC 4x250mm KPRPP-X250

5.4 MEASURING DEVICES

- Pipettes – air displacement/conical tip, or equivalent, various µL ranges; operated as prescribed in SOP 321
- Volumetric Flasks (Class A) – various sizes
- Graduated cylinders – 5 to 1000mL glass or polymer (translucent plastic, PMP), or equivalent
- Analytical Balance (for preparation of standards and matrix challenge solution); operated as prescribed in SOP 305
- Top-Loader Balance: to 0.01g (for sample aliquot prior to extraction extraction) ; operated as prescribed in SOP 305
- VWR Conductivity Meter Model 23226-523 or equivalent

5.5 CONSUMABLES

- Filter for Mobile Phase: Filter the mobile phase using vacuum filtration with a 0.45µm nylon membrane filter; 47mm (Whatman 7404-004) or equivalent
- Disposable 50mL centrifuge tubes, Falcon #35720 or equivalent
- Disposable transfer pipettes, SAMCO #202 or equivalent
- Syringe Filter, Restek 25mm, 0.22µm PTFE #26146, 0.45µm or equivalent
- Autosampler vials and caps
- C_{18} Solid Phase Extraction (SPE) Cartridges (optional cleanup)
- Ion exchange cartridges: Ba^{2+}, –H and/or Ag (optional cleanup)

NOTE: **High Density Polyethylene** (HDPE) instead of glass is acceptable for perchlorate per EPA 331.0.

6. REAGENTS - All reagents must be HPLC grade or better

6.1 Mobile Phase: 50:50 Acetonitrile (ACN): HPLC H_2O, with 0.1% Acetic Acid (HOAc) – Make by mixing 500mL HPLC reagent water and 500mL ACN, add 1.0mL of acetic acid. Filter as per Section 5.5.

6.2 Internal Standard (IS) Stock Solution
Isotopically labeled perchlorate ($^{35}Cl^{18}O_4$) as neat salt or in HPLC water (concentration as received from manufacturer)

6.3 Working Internal Standard Solution (WIS)
Typically the concentration of the WIS is 50µg/L of isotopically labeled perchlorate ($^{35}Cl^{18}O_4$) in HPLC water (final IS concentration in samples is

0.5µg/L). The absolute concentration is not critical as long as all samples and standards are spiked equivalently.

6.4 Acetonitrile/Acetic Acid Solution: ACN + 0.1% HOAc.

6.5 Solid phase column activation (optional cleanup)
Methanol, HPLC grade

6.6 Ottawa sand

6.7 STANDARDS
All standards are maintained per SOP 300. In the event of a conflict, the specific guidance in this SOP shall supercede that of SOP 300. All stock and intermediate standards are documented in the laboratory's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Certificates of Analysis from vendor materials are maintained by the applicable laboratory Department.

6.7.1 At minimum, two independent sources of target analyte are required. First source materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards. Second source materials are used to create the initial calibration verification (ICV) solution (used to independently verify the accuracy of the initial calibration, ICAL).

6.7.2 An appropriate volume of commercial stock standard is diluted to a specific volume to create both Intermediate and Working Standards; these dilutions are shown below. Perform all dilutions using calibrated pipettes (SOP 321). Do not use standards beyond their expiration date. EPA 6850 specifies a one-year expiration period for intermediate perchlorate standards. This applies to labeled internal standard as well as native perchlorate standards.

Intermediate standards are prepared from 1000µg/mL perchlorate stock (first source for calibration standards, second source for ICV) as follows:

Intermediate Perchlorate Solution A:
500µg/L (50µL of 1000µg/mL perchlorate to 100mL HPLC water)

Intermediate Perchlorate Solution B:
5µg/L (100µL of A to 10mL HPLC water)

TABLE 4
CALIBRATION STANDARDS

Level	Analyte Conc. (µg/L)	Standard Diluted (Intermediate Solutions Above)	Standard Added (µL)	Final Volume (mL)
ICAL 9	100	A: 500 µg/L Stock	2000	10.0
ICAL 8	50	A: 500 µg/L Stock	1000	10.0
ICAL 7	10	A: 500 µg/L Stock	200	10.0
ICAL 6	5.0	A: 500 µg/L Stock	100	10.0
ICAL 5	1.0	B: 5.0 µg/L	2000	10.0
ICAL 4	0.5	B: 5.0 µg/L	1000	10.0
ICAL 3	0.1	B: 5.0 µg/L	200	10.0
ICAL 2	0.05	B: 5.0 µg/L	100	10.0
ICAL 1	0.01	B: 5.0 µg/L	20	10.0
ICV	1.0	B: 5.0 µg/L (2^{nd} source)	2000	10.0

NOTE: Alternate equivalent dilution schemes may be used as appropriate.

NOTE: The ICV is to be utilized at the midpoint of the calibration curve. Based on a logarithmic (i.e., order-of-magnitude) view of the calibration, the ICV has currently been established as 1.0ug/L, which is two orders of magnitude above the low standard and two orders of magnitude below the high standard. This interpretation provides for the best quantitation of perchlorate, particularly because it retains focus at a concentration level most likely to be of primary interest regarding environmental perchlorate samples.

6.8 Interference Check Solution Stock (ICSS) 20mg/mL of each ion: Cl^-, SO_4-, CO_3^-, and $HCO_3^=$. Make by weighing 3.30g NaCl; 2.96g Na_2SO_4; 3.53g Na_2CO_3; and 2.76g $NaHCO_3$ and bring to 100mL with HPLC water. Mix thoroughly, then filter solution through a 0.45µm filter.

6.9 Interference Check Standard for LC/MS (ICSL). For 2000ppm of each anion and 0.05µg/L perchlorate, add 1mL ICSS and 100µL Intermediate Perchlorate Solution B (5µg/L) and bring to 10mL with HPLC water.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Water samples are collected in 125mL sterile HDPE bottles; solid samples are collected in a 4oz amber glass jar. Headspace (one third of total volume) **should** be present to minimize anaerobic biodegradation.

7.3 Store samples at 4±2°C.

7.4 Liquid samples must be analyzed within 28 days of collection. Extracts must be generated from solid samples, within 28 days of collection; the extracts must then be analyzed within 28 days thereafter. A Q flag is appended if samples are out of holding time when received by the laboratory.

8. PROCEDURES

8.1 TYPICAL SYSTEM OPERATING CONDITIONS

HPLC DEVICE

Flow Rate (mobile phase):	0.5 mL/min
Auto Sampler Temperature	15°C
Injection Volume:	100 µL
Column Temperature:	30°C
Run Time:	16 min. (2 min. beyond peak tail)
Ionization Mode:	Turbo Spray (ESI)
Polarity:	Negative

8.2 LCMS-MS MAINTENANCE

Prior to analyzing samples or establishing calibration curves, the following suggested maintenance may be performed/documented to aid in achieving more consistent results:

- Change the column frits as needed (i.e., if pressure increase is observed).
- Ensure that mobile phase provides expected chromatography for perchlorate.
- Flush the entire analytical system and back-flush the column with 50:50 ACN:H2O after each use with this method.
- Clean the K' column by pumping 90:10 ACN:Water. Store the column in the same solution.

  NOTE: The column should be flushed with cleaning solution every 2 months if storing for longer than 2 months.

- Clean or change inlet or outlet valves as appropriate to maintain acceptable flow and accurate flow rate.
- Clean the curtain plate. **CAUTION - source housing and curtain plate may be extremely hot!** Remove the ion source (not necessary to break vacuum); carefully remove the curtain plate and clean on a dust-free surface. Use a dust-free wipe with HPLC water and methanol or 1:1 HPLC

water:ACN with 0.1% formic acid. Carefully reassemble.

8.3 INSTRUMENT MASS CALIBRATION AND TUNING; ANALYTE OPTIMIZATION

The LCMS-MS must have valid mass calibration and tuning, and analyte optimization prior to the performance of any sample analysis.

8.3.1 Mass Calibration and Tuning

Mass calibration ensures that mass peaks are assigned the correct mass-to-charge values. Tuning is the adjustment of the instrument's resolution off-sets to ensure the best peak response. Mass calibration and tuning are performed per manufacturer's instructions.

- The calibration is updated on an as needed basis (i.e., when QC failures are observed, ion masses show large deviation from known masses, major instrument maintenance is performed, or if the instrument is moved).
- If problem is suspected, check calibration with polypropylene glycol (PPG) infusion per manufacturer's recommendation. Adjust as necessary or appropriate.
- Acceptance Range: 0.7 +/- 0.1 (unit resolution)

8.3.2 Analyte Optimization - Analyte optimization considerations consist of both Compound Dependent Parameters and Source Dependent Parameters.

Compound Dependent Parameters:

Declustering Potential (DP)

Entrance Potential (EP)

Pressure of the collision gas during MS/MS scan (CAD gas)

Collision Energy (CE)

Collision Cell Entrance Potential (CEP)

Collision Cell Exit Potential (CXP)

Compound dependent optimization is performed per manufacturer's recommendation (i.e., at method development only, then determined parameters are used). Re-optimization may be performed if needed to improve or restore method performance (for example, after significant maintenance is performed, following a significant failure or event such as moving the instrument, or after the instrument is retuned or recalibrated).

Source Dependent Parameters:

Temperature

Ion Spray Voltage

Gasses

Probe position

Source dependent parameters are more susceptible to change because they are dependent on mobile phase composition and flow. Hence, these parameters are updated when mobile phase flow or composition changes.

8.3.3 Daily Check

Overall system performance is monitored daily through the injection of a perchlorate 'Shooter', which is a known concentration of perchlorate in mobile phase. The Shooter monitors target compound response from the detector, and is injected prior to any analysis. This daily check is evaluated in terms of reasonable peak retention time, shape and response. If the Shooter does not yield reasonable characteristics, problems with the system are looked for and corrected. If the Shooter characteristics are reasonable, analysis proceeds.

8.4 GENERAL SAMPLE PREPARATION

8.4.1 Every standard, sample and quality control (QC) sample must have an equivalent amount of IS added, and each sample must have similar amount of ACN/HOAc solution added in order to improve chromatography and ensure consistent peak shape in samples.

8.4.2 Standards and controls used for calibration and analytical QC such as ICAL standards, ICV, CCV, ICB, CCB are prepared as follows without filtration:

Pipette one mL of standard or control into an autosampler vial, add 10uL of WIS, 200uL of ACN/HOAc, cap tightly. Prefiltered field samples may also be prepared in this manner.

8.4.3 Soil samples, unfiltered water samples and batch preparation QC such as method blanks (MB) and Laboratory Control Sample (LCS) must be prepared with the internal standard added prior to filtering and water extraction from soils.

Samples are spiked with an equivalent amount of WIS as was added for the analytical standards above (8.4.2). For example, if 3mL of a water sample are filtered, then 30uL of WIS is added.

After samples are extracted and/or filtered, 1mL of filtrate is added to the autosampler vial with 200uL of ACN/HOAc solution added.

8.5 INITIAL CALIBRATION

Initial calibration standards are prepared with a minimum of six concentrations (see Section 6.7.2). The range of concentrations of the initial calibration is intended to define the working range of the analytical system. One of the concentrations must be at or below the analyte reporting limit (RL). In addition, a 'Shooter' (high concentration of analyte in MP), may be prepared to show system suitability, and a reagent blank may be injected without IS added in order to show that no interference or residual Perchlorate is present in the reagents used.

8.5.1 Inject 100µL of each calibration standard solution (with internal standard and organic compound mix added) into the HPLC and acquire data. Generate the calibration curve using the internal standard (isotope dilution) method.

8.5.2 A first order regression fit of six or more calibration points that is not forced through zero (e.g., least squares method) is constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be >0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit" with perfect fit being a value of 1.0. Also note that an r-value of 0.995 is equal to an r squared value of 0.99.

8.5.3 Non-linear (quadratic) regression curve fitting may be employed, with a minimum of 6 points, following the guidelines in SW-846 Method 8000. A quadratic regression may not be used to compensate for detector saturation.

8.5.4 The type of curve fit applied should be chosen to best represent the data. Strong linearity is expected for this method. If other response is observed, check for system problems. If regression criteria cannot be met, a new initial calibration (ICAL) must be performed.

8.6 INITIAL CALIBRATION VERIFICATION (ICV)

A second source (ICV) standard is analyzed immediately after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV must be within the quantitative range of the method. The acceptance criteria for the ICV are identical to those of CCV (see Section 8.8). If the acceptance criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

8.7 PREPARATION OF SAMPLE ALIQUOT

8.7.1 Water samples are prepared by measuring a representative volume of sample into a test tube. Sample amounts depend on sample prep and cartridge clean up and may be scaled up or down as necessary. The following example is based on a 3mL sample preparation:

- Add internal standard (30µL of 50µg/L WIS).
- Mix well and then filter with (0.45 or 0.2µm PTFE membrane or equivalent).
- Transfer 1.0mL to an autosampler vial and add 200uL of the acetonitrile/acetic acid solution.

8.7.2 Solid samples are prepared by first weighing a representative 1g solid sample aliquot into a labeled 50mL centrifuge tube. MB or LCS samples are prepared with 1g of Ottawa sand. The solid sample preparation may be scaled up (i.e., 2.0g to 20mL reagent water) if additional extract volume is needed for column and/or cartridge cleanups. The following steps are based on a 1.0g sample preparation:

- Add internal standard (100µL of 50µg/L IS spiking solution).
- Add 10.0mL reagent water (resultant IS concentration is 0.5µg/L).
- Vortex the mixture, followed by sonication for a minimum of 10 minutes, followed by additional shaking and vortex mixing.
- Visually adequate separation of solids must be achieved prior to filtering the sample. Use a centrifuge to spin the samples if appropriate (i.e., centrifuge at approximately 3200rpm for 15-25 minutes).
- Filter the supernatant extract solution using a plastic syringe fitted with a 0.45 or 0.2µm PTFE membrane filter. Dispense the filtrate into an autosampler vial for analysis.
- Cleanups may be performed per SW6850 (C_{18} cartridges for removal of organic interference) and/or EPA 331.0 (Ag, H^+, Ba^{2+} cartridges) if useful for achieving performance goals.
- Transfer 1.0mL to an autosampler vial and add 200uL of the acetonitrile/acetic acid solution.

NOTE: If sample dilution is required due to high analyte concentration or high interference, the sample may have IS added after the dilution if the dilution exceeds a factor of 10. If the dilution factor is less than 10, the sample may be

reanalyzed with the original IS.

8.7.3 Quality control samples are prepared with each extraction batch of ≤20 samples:

- Method Blank - Reagent water added (water matrix) or Ottawa sand added (solid matrices), all reagents and steps are equivalent to field sample.
- LCS - Reagent water or clean (Ottawa sand) matrix spiked at a midpoint level, prepared as is field sample.
- MS - Field sample fortified with perchlorate spike.
- Duplicate - Dup a field sample or MS

8.8 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or around the midpoint of the initial calibration. Acquire a CCV at the start of each analytical sequence, after each ten injections, and at the end of each sequence. QC samples are counted as part of the number of injections, instrument blanks are not.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when % D is $\leq$15% at midlevel, and $\leq$50% at low level (also called LODV). If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Reanalyze the CCV. If the CCV still fails, the instrument must be recalibrated and all samples injected since the last compliant CCV must be reanalyzed.

8.9 RT AND ISOTOPE RATIO (^{35}CL/^{37}CL) CONFIRMATION

- RT will vary due to matrix effects.
- Peak is identified by coelution of the analyte with the IS. Perchlorate identity is confirmed by evaluating the 35Cl/37Cl isotope ratio.
- Perform evaluation of the 35Cl/37Cl isotope ratio for every sample, batch QC sample and standard.
- The theoretical ratio for daughter ions m/z 83/85 is approximately 3.05.
- 83/85 peak area ratio acceptance limit - should be within $\pm$30% of the mid range calibration standard or average of all of the CCV runs of the

analytical batch if calibration was performed previously. If ratio limits are not met, inject a new aliquot of sample. If interference is suspected, dilute the sample with HPLC water if sensitivity is adequate, otherwise use cartridge cleanup. If ratio is not improved, flag sample data as suspect. Note that other criteria and corrective actions may apply, consult the applicable client LIMS program specification.

- Internal Standard Response Verification: The IS area counts must be monitored throughout the run. IS area counts must be within ±50% of the average of the IS area counts of the calibration standards if calibration is performed on the same day as analysis, otherwise use the IS area counts for the first CCV of the analytical batch. If sample IS area counts do not meet the criterion, reanalyze a fresh aliquot of the sample. If the IS counts are still outside of the criterion, check the most recent CCV IS area counts. If the most recent CCV IS area counts meet the criterion, then the sample results should be considered suspect. If the most recent CCV IS area counts do not meet the criterion, corrective action must be taken to resolve the problem. Evaluate and correct as directed in the applicable LIMS program specification.

8.10 SAMPLE ANALYSIS (IDENTIFICATION, CALCULATIONS, REPORTING)
Aqueous sample extracts (with isotopically labeled perchlorate standard) are mixed with acetonitrile-acetic acid and injected for HPLC/ESI/MS/MS determination of perchlorate:

8.10.1 Confirmation is achieved via observation of coelution between perchlorate analyte ions (m/z 83 and 85) and isotopically labeled perchlorate internal standard ion (m/z 89). Relative retention time (RRT) is calculated by dividing the analyte RT by the IS RT. Acceptance limit is 1±0.02.

8.10.2 Linear regression is typically employed, quantitation of sample concentration is based on the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)\,(V_t)(DF)}{m}$$

where:

x = concentration of the analyte (ppb; µg/L or µg kg)

y = analyte instrument response (area units)

b = calculated intercept (area units)

m = calculated slope of the line (area/conc. in ppb; µg/L or µg/kg)

V_t = total volume of concentrated extract (L)

DF = Dilution Factor (if applicable); if no dilution, then DF = 1

NOTE: The calibration fit may be weighted (i.e., 1/x weighting) as described in SW8000.

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike sample (MS) and either field sample duplicate (DUP) or matrix spike duplicate (MSD). All batch QC samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

There are three types of blanks used in this analysis: Reagent Blanks (RB), Initial and Continuing Calibration Blanks (ICB/CCB), and Method Blanks (MB).

Reagent blanks are prepared with HPLC water, ACN/HOAc solution with NO WIS added.

Calibration Blanks are prepared with HPLC water, WIS and ACN/HOAc solution, but no filtration is performed.

Method Blanks (MBs) are aliquots of matrix (i.e., water or solid) that have been prepared and analyzed in the same manner as the associated field samples. HPLC or other analyte free water is used for water samples. Ottawa sand should be used in association with solid samples. MBs are analyzed to demonstrate that interferences from the analytical system, media, glassware, and reagents are under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. An LCS is similar to a matrix spike analysis (below) in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample, a field sample or matrix spike sample is performed in duplicate. The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$\text{RPD} = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

The matrix spike is analyzed to measure matrix effects on analyte recovery. To accomplish this, a measured amount of field sample is spiked with a known amount of analyte and % Recovery is calculated as above for the LCS. See QC Table for evaluation criteria. A minimum of one MS per day and at least one per batch of 20 is required.

$$\%R = \frac{\text{(MS Sample result-Sample result)}}{\text{Spike added}} \times 100$$

9.6 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

10.1 This SOP meets the requirements of EPA SW6850.

10.2 DoD Perchlorate Handbook Rev. 1 Change 1: See Program Specification and LIMS Nickname for the detailed conformance requirements of this reference.

10.3 EPA Method 331.0: See Program Specification and LIMS Nickname for the detailed conformance requirements of this reference.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals, or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.1.8 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 Mobile phase waste is collected and disposed of in accord with SOPs 003 and SOP 015.

11.2.2 All radioactive samples and sample preparations shall be disposed as per SOP 015.

11.2.3 All non-radioactive hazardous waste will be disposed of as per SOP 003.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

12. REFERENCES

12.1 EPA Method SW6850 Rev. 0 "Perchlorate in Waters, Soils and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry (HPLC/ESI/MS/MS)". January 2007.

12.2 DoD Perchlorate Handbook; August 2007 Revision 1, Change 1.

12.3 EPA 331.0 Rev. 1.0 January, 2005 "Determination of Perchlorate in Drinking water By Liquid Chromatography Electrospray Ionization Mass Spectrometry" EPA Document # 815-R-05-007.

DOCUMENT REVISION HISTORY

12/31/08: Updated SOP Header to reflect ALS. Added paragraph to SUMMARY referencing program specification concepts. Minor text edits throughout. Added ICSS and ICSL reagents as Sections 6.8 and 6.9, respectively. Calibration and Tuning Section 8.3 was expanded. The last three bullets of Section 8.9 were edited. QC Table was updated (RT, Isotope Area Ratio, IRCS); also included program specification caveat in Table header. Added DoD program specification as Appendix A.

Analytical Method: EPA SW6850	**Parameter:** Perchlorate		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Note: The QC requirements depicted in this Table represent the laboratory's standard requirements and those of EPA SW6850. Consult applicable client program specification for QC requirements that supercede these criteria.			
Method Reporting Limit (MRL)	Demonstrated with every initial calibration	MRL ≥ lowest calibration standard	Correct system problem if calibration including MRL fails.
Limit of Quantitation (LOQ)	Demonstrated with every initial calibration	Documented in the specific matrix of concern, at or below the applicable regulatory limit Demonstrated with low calibration standard. Must be within 50% of true value	Apply J-flag to all results between the LOD and LOQ
Method Detection Limit (MDL), (LOD)	Upon implementation of method; annually and when major method changes are made; quarterly MDL checks suffice provided no significant method changes are made	MDL study must be performed in the matrix of interest using a standard at 1-10x MDL MDL must be validated through the analysis of a low-level matrix spike at approximately 2x MDL, must have SN ≥3 and isotope ratio of ± 30% of the ICAL mean	Run MDL verification at higher level and set MDL higher or re-perform MDL study. A valid MDL must be completed prior to analyzing samples.
Initial Calibration (ICAL); minimum six-point	At method set up and as needed (i.e., when daily calibration verification does not meet criteria) and after major maintenance	Minimum of 6 calibration standards (+ blank) to establish linearity, r≥0.995 (r^2 ≥0.99) The calibration is linear and shall not be forced through the origin. The concentration corresponding to the absolute value of the calibration curve's Y-intercept should be ≤ LOD. Or use mean response if the RSD for each analyte is ≤20% (including MRL)	Repeat ICAL. No samples may be analyzed and reported until calibration has been achieved and verified.
Initial Calibration Verification (ICV); second source standard at midpoint concentration	After each ICAL (conc. within cal. range)	% Difference (%D) ≤15%D relative to true value	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards. Problem must be corrected prior to analyzing and reporting samples.
Matrix Conductivity Threshold (MCT) study, performed to determine the maximum tolerable	At initial setup and when major changes occur in method operating procedures	Conduct study and determine MCT as discussed in the method.	The MCT for this analytical system using this method has been determined to be 16620uS/cm (2000mg/mL)

Analytical Method: EPA SW6850	**Parameter:** Perchlorate		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Note: The QC requirements depicted in this Table represent the laboratory's standard requirements and those of EPA SW6850. Consult applicable client program specification for QC requirements that supercede these criteria.			
concentration of known ion suppressors			
Continuing Calibration Verification (CCV)	All samples must be bracketed by the analysis of a standard demonstrating detection and accurate quantitation Analysis of mid-level standard after every 10 field samples. and at end of seq. Alternate LL and mid level concentration.	±15% ML; ± 50% LL (LL = approx. RL) Note: LL CCV equiv. to LODV	Evaluate/correct instrument malfunction as needed (e.g., rinse column, lines); prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed after a failed CCV must be reanalyzed. - If a failed CCV for an autosampler analysis returns to acceptable calibration later in the sequence, samples following the acceptable CCV will be reported, and samples between the failed CCV and subsequent compliant CCV will be reanalyzed.
Relative Retention Time (RRT)	Evaluated with each acquisition	The RRT between m/z 83 and m/z 89 must be less than 1.0± 2% (0.98-1.02)	Determine cause of problem and take corrective action
Isotope Area Ratio (m/z 83/85) to confirm presence of perchlorate	Evaluated with each acquisition (for every standard, sample, and control)	83/85 peak area ratio must fall between ±30% of ratio of the mid range calibration standard or the average ratio of all CCVs of the analytical batch if calibration was performed on a previous day	If ratio limits are not met, inject a new aliquot of sample. If interference is suspected, dilute if sensitivity is adequate or use cartridge cleanup. If ratio is not improved, flag sample data and narrate. (Note: Laboratory practice; corrective action not specified in SW6850)
Internal Standard Response Verification (IS = IRCS)	Same level added to every standard sample or control.	IS area counts must be within ±50% of the average of the IS area counts of the calibration standards if calibration is on the same day as analysis, otherwise use the IS area counts for the 1st CCV of the analytical batch	If IS area counts do not meet acceptance criterion, analyze a second aliquot. If the IS counts are still outside of the criteria, check the most recent CCV IS area counts. If the most recent CCV IS area counts meet the criteria, then the sample results should be considered suspect. If the most recent CCV IS area counts do not meet the criteria, corrective action must be taken to

Analytical Method: EPA SW6850	**Parameter:** Perchlorate		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Note: The QC requirements depicted in this Table represent the laboratory's standard requirements and those of EPA SW6850. Consult applicable client program specification for QC requirements that supercede these criteria.			
			resolve the problem.
ICB and CCB (Note: not required SW6850)	Immediately following the corresponding calibration verification samples	<RL, or as otherwise specified in the applicable LIMS program specification	Correct problem, demonstrate freedom from blank interferences and quantitative performance.
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	Perchlorate concentration <RL, or as otherwise specified in the applicable LIMS program specification	Reanalyze to determine if instrument contamination was the cause. If MB still non-compliant, initiate corrective action: - if a sample contains target compounds at ≥10X amount found in MB or if target compounds are not detected in the sample, then results may be reported; otherwise - if the samples are within the extraction holding time, then re-extract and reanalyze all associated samples containing target compounds at <10X amount found in MB - if the samples are beyond the extraction holding time, then complete an NCR and contact PM for sample disposition.
Laboratory Control Sample (LCS)	1 per preparation batch of ≤20 samples of like matrix, spiked at the RL.	Recovery within 80-120%, or as otherwise specified in the applicable LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may need to be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration

Analytical Method: EPA SW6850	**Parameter:** Perchlorate		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Note: The QC requirements depicted in this Table represent the laboratory's standard requirements and those of EPA SW6850. Consult applicable client program specification for QC requirements that supercede these criteria.			
Matrix Spike (MS)	1 per preparation batch of ≤20 samples of like matrix	Recovery within MS limits: 80-120%. Liquid; 70-130%. Solid, or as otherwise specified in the applicable LIMS program specification	Evaluate data to determine the source of the recovery problem or difference in replicates.
Matrix Spike Duplicate (MSD) or Field Sample Duplicate (DUP)	One MSD or sample Dup. per batch	RPD < 15% when at or above mid range of the ICAL; RPD < 50% when at low end of the ICAL	Examine data, check IS performance and integration. Re-prep. if appropriate.

Page ___ of ___

ALS Laboratory Group - Fort Collins

Perchlorate 6850 Bench Prep Sheet

Shooter __ul Inter A 1st Source in ____mL MP - System Check OK ___ Date _____ Operator _____ WO # (s)_____ Nickname(s) _____

Instrument ID **LC/MS/MS** SOP ____ / Rev ___ Matrix _____ Filter lot_____ Cartridge lot(s) (if applicable) _____

D:Analyst Data\Projects\Perchlorate\... Acquisition Method:..PercMRM___112808___.divert Batch Name: ...Batch_____.dab \Data Path: ...Data_____.wiff

Quantitation Method:.. _____.qmf Results table:._____.rdb ICAL Result File: _____ ICAL mean IS Area _____ ICAL Isotope Ratio _____

Stock Int. A ST080208-5 **Int. B** ST080208-6 **LODV** ST080212-2 **CCV**(m) ST080212-4 **CCV**(h) ST080212-7 **ICSL** ST080212-5 **LCS**(rl) ST080212-3 **LCS**(m) ST080212-6 **LCS**(h) ST080212-8 **Exp.** 2/1/2009

WIS ST080212-9 exp.9/21/2008; **ICV** ST071202-22 exp.8/6/2008; **ACN/HOAc** RG080213-1 **HPLC Water** 072343 **Others**_____

#	Sample Name	Method / Nickname	Sample Head Space? **Y** or **N**	Conductivity (µS/cm) (if done)	Matrix	Starting Matrix / Amt.	Extract H_2O Added (mL)	ID Stock Added	Amount Stock Added (varies)	WIS Added (µL)	Filtered? **Y** or **N**	Amount Prep. Added to AS Vial (mL)	ACN/ HOAc Added (mL)	Vial Position	Comments
						Example - use most current iteration									

Reviewed by / date _____

Form 415r1.xls (3/27/08)

APPENDIX A (INTERNAL USE ONLY)
DoD Program Specification

(per DoD Perchlorate Handbook, Rev1, Change1)

QC Check	Frequency	Acceptance Criteria	Summary of Quality Control (QC) Procedures and Corrective Actions
Reagent Blank	Prior to calibration, after over-range samples; after batch analysis	<½ RL	Reanalyze reagent blank and determine source of problem. If reagent contamination is determined, replace source and reanalyze. If carryover is determined, correct problem and reanalyze. Apply B-flag to all samples that cannot be reanalyzed.
ICAL	At method setup and after major maintenance	RSD <20% ea. Linear Fit-No Force Conc. = [Y-inter.] ≤ LOD r= > 0.995; ≥ 5 stds	Correct problem and repeat ICAL. No sample may be run until ICAL has passed.
ICV (2nd Source)	After every ICAL	±15% (mid-range conc.)	Correct problem and re-run. No samples may be run until ICV has passed.
MCT	At initial setup and when major changes occur in method operating procedures	Conduct study and determine MCT	The MCT for this analytical system by this method has been determined to be 16620uS/cm (2000mg/mL)
ICS (ICSL)	1x/20 samp. Batch	Same pretreatment as samples Conc. @ RL [Anion] at MCT Result ±30%	Correct problem then reanalyze batch. No samples may be reported with a failing ICSL.
CCV	After every 10 samples	Rec.±15% (mid-range conc.)	Correct and re-run all samples since the last acceptable CCV. If that fails, or samples cannot be re-run, Q flag all affected samples.
MB	At least one per batch of 20 samples < ½ RL	MB conc. < ½ RL	Correct problem, re-prep and reanalyze MB and all samples associated with the batch. Apply a B-flag to all results if the samples cannot be successfully reanalyzed.
LCS	1x/20 @RL	Rec.±20%, or within laboratory-generated limits, whichever is more stringent	Correct the problem then re-prep and re-analyze LCS and all associated samples. If that fails, or samples cannot be re-run, Q flag all affected samples.
LODV	Bracket Batch of 20 samples. @ 2x LOD	Rec. ±30% LODV Failure: Samples in the batch at > LOD < RL must be re-evaluated. Samples above the RL may be reported.	Correct problem and rerun the LODV and all samples since the last failing LODV (as described under acceptance criteria). Apply a Q flag to all samples since the last unacceptable Q-flag if reanalysis is not possible.
MS	≥1per prep. Batch of 20 samples; @RL	Rec.±20%, or within laboratory-generated limits,	In parent sample apply J flag if acceptance criteria are not met.

APPENDIX A (INTERNAL USE ONLY)
DoD Program Specification

(per DoD Perchlorate Handbook, Rev1, Change1)

QC Check	Frequency	Acceptance Criteria	Summary of Quality Control (QC) Procedures and Corrective Actions
		whichever is more stringent	
Laboratory Dup. or MSD	≥1per prep. Batch of 20 samples spiked at RL.	RPD <15%	In parent sample apply J flag if criteria not met.
IS Recovery (IS = IRCS)	Same level added to every standard sample or control.	±50% of the average IS area counts of original ICAL	Determine cause of problem and take corrective action. If interference is suspected dilute and reanalyze. If correction is not possible Q flag and narrate.
Relative Retention Time	Evaluated with each acquisition	The RRT between m/z 83 and m/z 89must be less than 1.0±2% (0.98-1.02)	Determine cause of problem and take corrective action. If interference is suspected dilute and re-analyze. If correction is not possible Q flag and narrate.
Isotope Area Ratio (m/z 83/85)	Evaluated with each acquisition (for every standard, sample, and control)	Theoretical 3.06; must fall 2.3-3.8 (25% window)	If ratio limits are not met, inject a new aliquot of sample. If interference is suspected, dilute if sensitivity is adequate or use cartridge cleanup. If ratio is not improved, flag sample data and narrate.

Note that a valid MDL study and check per ALS-FC standard practice are required for DoD analyses.

STANDARD OPERATING PROCEDURE 449 REVISION 0

TITLE: DETERMINATION OF DISSOLVED GASES IN WATER SAMPLES USING GAS CHROMATOGRAPHY

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 4.7.09

QUALITY ASSURANCE MANAGER _____ DATE 4/7/09

LABORATORY MANAGER _____ DATE 4-8-09

HISTORY: DRAFT 3/25/08; Rev0, 3/20/09.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references – RSKSOP-175 and EPA Region I Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane and Ethene, is used to determine concentration of dissolved gases (methane, ethane and ethane) in water samples.

Analyte	CAS #	Molecular Weight
CH_4	74-82-8	16
$C2H_4$	74-85-1	28
$C2H_6$	74-84-0	30

Other compounds may be analyzed if successful demonstration of capability (DOC) and method detection limit (MDL) studies are performed.

2. SUMMARY

A headspace volume is created in each water matrix blank, calibration standard, sample and quality control sample, by displacing water with helium at ambient pressure. Equilibrium is then attained by vortex mixing (or equivalent equilibration), and an aliquot from the headspace is then introduced to a gas chromatograph with flame ionization detection (GC/FID), to determine the concentration of dissolved gases in the water sample.

Every water blank, calibration standard, sample and quality control (QC) sample is treated equivalently. The temperature, pressure, headspace volume, equilibration procedure and injection volume are kept constant.

Standards are prepared by introduction of a selected volume of gas phase standard to the headspace of a laboratory reagent blank. The standard concentrations are calculated to reflect the total concentration (TC) of analyte per volume of water. After equilibration, a portion of the headspace in each standard is analyzed, and a linear or 2nd order calibration curve is generated that describes the relationship between instrument response and standard

concentration.

The TC of each dissolved gas in each water sample is then determined by analysis and comparison of the resulting instrument response to the calibration curve.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 ALSLG-FC's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALSLG-FC's's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Any co-eluting entity that responds via FID. Few method interferences are known because methane, ethene and ethane are very small and highly volatile molecules. Interfering compounds are likely to be much more highly retained on the analytical column and separated from these analytes. Typically, chromatographic interferences are not observed with this procedure.

4.2 Interferences are also minimized by the use of high purity reagents (helium or nitrogen, analyte-free water).

4.3 Methane, ethene and ethane are present in the atmosphere (methane more so than ethene and ethane). Precautions should be taken to ensure that interference from room air is avoided. The helium and method blanks serve to demonstrate adequate control of ambient interference. Refer to QC Table for guidance and corrective actions pertaining to method blank analyses.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH (GC) AND DETECTORS

Hewlett Packard 5890 Series II GC or equivalent equipped with a flame ionization detector (FID)

5.2 DATA ACQUISITION

Any data acquisition system capable of acquiring, storing and processing GC/FID data (e.g. Agilent EZChrome™ or equivalent) to support the qualitative and quantitative requirements of this method may be used.

5.3 GASES - use only ultra high purity (99.999%)

Helium (purge and carrier gas)

Hydrogen (FID detector gas)
Compressed Air (FID detector gas)

5.3 COLUMNS - Equivalent columns may also be used
Analytical Column: J&W GS-CARBONPLOT; 30m x 0.533mm x 3.00µm; 0-360ºC operating range

5.4 MEASURING DEVICES
Gas Tight Syringes, various µL ranges

5.5 CONSUMABLES

- GC septa
- VOA Vials, 40mL size
- Replacement caps with septa, for 40mL VOA vials

5.6 Vortex mixer

6. REAGENTS

6.1 GAS PHASE STANDARDS:

6.1.1 Air Liquide-Scott Specialty Gases™: Scotty® mix; methane, ethane, ethane at various applicable concentration such as 100ppm (mole), 1% (mole) and 30% (mole) in nitrogen, or equivalent

6.1.2 Alternate source check standard, if available, otherwise two different lots may be used to confirm accuracy (ICV). Other reference material concentrations may be used, as long as an appropriate calibration range is

accomplished.

6.2 Organic-free reagent water; carbon-filtered, boiled and purged with helium prior to use (SOP 511)

6.3 Methanol, HPLC grade

6.4 STANDARDS

6.4.1 All standards are maintained per SOP 300. Specific SOP instructions take precedence with regard to management of standards.

6.4.2 At minimum, two independent sources of target analyte are recommended. First source materials are used to create calibration, continuing calibration verification (CCV) and QC sample spike standards. Second source materials are used to create the initial calibration verification (ICV), which is used to independently verify the accuracy of the initial calibration (ICAL). Use a second certified standard lot if a suitable alternate standard supply is not available.

6.4.3 An appropriate volume of stock standard is aliquoted to create working standards. All standards are delivered using gas tight syringes or a vacuum manifold system or other accurate gas delivery technique. Standards diluted from stock should be prepared daily.

6.4.4 All stock and intermediate standards are documented in ALSLG-FC's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Samples should be acidified with hydrochloric acid (HCl) to pH < 2. Water samples are usually preserved by adding approximately four (4) drops of concentrated hydrochloric acid (HCl) to each 40mL VOA vial. The purpose of the hydrochloric acid is to prevent microbially induced bias of target compound concentration. If the water sample is unpreserved, the holding time is not defined. Sample analysis of unpreserved samples may proceed given client approval.

7.3 Aqueous samples are collected in 40mL glass VOA vials with screw tops and Teflon ^{TM}-lined septa. Aqueous samples should be headspace-free. It is recommended that a minimum of three vials should be collected for each field

sample. For a designated matrix spiked (MS) analysis, the client may need to provide as many as six vials. Note that a matrix spiked duplicate (MSD) analysis is not typically performed with this procedure.

7.4 Store samples at 4±2 ° C

7.5 Samples must be analyzed within 14 days of sample collection.

7.6 To prevent loss of volatile organic compounds, samples must not be opened until the time of analysis.

8. PROCEDURES

8.1 TYPICAL SYSTEM OPERATING CONDITIONS

Gas Chromatograph

Column Flow Rate (helium):	4.8 ± 0.5mL/min
Air Flow Rate:	per manufacturer's recommendation
Hydrogen Flow Rate:	per manufacturer's recommendation
Purge Valve:	On at 90s (off at 7 minute)
Injector Temp.	250°C
Detector Temp.	350°C
Column Temperature:	150°C
[1]Ramp:	150°C, 4min., 40°C/min., 240°C, 0.8min.
[1]Run Time:	8 min. (includes ramp)
Injection Volume:	300 µL

Expected Retention Times:
Methane 1.7 minute; Ethene 1.9 minute; Ethane 2.03 minute

[1] The run time may be shortened to 3 minutes by omitting the ramp. The shortened run is then an isothermal run. Periodic bake out or use of the temperature ramp may be important to avoid carryover effects in some sample matrices.

8.2 GC MAINTENANCE

Prior to establishing calibration curve or analyzing samples, the following suggested maintenance can be performed to aid in achieving more consistent results:

- Change the GC injection port septum regularly (after approximately each 50 injections).
- Bake out the GC at 250°C until the background signal reaches approximately 4 mV.
- Clean or change the GC liner if pieces of septa or other contamination begin to cause a rise in background signal or column bleed.

- Syringes may be purged with helium or nitrogen to control potential carryover effects.
- Additional GC bake-out may be added to routine sample runs to control moisture or late eluting interferences.

8.3 DISSOLVED GASES CONCEPTS

The purpose of this procedure is to identify and quantitate the concentration of a dissolved gas (methane, ethene or ethane) in an aqueous field sample.

8.3.1 Starting with a 40mL VOA vial (42.5 mL of volume), a 4.0mL headspace is created using helium supplied at near ambient pressure. Thus, 38.5mL of water sample remains.

At this point, any target analytes in the water, partition into the headspace until equilibrium between the two phases is reached.

The concentration of target analyte in the original sample, can be said to be equal to the mass of analyte partitioned to the headspace plus that remaining in the water, divided by the 38.5mL of water sample remaining in the vial.

8.3.2 A standard can be prepared in the same manner as the sample. 4.0mL of headspace is created in a vial of blank reagent water. A known amount of a reference gas standard is then added to the headspace (an equivalent amount of headspace is first withdrawn to maintain ambient pressure inside the vial), and the standard is allowed to equilibrate (same conditions as a field sample). The resulting concentration can be defined as the total mass of analyte added, divided by the water volume in the vial (38.5mL).

If a series of initial calibration standards (at different concentrations) is thusly prepared and analyzed, a calibration curve may be generated from the detector responses obtained.

Field samples may then be analyzed and their detector responses compared to the calibration curve for quantitation.

Since water volume, headspace volume, total VOA vial volume, equilibration conditions, pressure and temperature are all kept constant between standards and samples, one may calibrate and quantitate without the need to determine the concentration in the water phase using the Henry's law calculation approach.

Reference gas standards are supplied with the analyte concentration stated in ppm as calculated on a mole basis. It is necessary to first

calculate the weight per unit volume concentration of each analyte in each standard. This concentration is then used to calculate the total mass of analyte added to a standard or QC sample (via addition into the headspace).

8.3.3 CALCULATIONS

A. Unit Conversion of ppm (mole basis) to gram/liter for Gas Mixtures:

Example Given a 100 ppm (mole basis) gas mixture of CH_4 in nitrogen, calculate the concentration (g/L) of CH_4 in a 1 liter volume:

Key Assumptions

- Temperature of sample assumed to be at 22°C
- Pressure of sample assumed to be 840 bar (0.829 atm; typical Fort Collins atmospheric pressure) just before injection.

  At around atmospheric pressure, gases behave in close to ideal manner.

Using the Ideal Gas Law (PV = nRT) for a temperature of 295.15°K (22°C), a pressure of 0.829 atm (= 840mbar barometric pressure), and the gas constant R of 0.0821 liter-atm/mole-°K, it is determined that:

1 mole of ideal gas occupies 29.21 liters.

One liter of gas will then contain (1/29.21) moles.

Since the concentration of CH_4 is 100 ppm:

(total # moles per liter)(concentration of CH_4) = total number of moles of CH_4 in 1L

The concentration of 100 ppm (parts per million) is unit-less, and equals 100 mole-parts per 1,000,000 total moles = 0.000100 in decimal form; thus the amount of moles of CH4 in one liter of mixture is:

(1/29.21 moles/L)(0.000100) = 0.00000342 moles of CH_4 per liter

The analyte's molecular weight is used to determine the weight of analyte in the mixture:

Example For methane (molecular weight 16 gram/mole):

(16 gram/mole)(0.00000342 moles/L) = 0.0000547 g/L or 0.0547 mg/L

B. General Formula for Conversion of ppm (mole) to gram/liter for Gas Mixture (22°C, 0.829 atm):

$$\frac{\text{Gas Conc. (ppm in decimal form) x mole-weight (gram/mole)}}{\text{29.21 L / mole}} = \text{Conc. (g/L)}$$

C. Calculation of Concentration for Standards:

$$\frac{\text{Gas Conc. (ppm in decimal form) x mole-weight (g/mole) x Vol. Std. Added to Headspace (L)}}{\text{Volume at ambient P and T (L/mole) x Vol. Sample (L)}} = \text{Conc. (mg/L)}$$

Unit Conversions: mg/L (1000 µg/mg) = µg/L

NOTE: The gas volume to be added is first withdrawn from the headspace to maintain ambient pressure (equivalent headspace volume and pressure to that of the samples).

Concentration = total mass of analyte (in the entire vial)/volume of water in vial, mg/L or µg/L

MW = Molecular weight of analyte (g/mole)

T = Temperature

P = Pressure

Example Calculation Standard Concentration for methane (injection of 4µL of 1% mole/mole standard into a VOA vial with 4.0mL headspace):

$$\frac{\text{(0.0100 mole ratio; 1\% std.)(16g/mole)}(4\text{x}10^{-6}\text{L injected})(1\text{x}10^{6}\mu\text{g/g})}{\text{(29.21 L std. Vol. for 1 mole) (0.0385 L water)}} = 0.569\ \mu\text{gCH}_4\text{/L}$$

Calculation of sample results may be done directly by comparison to the standard total concentration curve.

8.4 INITIAL CALIBRATION

8.4.1 Initial calibration standards are prepared at a minimum of five concentrations. The range of concentrations of the initial calibration is intended to define the working range of the analytical system. One of the concentrations must be at or below the analyte reporting limit.

8.4.2 Certified gas standards, containing target analytes in nitrogen, are used to prepare the working standards. The calibration standards are prepared from water blanks and are handled as samples would be (equivalent headspace, pressure, temperature, equilibration).

8.4.3 Example standard levels are provided in the following Table. Standard concentrations were calculated based on a room temperature of 22 ºC and a barometric pressure of 840mbar. As the barometric pressure varies by less than 3% from 840mbar in Fort Collins, CO and room temperature is maintained at close to 22ºC in the laboratory, these conditions will be

routinely applied to calculate standard concentrations. Standard concentrations should be corrected if ambient conditions vary significantly.

TABLE 3
CALIBRATION STANDARDS

Target	Standard Preparation	Total Conc. ppm	TC ppb
CH4	4uL 1%	0.0005690	0.5690
	25uL 1%	0.0035563	3.5563
	100uL 1%	0.0142253	14.2253
	1000uL 1%	0.1422532	142.2532
	300uL of 30%	1.2802789	1280.2789
	3000uL of 30%	12.8027886	12802.7886
C2H4	4uL 1%	0.0009958	0.9958
	25uL 1%	0.0062236	6.2236
	100uL 1%	0.0248943	24.8943
	1000uL 1%	0.2489431	248.9431
	300uL of 30%	2.2404880	2240.4880
	3000uL of 30%	22.4048801	22404.8801
C2H6	4uL 1%	0.0010669	1.0669
	25uL 1%	0.0066681	6.6681
	100uL 1%	0.0266725	26.6725
	1000uL 1%	0.2667248	266.7248
	300uL of 30%	2.4005229	2400.5229
	3000uL of 30%	24.0052287	24005.2287

NOTE: Alternate equivalent dilution schemes may be used as appropriate. Five or more calibration levels are required. Sample injection size, headspace volume, water volume, pressure and temperature must be equal for all standards and samples (keep constant throughout each run).

8.4.4 Inject 300µL of each equilibrated calibration standard into the GC and acquire data.

8.4.5 Electronically integrated peak area responses are tabulated and quantitated using external standard quantitation. Calibration Factors (CFs) for each compound are calculated as follows:

$$CF = A_s/C_s$$

where:

A_s = response (area) for the analyte to be measured

C_s = concentration of the analyte to be measured (µg/L)

8.4.6 Since each CF represents the slope of the line between the response for that standard and the origin, then if the observed deviation between the

CF's is constant (i.e., ≤20% RSD), then the response is assumed to be invariant and the average (mean) CF may be used to quantitate sample concentrations. Percent Relative Standard Deviation (%RSD) is calculated as:

$$\%RSD = \frac{\text{Standard Deviation (SD)} * 100}{\text{Average (mean) RF}}$$

If an initial calibration point is not used for any reason, the analyst must clearly notate why the data point was not used for instrument calibration. "Picking and choosing" among calibration points in order to meet criteria is NOT acceptable. Generally, calibration points are only discarded due to easily demonstratable causes.

8.4.7 When %RSD over the calibration range is greater than 20%, linearity through the origin cannot be assumed. A first or second order regression fit of five or more calibration points that does not pass through zero (e.g., least squares method) may be constructed. The regression calculation will yield a coefficient of determination (r^2 value) that must be >0.99 to be used for sample quantitation. Note that the coefficient of determination (COD) is an expression of "goodness of fit", with perfect fit being a value of 1.0. If non-linear (quadratic) regression curve fitting is used, a minimum of 6 calibration points is required (SW8000C). A quadratic regression should not be used to compensate for detector saturation.

8.4.8 The mathematics used in least squares regression have a tendency to favor numbers of larger value over numbers of smaller value. The regression curves that are generated will therefore tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels. To compensate for this, a "weighting" factor which reduces this tendency can be used. The analyst may weight the curve to either the inverse of the concentration (1/x) or to the inverse of the square of the concentration (1/x2). If regression criteria cannot be met, system repair or maintenance may be necessary and a new initial calibration must be performed.

The type of curve fit applied should be chosen to best represent the data.

8.5 INITIAL CALIBRATION VERIFICATION (ICV)

A second source (ICV) standard is analyzed immediately after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. The acceptance criteria for the ICV are identical to those of the CCV (described below). Refer to the QC Table for corrective action should the ICV analysis fail.

8.6 SAMPLE PREPARATION / ANALYSIS

8.6.1 The reagent gas (nitrogen or helium) used to create sample headspace must be sufficiently pure to support low level quantitation requirements. A system blank of helium is injected to demonstrate that helium and system background are low enough to support analytical goals.

8.6.2 A known volume of 10% or more of headspace must be generated using nitrogen or helium at close to ambient pressure. Ensure that the gas source flows at a low pressure (observe approximately one bubble per second if the gas delivery needle is monitored in vial with methanol).

8.6.3 Each VOA vial contains 42.5mL of volume. A 4.0mL helium headspace was created for the initial MDL study, calibrations and sample analyses, and should therefore be used unless further study is performed to support changing the headspace volume. The displaced water may be measured in a syringe or by weight.

8.6.4 Record the room temperature and barometric pressure in the sequence log. The value for barometric pressure may be taken from Colorado State University's weather observation station. These data show that a value of 840mbar may be used for Fort Collins' barometric pressure with minimal error.

8.6.5 The sample is equilibrated by vortex mixing at approximately 3000 rpm for at least 2 minutes. A 300µL aliquot of headspace is then injected into the GC.

8.6.6 Dilutions. If less than 10% of the original sample headspace was used in a sample analysis, a smaller aliquot, from the same headspace, may be used for gas-phase dilution. The injection size is kept constant. Otherwise, a new sample is prepared at an appropriate dilution. For example, if the head space is 4mL from a 40mL VOA vial and the sample injection is 300µL (7.5% of the headspace), a smaller aliquot of headspace can be used for dilution. The dilution to be performed is chosen to keep the response in the upper half of the calibration curve.

Example Vapor-Phase Dilution: 50µL to 42.5mL (42,500 µL) = 850x

8.7 QC SAMPLES

8.7.1 The following types of QC samples are prepared with each extraction batch of ≤20samples (see QC table for frequency, acceptance criteria and corrective actions):

- Method Blank (MB): No sample added; all reagents and Steps are equivalent to field sample.

- LCS (CCV)/LCSD: Reagent water with equivalent headspace to standard after addition of gas-phase standard. Note that for this procedure, the LCS is equivalent to a CCV (referenced by the method as a CCS). The LCSD is a Duplicate of the LCS.

- MS/MSD: Field sample (and field sample duplicate) fortified with midpoint analyte spike. MSD not required unless specified in the Program Specification or Nickname.

- Duplicate: a field sample duplicate (Dup).

8.7.2 To prepare QC samples, 40mL VOA vials are filled with reagent water (SOP 511) with zero headspace.

8.7.3 Create a 4.0mL headspace by displacing water with helium or nitrogen at close to ambient pressure.

8.7.4 Vials thusly prepared can be method blanks, or can be spiked to create working standards. Note that working standards are equivalent to LCSs for this procedure.

8.7.5 Vapor phase dilutions are performed as necessary to ensure that each analyte is quantitated within the working range of the calibration.

8.8 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to confirm system response throughout an analytical sequence. The concentration of the CCV is at or around the midpoint of the initial calibration. Acquire a CCV at the start of each analytical sequence, after each twenty injections (or less), and at the end of each sequence. ALSLG-FC commonly analyses 10 samples between CCVs to reduce the amount of repeat injections, should they be required. QC samples are counted as part of the number of injections, instrument blanks are not.

The percent difference (%D, drift) must be calculated for each CCV (see equation below):

$$\%D = \left[\frac{(\text{calculated concentration}) - (\text{expected concentration})}{\text{expected concentration}} \right] (100)$$

Calibration is verified when all compounds are within 20%D. Individual compounds that exceeded 20% are noted in the data package narrative. If any CCV does not meet acceptance criteria, analyses should be halted and corrective action taken. Refer to the QC Table for corrective action in the event of CCV analysis failure.

8.9 RETENTION TIME WINDOWS

For GC methods utilizing external standard quantitation, retention times are used for analyte identification. Retention Time Windows (RTWs) are established each time a new column is installed and are used to compensate for minor retention time shifts. It is important to establish valid retention RTWs. If too tight, false negatives may result. If too loose, false positives may occur. Determine RTWs by analyzing replicates (typically three injections), of a mid-level standard containing all analytes, non-consecutively, over a 72-hour period (this approach captures system variation). Calculate the standard deviation of absolute retention time for each analyte for the set of analyses used in the RTW study. Define each analytes' RTW as the mean retention time ±3σ, such that the Upper Limit = + 3σ and the Lower Limit = -3σ.

8.10 SAMPLE IDENTIFICATION, CALCULATIONS, REPORTING

8.10.1 Dual column confirmation is not required because interferences are not observed due to strong separation/greater retention of interferences on the chromatographic column.

8.10.2 The following equation is used to quantify sample concentration when CF (or mean CF) is employed:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(DF)}{(\text{mean CF})(V_s)}$$

where:

A_x	=	analyte response (area units)
DF	=	dilution factor (if applicable); if no dilution was made, DF = 1 (dimensionless)
CF or mean CF	=	standard response (area units/concentration)
Vs	=	volume of sample analyzed (L)

8.10.3 Where linear regression is employed, quantitation of sample concentration is based on the equation of the linear curve generated during initial calibration (i.e., y = mx + b), as follows:

$$x = \frac{(y - b)\,(V_t)(DF)}{m}$$

where:

x = concentration of the analyte (µg/L)

y = analyte instrument response (area units)

b = calculated intercept (area units)

m = calculated slope of the line (area/conc. in µg/L)

V_t = total volume of concentrated extract (L)

DF = Dilution Factor (if applicable);

if no dilution, then DF = 1

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS) and laboratory control sample duplicate (LCSD). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specifications for additional or alternative requirements.

9.2 BLANKS

Method Blanks (MBs) are aliquots of matrix (i.e., water) that have been prepared and analyzed in the same manner as the associated field samples. MBs are analyzed to demonstrate that the system overall is under control. Concentrations of target analytes, if any, must be less than the reporting limit (RL), or as otherwise prescribed in the LIMS program specification.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the analytical system. An LCS is similar to a matrix spike analysis in that known concentrations of target analytes are spiked into reagent matrix (as opposed to sample matrix, as with the MS) and the percent recoveries for the analytes are calculated as shown below. See QC Table for evaluation criteria.

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right)(100)$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this measurement, the laboratory control sample and/or matrix spike sample is performed in duplicate (LCSD, MSD). The results of the duplicate analyses are evaluated in terms of Relative Percent Difference (RPD), which is calculated as shown below. See QC Table for evaluation criteria.

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

9.5 MATRIX SPIKE

The matrix spike is analyzed to measure matrix effects on analyte recovery. To accomplish this, a measured amount of field sample is spiked with a known amount of analyte and % Recovery is calculated as above for the LCS. See the QC Table for evaluation criteria.

$$\%R = \frac{\text{(MS Sample result-Sample result)}}{\text{Spike added}} \times 100$$

9.6 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven (7) replicates for each target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

10.1 Method RSK175: Specifies that the instrument blank (helium or nitrogen) acceptance is less than the MDL. ALSLG-FC uses less than the reporting limit (RL).

10.2 EPA Region 1, Analysis of Dissolved Methane, Ethane, and Ethene in Groundwater by a Standard Gas Chromatographic Technique: Butyl rubber VOA vial septa are specified in the EPA Region 1 method. Teflon-faced silicone septa are commonly employed by ALSLG-FC for volatile analytes. Adaptation of butyl rubber septa may be validated and adapted for this assay. ALSLG-FC has tested septa supplied to clients.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.7 All compressed gas cylinders must be secured at all times. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.1.8 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The aqueous sample waste shall be disposed of in the aqueous lab waste stream. A satellite waste collection vessel may be obtained from the Waste Manager.

11.2.2 Solvent wastes must be disposed of in the appropriate waste containers.

11.2.3 Any methanol, hexane or other non-halogenated organic solvents that has not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Non-halogenated Waste.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs (003, 015). Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 Felisa Hudson. RSKSOP-175. Revision No.2, May 2004.

12.2 Don H. Kampbell and Steve A. Vandegrift. "Analysis of Dissolved Methane, Ethane, and Ethene in Groundwater by a Standard Gas Chromatographic Technique". EPA, Ada, OK. Journal of Chromatography, Vol. 36, May 1998.

12.3 "Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane, and Ethene", Methane, Ethane, Ethene Analysis Guidance, Revision 1. US EPA - REGION 1, New England, NATATTEN.WPD. 11 Technology Dr. North. Chelmsford, MA 01863. February 21, 2002.

Analytical Method: RSK175	**Parameter:** Methane, Ethene, Ethane		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	QC Check
Initial Calibration; minimum 5-point; all analytes	As needed (i.e., when the daily calibration does not meet criteria)	Calculate linear regression (not forced through origin); use for quantitation if coefficient of determination (r^2) ≥0.990 (or r = ≥0.995) or calculate quadratic regression (minimum of six points required); use for quantitation if COD ≥0.990 ≤20%D each point	Evaluate/correct instrument malfunction and reanalyze ICAL to obtain acceptable curve
Independent Calibration Verification (ICV); all analytes	After each new initial calibration	≤20%D of each compound Note: Second lot is acceptable if second source is unavailable.	Prepare another ICV and analyze. If second ICV fails, system must be recalibrated with freshly prepared standards.
Continuing Calibration Verification (CCV); analyzed at approximately midpoint concentration level of the calibration curve	Run at start of sequence if ICAL not performed; brackets each set of 10 (or max. of 20) field sample analyses	≤20%D for each analyte or as otherwise specified in applicable LIMS program specification	Evaluate/correct instrument malfunction as needed (e.g. change septum, rinse or change liner; prepare a new standard and reanalyze. - If CCV still non-compliant, recalibrate. Samples analyzed before and after a failed CCV must be reanalyzed.
Retention Time Window (RTW); based on minimum of 3 non-consecutive injections throughout at least a 72-hour period to be representative of variation	Update whenever a new column is installed or target analytes are misidentified in a standard, LCS or MS	Column and compound specific Window is ±3x the standard deviation of the 3-injection average for the respective column Note that the ICV and CCV analyses are also used to monitor RT drift	Wider windows can be used to screen for compounds; if zero, substitute window of close eluting similar compound. Experience of analyst weighs heavily in interpretation of chromatograms (refer also to RT Shift).
Retention Time Shift; RT of analytes in CCV are evaluated against the midpoint of the ICAL	Each CCV; RT of analytes evaluated against the ICAL	Column and compound specific, must support consistent identification of analytes in know samples.	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate Evaluate data based on comparison with other standards run during sequence, consider RTs for the surrogates and spiked compounds analyzed before and after the sample in question: - adjust the RTW to correct the shift in compound location - if no peaks are found in the adjusted window, report the compound as a

Analytical Method: RSK175	**Parameter:** Methane, Ethene, Ethane		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	QC Check
			non-detect - if peaks are present, use the confirmation column to verify identification
Method Blank (MB)	1 per preparation batch of ≤20 samples of like matrix	<RL: MB should not contain any target compounds at or above the reporting limit (RL) or per other criteria as specified in the applicable LIMS program specification	If not less than acceptable limit, correct contamination and re-analyze associated samples if possible. Note: Due to the ubiquitous nature of methane, method blanks may occasionally have concentrations >RL. Such incidents are acceptable if concentrations of methane in associated samples are either ≥5x the concentration in the method blank OR <RL for methane. If the above conditions are met, then no Non-Conformance Report (NCR) needs to be generated. If the above conditions are not met, then consult the Project Manager for guidance regarding an NCR and corrective action.
Blank Spike (BS); Laboratory Control Sample (LCS); Since an LCS is physically equivalent to a CCV, a CCV may be designated as "CCS" and used as an LCS.	1 per preparation batch of ≤20 samples of like matrix	80-120% Recovery or as specified in individual nicknames; recoveries for spiked compounds must be within these limits or other limits as specified in the LIMS program specification	Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed) - if the samples are beyond the extraction holding time, then contact PM via NCR for sample disposition. Unless otherwise directed, samples will not be extracted outside of the holding time and the data will be submitted with appropriate narration
Matrix Spike (MS) Matrix Spike Duplicate (MSD) or sample Duplicate	1 per preparation batch of ≤20 samples of like matrix	70-130% Recovery or per applicable Nickname/Program Specification; recoveries for spiked compounds should be within advisory limits The relative percent difference	See Matrix Spike actions above for recoveries outside of advisory limits. If RPDs for the spiked compounds are not within advisory limits, check for documentable errors (e.g., calculations and spike preparation). Check unspiked sample results and surrogate

Analytical Method: RSK175	**Parameter:** Methane, Ethene, Ethane		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	QC Check
		(RPD) between duplicate analysis (sample/sample duplicate or MS/MSD) should be ≤ 20 (or per Nickname/Program Specification requirement)	recoveries for indications of matrix effects. Note in narrative. If significant differences between the MS and MSD exist, reanalysis of the sample and spikes may be necessary. Discuss with Department/ Project/QA Managers. Check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze to determine if instrumental conditions were the cause. - if still non-compliant and the samples are within the extraction holding time, initiate an NCR (associated samples may be reanalyzed)
Method Detection Limit (MDL) Study; run at analyte concentrations near to the minimum detection capabilities of the method	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level lower than that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Must Discard 30 Days from _____ (date printed)

Editorial amendment made (see red font) Section 8.12.1 following bullets (minor word re-structuring to include acronym TIC).
1/3/08 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 506 REVISION 15

TITLE: SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY, CAPILLARY COLUMN TECHNIQUE – METHODS SW8270D and EPA 625

FORMS: NONE (instrument printout used as run log)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3/1/07

QUALITY ASSURANCE MANAGER _____ DATE 3/1/07

LABORATORY MANGER _____ DATE 3-1-07

HISTORY: Rev0, 5/29/92; Rev1, PCN #140, 2/21/94; Rev2, 12/28/94; Rev3, 4/1/96; Rev4, 6/10/96; Rev5, 9/21/97; Rev6, 4/15/98; Rev7, 6/15/99; Rev8, 10/27/99; Rev9, 6/14/01; Rev10, 1/23/02; Rev11, 3/25/02; Rev12, 6/25/02; Rev13, 4/16/04; Rev14, 3/13/06; Rev15, 3/1/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references – Method SW8270D - describe a procedure to determine the concentration of semivolatile organic compounds (SVOCs) in extracts prepared from all types of solid waste matrices, soils, TCLP leachates and ground water. Direct injection of a sample may be used in limited applications.

The body of this SOP specifies the procedures to be used for SW-846 Method 8270D. Any additional or contradictory requirements for EPA Method 625 are contained in Section 10.

The following analytes have been successfully determined utilizing this analytical procedure after appropriate preparation methods are utilized. Other compounds may be determined after successful demonstration of capability (i.e., method detection limit studies and other demonstration of capability, as applicable). Analytes in the Table below are listed in elution order. Analytes that are part of Paragon's typical reporting list are presented in bold text.

TABLE 1
APPLICABLE COMPOUNDS FOR SEMIVOLATILE ANALYSIS BY SW8270D

COMPOUND	CAS Number
pyridine	110-86-1
N-nitrosodimethylamine	62-75-9
aniline	62-53-3
phenol	108-95-2
bis(2-chloroethyl)ether	111-44-4
2-chlorophenol	95-57-8
1,3-dichlorobenzene	541-73-1

TABLE 1
APPLICABLE COMPOUNDS FOR SEMIVOLATILE ANALYSIS BY SW8270D

COMPOUND	CAS Number
1,4-dichlorobenzene	106-46-7
1,2-dichlorobenzene	95-50-1
benzyl alcohol	100-51-6
bis(2-chloroisopropyl)ether	108-60-1
2-methylphenol	95-48-7
N-nitroso-di-n-propylamine	621-64-7
3-methylphenol	108-39-4
4-methylphenol	106-44-5
hexachloroethane	67-72-1
nitrobenzene	98-95-3
isophorone	78-59-1
2-nitrophenol	88-75-5
2,4-dimethylphenol	105-67-9
bis(2-choloroethoxy)methane	111-91-1
2,4-dichlorophenol	120-83-2
benzoic acid	65-85-0
1,2,4-trichlorobenzene	120-82-1
naphthalene	91-20-3
4-chloroaniline	106-47-8
hexachlorobutadiene	87-68-3
4-chloro-3-methylphenol	59-50-7
2-methylnaphthalene	91-57-6
hexachlorocyclopentadiene	77-47-4
2,4,6-trichlorophenol	88-06-2
2,4,5-trichlorophenol	95-95-4
2-chloronaphthalene	91-58-7
2-nitroaniline	88-74-4
dimethyl phthalate	131-11-3
2,6-dinitrotoluene	606-20-2
acenaphthylene	208-96-8
3-nitroaniline	99-09-2
acenaphthene	83-32-9
2,4-dinitrophenol	51-28-5
4-nitrophenol	100-02-7
dibenzofuran	132-64-9
2,4-dinitrotoluene	121-14-2
diethyl phthalate	84-66-2
fluorene	86-73-7
4-chlorophenyl phenyl ether	7005-72-3
4-nitroaniline	100-01-6
azobenzene	103-33-3
4,6-dinitro-2-methylphenol	534-52-1
N-nitrosodiphenylamine	86-30-6

TABLE 1
APPLICABLE COMPOUNDS FOR SEMIVOLATILE ANALYSIS BY SW8270D

COMPOUND	CAS Number
4-bromophenyl phenyl ether	101-55-3
hexachlorobenzene	118-74-1
2,3,4,6-tetrachlorophenol	58-90-2
pentachlorophenol	87-86-5
phenanthrene	85-01-8
anthracene	120-12-7
carbazole	86-74-8
di-n-butyl phthalate	84-74-2
fluoranthene	206-44-0
benzidine	92-87-5
pyrene	129-00-0
butyl benzyl phthalate	85-68-7
benzo(a)anthracene	56-55-3
3,3'-dichlorobenzidine	91-94-1
chrysene	218-01-9
bis(2-ethylhexyl)phthalate	117-81-7
di-n-octyl phthalate	117-84-0
benzo(b)fluoranthene	205-99-2
benzo(k)fluoranthene	207-08-9
benzo(a)pyrene	50-32-8
indeno(1,2,3-CD)pyrene	193-39-5
dibenzo(a,h)anthracene	53-70-3
benzo(g,h,i)perylene	191-24-2
2-acetylaminofluorene	53-96-3
acetophenone	98-86-2
4-aminobiphenyl	92-67-1
aramite	140-57-8
atrazine	1912-24-9
benzaldehyde	100-52-7
1,1'-biphenyl	92-52-4
caprolactam	105-60-2
chlorobenzilate	510-15-6
1-chloronaphthalene	90-13-1
diallate	2303-16-4
dibenz(a,j)acridine	224-42-0
2,6-dichlorophenol	87-65-0
dimethoate	60-51-5
4-dimethylaminoazobenzene	60-11-7
N,N-dimethylaniline	121-69-7
7,12-dimethylbenz(a)anthracene	57-97-6
3,3'-dimethylbenzidine	119-93-7
A,A-dimethylphenethylamine	122-09-8
1,2-dinitrobenzene	528-29-0

TABLE 1

APPLICABLE COMPOUNDS FOR SEMIVOLATILE ANALYSIS BY SW8270D

COMPOUND	CAS Number
1,3-dinitrobenzene	99-65-0
1,4-dinitrobenzene	100-25-4
disulfoton	298-04-4
N-ethylaniline	103-69-5
ethyl methanesulfonate	62-50-0
ethyl parathion	56-38-2
famphur	52-85-7
hexachloropropene	1888-71-7
isodrin	465-73-6
isosafrole	120-58-1
kepone	143-50-0
N-methylaniline	100-61-8
tetramethylurea	632-22-4
4-nitroquinoline-n-oxide	56-57-5
N-nitrosodi-n-butylamine	924-16-3
N-nitrosodiethylamine	55-18-5
phorate	298-02-2
pronamide	23950-58-5
safrole	94-59-7
methapyrilene	91-80-5
3-methylcholanthrene	56-49-5
methyl methanesulfonate	66-27-3
1,4-naphthoquinone	130-15-4
1-naphthylamine	134-32-7
2-naphthylamine	91-59-8
N-nitrosomethylethylamine	10595-95-6
N-nitrosomorpholine	59-89-2
N-nitrosopiperidine	100-75-4
N-nitrosopyrrolidine	930-55-2
5-nitro-o-toluidine	99-55-8
pentachlorobenzene	608-93-5
pentachloroethane	76-01-7
pentachloronitrobenzene	82-68-8
phenacetin	62-44-2
2-picoline	109-06-8
1,2,4,5-tetrachlorobenzene	95-94-3
sulfotepp	3689-24-5
o,o,o-triethylphosphorothioate	126-68-1
1,3,5-trinitrobenzene	99-35-4
4-phenylenediamine	106-50-3
2-toluidine	95-53-4
thionazin	297-97-2
bis(2-ethylhexyl)adipate	103-23-1
1-methylnaphthalene	90-12-0

TABLE 1
APPLICABLE COMPOUNDS FOR SEMIVOLATILE ANALYSIS BY SW8270D

COMPOUND	CAS Number
2,3,5,6-tetrachlorophenol	935-95-5
methyl parathion	298-00-0
1,4-dioxane	123-91-1
ethyl methacrylate	97-63-2
diphenyl ether	101-84-8
hydroquinone	123-31-9
quinone	106-51-4
SURROGATES	
1,2-dichlorobenzene-d_4	2199-69-1
2,4,6-tribromophenol	118-79-6
2-chlorophenol-d_4	93951-73-6
2-fluorobiphenyl	321-60-8
2-fluorophenol	367-12-4
phenol-d_6 (d_5)	13127-88-3
terphenyl-d_{14}	1718-51-0
nitrobenzene-d_5	4165-60-0
hydroquinone-d_6 (surr); optional	
INTERNAL STANDARDS	
acenapthene-d_{10}	15067-26-2
1,4-dichlorobenzene-d_4	3855-82-1
chrysene-d_{12}	1719-03-5
naphthalene-d_8	1146-65-2
perylene-d_{12}	1520-96-3
phenanthrene-d_{10}	1517-22-2

2. SUMMARY

Prior to using this instrumental analytical method, the samples are extracted and appropriate concentration and cleanups are performed to prepare the extract for analysis. The semivolatile compounds are introduced into the GC/MS by injecting the extract into a gas chromatograph (GC), equipped with a narrow-bore, fused-silica capillary column. The GC oven housing the column, is temperature-programmed to facilitate analyte separation. As analytes elute from the column, they are introduced into the mass spectrometer (MS) detector via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major quantitation ion relative to an internal standard, using a calibration curve (at minimum, 5 points for quantitation by average response factor, or 6 points for use of a quadratic fit).

Method 8270D can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride, and capable of being eluted without

derivatization as sharp peaks from a fused-silica capillary GC column, coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons (PAHs), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, and aromatic nitro compounds and phenols, including nitrophenols.

The following compounds may require special treatment when being determined by this method:

- *Benzidine* can be subject to oxidative losses during solvent concentration. Also, chromatography is poor.
- *Hexachlorocyclopentadiene* is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- *N-nitrosodimethylamine*, *pyridine* and *1,4-dioxane* are difficult to separate from the solvent front under the chromatographic conditions described in the method.
- *N-nitrosodiphenylamine* decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
- *Pentachlorophenol*, *2,4-dinitrophenol*, *4-nitrophenol*, *4,6-dinitro-2-methylphenol*, *4-chloro-3-methylphenol*, *benzoic acid*, *2-nitroaniline*, *3-nitroaniline*, *4-chloroaniline*, and *benzyl alcohol* are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analyses according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Paragon Project Manager is responsible for directing a chlorine residual check to be performed just prior to analysis, as applicable.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon’s standard criteria. It is the responsibility of all personnel who work with samples or data

involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the review sheet indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to correct any errors found during the review.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples, and take corrective action to eliminate the problem.

4.2 Contamination by carryover can occur whenever high-concentration and low-concentration extracts are sequentially analyzed. To reduce carryover, the sample syringe must be thoroughly rinsed with solvent between sample introductions.

Whenever an unusually concentrated sample is encountered, a solvent blank may be injected to check for carryover contamination, thus ensuring that the autosampler, injector, and also column bleed, are not contributing carryover contamination.

4.3 Phthalate esters are used in the production of plasticizers and are ubiquitous in many commercial products used in laboratories. In particular, bis(2-ethylhexyl) phthalate is the only one of this class of compounds that is typically present in all extracts analyzed using this procedure.

5. APPARATUS AND MATERIALS

5.1 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM
Hewlett Packard (HP) Model 6890 GC or equivalent (temperature-programmable oven, capable of splitless or split/splitless injection, constant differential flow controllers).

HP Model 5973 or equivalent MS detector (capable of scanning from 35 to 500amu every 1sec or less; using 70 volts, nominal, electron energy in the electron impact ionization mode; capable of producing a mass spectrum for decafluorotriphenylphosphine, DFTPP, which meets all of the tune criteria in Table 3 for a 0.5µL, 25ng, injection of tuning standard; and to ensure sufficient

precision of mass spectral data, the MS scan rate shall allow acquisition of at least five spectra, while a sample component elutes from the GC).

5.2 DATA ACQUISITION AND PROCESSING SYSTEM

A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.

The computer must have software that can search any GC/MS data file for ions of a specific mass, and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits.

The most recent version of the EPA/NIST Mass Spectral Library, or similar spectral search library, should also be available. This library is used to help to identify non-target compounds generally referred to as tentatively identified compounds (TICs). Paragon's Windows NT software uses a NIST 98K library.

5.3 COLUMNS*

Capillary Column - 30m x 0.25mm ID (or 0. 32mm ID), 0.5µm film thickness; J&W Scientific DB-5.625 or equivalent.

* equivalent columns/guard columns may also be used, providing that all method QC criteria can be met

5.4 GASES- use only ultra high purity (99.999%)

Helium: carrier gas

5.5 MEASURING DEVICES

- microsyringes, gas-tight, Precision Hamilton™ or equivalent, 1µL - 1.0mL sizes (used for spiking)
- Luer-lock syringes, Becton & Dickinson or equivalent, disposable, 5mL or 25mL (used for sample introduction)
- balance, 0.01g sensitivity (used for weighing solid sample aliquots)
- volumetric flasks, Class A, with ground glass stoppers, various sizes

5.6 CONSUMEABLE SUPPLIES

- Septa, 11mm, Restek #20365 or equivalent
- fluorocarbon O-ring, 6.5mm, Restek #20372 or equivalent
- ID splitless liner, 2mm, Restek #20796 or equivalent

- gold seal, Agilent #18740-20885 or equivalent
- bottles, glass, with Teflon™-lined screw caps or crimp tops

6. REAGENTS- Only pesticide residue grade or equivalent may be used.

6.1 methylene chloride, Burdick and Jackson #299-4 or equivalent

6.2 methanol, Burdick and Jackson #230-4 or equivalent

6.3 STANDARDS

6.3.1 All standards are maintained per PAR SOP 300, refer to this SOP for expiration information. Note that any standard or reagent must be replaced sooner that its expiration, if laboratory control samples indicate a problem, or deterioration is evident.

All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer.

Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

6.3.2 Care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards (typically in methylene chloride) be stored in a freezer (-10°C to -20°C) in amber vials with firmly sealed Teflon™-lined screw-caps. If permitted by the manufacturer, unopened stock standards may be stored at room temperature in flame-sealed ampules. Standards for this procedure are sonicated, and allowed to equilibrate to room temperature before opening.

6.3.3 Two independent sources of commercial target analyte stock standards are required. The stock standards are purchased as certified solutions from suitable suppliers. Typically, concentrations of stock solutions vary from 1,000-5000µg/mL.

First source materials are used to create calibration and continuing calibration verification (CCV) standards. Second source materials are used to create the initial calibration verification (ICV) solution. Laboratory control and matrix spike standards, consisting of compounds that will be representative of the compounds being investigated, may be from either source (a third source is often used for spiking).

6.3.4 Non-target analyte internal standard (IS) and surrogate (SS) stock standards are also purchased. The IS is used to quantitate analytes detected in samples. The SS is used to monitor system performance and method effectiveness for each sample matrix.

The internal standards (ISs) used for this method are: 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} (see also Table 6). These internal standards are purchased in a mix with all compounds at a concentration of 2,000µg/mL and diluted to an intermediate concentration of 1,000µg/mL. Alternative internal standard stock concentrations may be used.

An appropriate aliquot of IS solution is added to an aliquot of calibration standard or extract prior to analysis so that the resulting concentration is 40ng/µL of each internal standard. In the case of sample extracts that require dilution, the extract is first diluted and then IS is added.

If selected ion monitoring (SIM) is being used to reach lower reporting limits, a less concentrated IS solution is recommended. As a general rule, use an IS concentration that will produce a response factor of approximately 1. For most SIM applications, an IS concentration of 4ng/µL will be sufficient.

The surrogate standards currently utilized are: phenol-d_5, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{l4}, 2-chlorophenol-d_4, and 1,2-dichlorobenzene-d_4. A surrogate intermediate standard is prepared in methanol at a concentration of 50µg/mL for base/neutral compounds and 75µg/mL for acid compounds. Other compounds may be used as surrogates if required by the client. During preparation, 1.0mL of this standard is typically spiked into all client and QC samples

6.3.5 Intermediate standards are created by diluting the stock standards. All dilutions should be performed using syringes, and pesticide grade solvent. The intermediate standard may contain the compounds of interest singly or mixed together. After opening/initial use, transfer the remaining stock standard to a suitable vial, such as an amber vial with a Teflon™-lined screw-cap; store with minimal headspace in a freezer (-10 to -20°C). Dilute target analyte stock standards with dichloromethane. Dilute QC standards with methanol. Intermediate standards should be checked frequently for signs of degradation,

especially just prior to preparing working calibration standards from them.

6.3.6 For tuning purposes, a methylene chloride solution containing 50ng/µL of decafluorotriphenylphosphine (DFTPP) should be purchased or prepared. The standard should also contain 50ng/µL each of 4,4'-DDT, pentachlorophenol and benzidine to verify injection port inertness and GC column performance. Also, it is possible to check the degradation of these compounds in the ICV or CCV as long as co-elution with other compounds is not present.

6.3.7 Target analyte intermediate standards are further diluted in dichloromethane to create calibration (working) standards. Prepare, at minimum, five concentrations, a minimum of six concentrations is required if higher order fits (e.g., quadratic) are to be used. One of the calibration standards should be created at a level that yields concentrations less than or equal to the reporting limit (RL). The remaining concentrations should correspond to the expected range of concentrations found in real samples, but should not exceed the working range of the GC/MS system. The laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standards.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 All samples must be kept chilled (4±2°C).

7.3 Aqueous samples must be collected in one-liter amber glass bottles with Teflon™-lined caps. Soil samples must be collected in glass containers with Teflon™-lined caps.

7.4 Samples are not chemically preserved, however, sodium thiosulfate may be used to dechlorinate liquid samples that contain residual chlorine. When applicable, the Project Manager will designate the need for residual chlorine check.

7.5 Aqueous samples must be extracted within 7 days of collection, soil samples must be extracted within 14 days of collection. Extracts must be analyzed within 40 days of extraction.

8. PROCEDURE

8.1 Several techniques are available for sample preparation (i.e., extraction and concentration):

MATRIX	SW-846 METHODS
Water	3520, 3510
Soil/Sediment	3540, 3550
Waste	3540, 3580

All surrogates, and matrix spikes (as applicable) must be added to samples prior to performing the extraction step. Internal standards must be added to the resultant extracts prior to performing the GC/MS instrumental analysis.

Extracts may be cleaned up using Gel Permeation Chromatography (GPC) by Method SW3640. See SOP 641 for GPC procedures. On a limited basis, contingent upon the list of compounds to be analyzed, silica gel cleanup may be performed for semivolatile compounds. See SOP 604 for further details. All compound recoveries must be verified prior to using silica gel as a clean up technique.

8.2 DIRECT INJECTION

In very limited applications, direct injection of the non-aqueous liquid sample into the GC/MS system with a μL syringe may be appropriate. The detection limit is very high (approximately 10,000μg/L), therefore, it is only permitted where concentrations in excess of 10,000μg/L are expected.

8.3 MODES OF DATA ACQUISITION

Mass spectra may be collected in one of two ways: scan mode or selected ion monitoring (SIM) mode. Each mode of type of acquisition is discussed below:

8.3.1 SCAN MODE

A selected mass range is scanned repeatedly over the course of analysis. The typical mass range for Method 8270D is 35-500amu. A scan rate of ~1scan/sec or manufacturer's specifications should be consistent throughout the analysis.

8.3.2 SIM MODE

Specified masses are monitored at specified retention times over the course of analysis. The dwell time (length of time each ion response is measured) can also be adjusted from ion to ion. Instrument conditions, however, must be consistent for all standards, samples and quality control samples.

An example of a SIM method for polyaromatic hydrocarbons (PAHs) is listed below. In this example at the retention time of 2.80 minutes, each ion in the associated group of six ions is searched for 50msec. This monitoring will continue until 9.60 minutes when the next group

of fourteen ions is searched for 50msec each. These groups include only the primary and major secondary ions of the compounds of interest. Because the mass spectrometer is looking for fewer ions (less than 15 per scan in the example below vs 465 per scan during a standard scan mode), lower reporting limits can be achieved.

Retention Time (min)	Selected Ions	Dwell Time (msec)
2.80 (start scan time)	82, 108, 127, 128, 129, 136	50
9.60	115, 141, 142, 151, 152, 153, 154, 162, 164, 165, 166, 167, 171, 172	50
12.40	94, 122, 176, 178, 179, 188, 200, 201, 202, 203	50
15.00	125, 226, 228, 229, 236, 240, 252, 253, 260, 264	50
17.60	138, 139, 276, 277, 278, 279	50

If selected ion monitoring is being used, concentration ranges that are 10 to 100 times lower than standard scan mode may be achieved. However, a large amount of mass spectral confirmation and tentatively identified compound information is lost. Because much of the mass spectral confirmation data is not present in SIM mode, retention time confirmation becomes more important. It may be necessary to use tighter RT windows.

8.4 INSTRUMENT OPERATING CONDITIONS

Whether using scan or SIM mode, instrument operating condition may be the same. Typical instrument operation conditions are shown below:

Initial temperature:	60°C, hold for 3 minutes; 2.80 (start scan time)
Temperature program:	65-100°C at 20°C/min, hold for 1 minute; then
	100-335°C at 30°C/min
Final Temperature:	335°C, hold until benzo[g,h,i]perylene has eluted
Injector temperature:	240°C
Transfer line temperature:	280°C
Source Temperature:	According to manufacturer's specifications

Injector:	Grob-type, splitless
Injection volume:	0.5-2µL
Carrier Gas:	Helium at 40cm/sec

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

8.5 TUNING

8.5.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50ng injection of DFTPP. Analyses may not begin until all criteria are met. Acquisition of the mass spectrum of DFTPP must be performed as follows:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
- Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.
- The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. All subsequent standards, samples, MS/MSDs and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

8.5.2 DFTPP evaluation will always be done using scan mode so that the full mass range may be evaluated. Dwell times for ions during SIM mode will differ from those during the scan mode, but all other settings should be kept the same.

8.5.3 Benzidine and pentachlorophenol should be present at their normal responses. The tailing factor of benzidine must be less than 3.0 and of pentachlorophenol must be less than 5.0. The HP software performs the tailing factor calculation. Tailing factors are typically evaluated during the analysis of DFTPP, but may be evaluated using benzidine and pentachlorophenol from the calibration standards.

8.5.4 Degradation of DDT to DDE and DDD may not exceed 20%. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to

remove the first 6-12in. of the capillary column. The use of a guard column between the injection port and the analytical column may help prolong analytical column performance.

8.5.5 The internal standards selected should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 2). If interferences are noted, use the next most intense ion as the quantitation ion (i.e., for 1,4-dichlorobenzene-d4, use 152m/z for quantitation).

8.6 INITIAL CALIBRATION

8.6.1 Analyze a 0.5 to 2.0µL injection of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound. All standard and sample injections must use a consistent injection volume. The following Table is an example of the typical calibration levels associated with initial and continuing calibration standards:

Internal Standard (ng/µL on column)	**Final Concentration (ng/µL on column)**
40	120
40	100
40	80
40	60
40	40
40	20
40	10
40	5
40	1
40	50 ICV level

Each calibration standard should be carefully evaluated before inclusion in the calibration curve.

8.6.2 To confirm that a complete injection took place, the internal standard recovery results must be within the required acceptance range. The analyst must view the standard in the data analysis section of the software. The chromatography of the standard should be examined to ensure that peak shape and separation appear to be acceptable. Extra

care should be taken with the low and the high standards as these are useful to evaluate performance problems. Compounds that commonly have poor chromatographic characteristics should be checked in each standard. These compounds are:

pyridine	n-nitrosodimethylamine
aniline	phenol
bis(2-chloroethyl)ether	benzyl alcohol
bis(2-chloroisopropyl)ether	n-nitroso-di-n-propylamine
2,4-dimethylphenol	benzoic acid
2,4,5-trichlorophenol	4-nitroaniline
benzo(b) fluoranthene	benzo(k)fluoranthene

8.6.3 Isomeric compounds and compounds which exhibit similar spectra must be checked in the data analysis section of the software and on the quantitation report to ensure that the correct compound names have been assigned to each peak. The compounds that should be checked are:

aniline & bis(2-chloroethyl)ether
the dichlorobenzenes
benzyl alcohol, 2-methylphenol, 3-methylphenol & 4-methylphenol
2,4-dimethylphenol & benzoic acid
naphthalene & 4-chloroaniline
2,4,6- and 2,4,5-trichlorophenol
2-, 3- and 4-nitroaniline
2,6- and 2,4-dinitrotoluene
fluoranthene & pyrene
phenanthrene & anthracene
benzo(a)anthracene & chrysene
the phthalates
3,3'-dichlorobenzidine, benzo(b) and (k) fluoranthene, benzo(a)pyrene
indeno(1,2,3-c,d)pyrene & benzo(g,h,i)perylene

8.6.4 Calculate response factors (RFs) for each compound relative to one of the internal standards as follows:

$$RF=(A_xC_{IS})/(A_{IS}C_x)$$

where:

Ax = Area of the characteristic ion for the compound being measured
A_{IS} = Area of the characteristic ion for the specific internal standard
C_{IS} = Concentration of the specific internal standard (ng/µL)

C_x = Concentration of the compound being measured (ng/µL)

8.6.5 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitro-phenol, and 4-nitrophenol (see Table 4). The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

8.6.6 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

8.6.7 Calibration Check Compounds (CCCs) are used to evaluate the linearity of the curve and the integrity of the system. Variability for these compounds indicates a system leak and/or reactive sites on the column. The percent relative standard deviation (%RSD) should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 5) must be less than 30%.

$$\%RSD = \frac{SD}{\overline{RF}} x100$$

where:

RSD = relative standard deviation

$\overline{RF}$ = Mean of all initial RFs for a compound. (Minimum, 5-point curve).

SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N-1}}$$

where:

RFi = RF for each of the calibration levels (minimum, 5-point cal)

N = Number of RF values (i.e., 5)

If the %RSD of any CCC is 30% or greater, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Section 8.4.

8.6.8 The relative retention times (RRT) of each compound are evaluated as defined in Section 8.8.

8.7 LINEARITY

If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

If the %RSD of any compound is greater than 15%, a calibration curve of area ratio (A/A_{is}) versus concentration ratio (C/C_{is}), using first or second order regression fit of the five or more calibration points may be constructed. The type of curve fit applied should be chosen to best represent the data. The use of calibration curves is a recommended alternative to average response factor calibration and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system. The coefficient of determination (COD, r^2 value) of the linear or higher order regression used to define the calibration curve, is an expression of "goodness of fit", and must be $\geq$0.99. Quadratic regressions may be used with a minimum of 6 calibration points, and must yield a COD (r^2 value) of $\geq$0.99.

Consult SW-846 Method 8000 for specific requirements pertaining to each calibration technique. Quadratic or higher order calibrations are not to be employed solely to extend the calibration range for compounds that show saturated or nearly saturated response at higher concentrations.

8.8 INITIAL CALIBRATION VERIFICATION (ICV)

An ICV must be analyzed each time a new initial calibration is performed. The ICV consists of a standard at or near the mid-point concentration of the initial calibration. The standard is prepared from a source independent from that used for the initial calibration standards.

The measured concentration of analytes in the ICV must be within 25% of the expected value for each analyte. Up to four analytes may be accepted as sporadic marginal results with percent differences of up to 50%. The ICV should be analyzed at a concentration level different from that of the CCV to ensure that the curve is valid over much of the range of the initial calibration.

8.9 ROUTINE MAINTENANCE

8.9.1 Bake out column. Extra blanks may be necessary to achieve an adequate baseline if carryover is observed. Replace the injection port

liner, pre-column, cut contaminated section from column, or replace column as necessary to alleviate sample effects limiting performance of the front of the system.

Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Oxidized columns will exhibit baselines that rise rapidly during temperature programming. If a column is oxidized, replacement may be necessary.

8.9.2 INJECTION PORT MAINTENANCE

- Cool injection port to room temperature.
- Disconnect column and plug with old septa.
- Open top of injection port and remove liner for cleaning.
- Remove inlet seal and clean with Q-tip and $MeCl_2$.
- Rinse inlet with $MeCl_2$, scrub with micro grit, rinse again with $MeCl_2$ to remove all traces of micro grit.
- Install cleaned or new injection port seal.
- Install cleaned or new injection port liner.
- Replace septa and insert O-ring as needed.
- Seal injection port and turn injection temperature on.
- When injection temperature is reached tighten seal and turn carrier gas on for about 30 seconds. Clip about 2 or 3 inches of column and re-install.
- Turn oven to the maximum temperature of the run and bake for 5 to 10 minutes.

8.10 DAILY GC/MS CALIBRATION

8.10.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50ng injection of DFTPP must result in a mass spectrum for DFTPP that meets the criteria given in Table 3. Also, benzidine and pentachlorophenol should be present at their normal responses. The tailing factor of benzidine must be less than 3.0 and the tailing factor of pentachlorophenol must be less than 5.0. The degradation of 4,4'-DDT must be ≤20%. These criteria must be demonstrated during each 12-hour shift.

8.10.2 CONTINUING CALIBRATION VERIFICATION (CCV)
A calibration standard(s) at mid-concentration containing all semivolatile analytes, including all required surrogates, must be analyzed every 12 hours prior to sample analysis. Compare the instrument response factor from this calibration check with the SPCC, CCC and %D criteria discussed below.

8.10.3 System Performance Check Compounds (SPCCs): A system performance check must be made during every 12-hour shift. For each SPCC compound in the daily calibration, a minimum response factor of 0.050 must be obtained. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This criterion must be achieved before analysis begins.

8.10.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Table 5 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RFC}_I - RFC_c}{\overline{RFC}_I} x100$$

where:

$\overline{RFC}_I$ = The average response of check compound in the initial calibration.
RFC_c = RF for CCC in continuing calibration.

If a least squares regression is used, the CCC must be evaluated using a percent drift calculation. Calculate the percent drift using:

$$\%\text{Drift} = \frac{\text{CC - TC}}{\text{TC}} \times 100$$

where:

CC = Calculated concentration
TC = Theoretical concentration

If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% difference) for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after

corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

The measured concentration of analytes other than CCCs in the CCV must be checked and all should be within 20% of the expected value for each analyte. Up to four analytes (Paragon standard target list) may be accepted as sporadic marginal results with percent differences of up to 40%. See introductory comments of this SOP for a listing of typical problematic compounds. Examples of non-standard target list compounds that may be problematic include benzidine and 3,3'-dichlorobenzidine. CCV responses for non-standard target list compounds >20% may be narrated or controlled as directed in the applicable LIMS program specification.

The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from that in the midpoint standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

8.11 EXTRACT ANALYSIS

8.11.1 Prior to analysis, the sample extract must be brought to room temperature and spiked with internal standards. The entire extract may be spiked, or an aliquot of the extract may be removed and spiked with an appropriate aliquot of the internal standard mixture. The resulting concentration in the extract to be analyzed must be the same as the concentration of the internal standards in the calibration standards (usually 40µg/mL).

8.11.2 Inject an aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for calibration. The injection volume must be the same volume used for the calibration standards.

8.11.3 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must be performed. A new aliquot of the extract is diluted and IS is added to achieve a concentration of 40µg/mL of each IS. The analyst should take care to

ensure that extracts are analyzed at the greatest concentration possible while avoiding damage to the instrument.

8.11.4 Extracts may be diluted for matrix interferences to a point at which the baseline rise is equal to one half the height of the nearest internal standard, or non-target compound is the same height or greater of the nearest internal standard. Further, extracts may be diluted if, in the opinion of the analyst, the color or viscosity of the extract indicates that the matrix will interfere with the instrument's future performance.

8.11.5 Perform all qualitative and quantitative measurements as described in Section 8.12 below. Return the extracts to refrigerated storage.

8.12 DATA INTERPRETATION

8.12.1 COMPOUND IDENTIFICATION

The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method or be obtained from the NIST mass spectral library. Because close co-elution of compounds commonly masks standard spectra and cannot be corrected with background subtraction, the use of NIST mass spectral library spectra, when available, is preferred. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met:

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion. Analyst judgment is critical in interpreting spectral data and target compound assignment by the software.
- The RT of the sample component is within ±0.06 RT units of the most recent standard component. If a retention time shift is suspected due to the sample matrix, the relative retention (RRT) time should be evaluated vs. the relative retention time of the most recent standard.

RRT = compound RT / internal standard RT

- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds.
- When analytes co-elute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of **tentative identification**. The necessity to perform this type of **tentatively identified compound (TIC) determination** will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

8.12.2 QUANTITATIVE ANALYSIS

When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion.

If the %RSD of a compound's average response factor is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data and the following equation:

$$C_{ex}(mg/L) = \frac{(A_x x C_{IS})}{(A_{IS} x \overline{RF})}$$

where:

Cex = The concentration of the compound in the extract
A_x = Area of the characteristic ion for the compound being measured
A_{IS} = Area of the characteristic ion for the specific internal standard
C_{IS} = Concentration of the specific internal standard (ng/μL)

Alternatively, the regression line fitted to the initial calibration may be used for determination of the extract concentration. See Method 8000, Section 7.0 for the equations describing internal standard calibration and either linear or non-linear calibrations.

Compute the concentration of the analyte in the sample using the equations below:

8.12.2.1 The concentration of the analyte in the liquid phase of the sample, is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid}\,(\mu g / L) = \frac{(C_{ex} x V_{ex})}{V_o}$$

where:

Vex = extract volume, in mL

Vo = volume of liquid extracted, in L

8.12.2.2 The concentration of the analyte in the solid phase of the sample, is calculated using the concentration of the analyte in the extract and the weight of the solids, as follows:

$$\text{Concentration in solid}\,(\mu g / kg) = \frac{(C_{ex} x V_{ex})}{W_s}$$

where:

Vex = extract volume, in mL

Ws = sample weight, in kg (typically reported on a dry weight basis)

8.12.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formula given above should be used with the following modifications: The areas Ax and Ais should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

For this method, an analysis batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of matrix spike samples.

All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch.

Consult LIMS program specification for additional or alternative requirements. See QC Table for additional details.

9.2 BLANK ANALYSIS

Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of 20 or fewer field samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. An MB must be analyzed for each 12-hour BFB tune.

Target compounds may not be detected above one-half the reporting limit (RL), or as otherwise directed in the applicable LIMS program specification. Common laboratory contaminants, such as bis(2-ethylhexyl) phthalate, are allowed at levels as high as the RL. Occurrence of common laboratory contaminants should be considered a warning and must be reported in the data package case narrative. See QC Table for further information.

9.3 SURROGATES

Surrogate recovery is monitored to assess method performance of the particular matrix. Surrogates are added to all standards, blanks, samples and QC samples prior to analysis. Recoveries should be compared to laboratory-established surrogate control limits or to client specified limits as listed in the LIMS program specification. See QC Table for corrective actions.

NOTE: Because of the number of surrogates used by this method, the laboratory will allow for samples to have one acid and one base/neutral surrogate outside limits if the remaining surrogates suggest the problem is matrix related and that there were no problems with the laboratory's performance during the extraction and analysis.

9.4 INTERNAL STANDARDS

Internal standards are added to all standards, field and quality control samples analyzed. Retention times and responses are evaluated for internal standards. See QC Table for acceptance limits and corrective actions.

9.5 LABORATORY CONTROL SAMPLES

A matrix-specific laboratory control sample (LCS) is analyzed per batch of 20 field samples. It is Paragon's practice to also analyze a laboratory control sample duplicate (LCSD) per batch of 20 field samples. LCS (LCSD) samples are

analyzed to evaluate the efficiency of the method performed. See QC Table for acceptance limits and corrective actions.

9.6 MATRIX SPIKE(S)
A matrix spike (MS) and matrix spike duplicate (MSD) sample are analyzed to evaluate the effect of the matrix. Additional sample volume of client samples is needed to perform these analyses. The frequency of the MS/MSD shall be one pair per batch of 20 field samples, assuming adequate volume has been provided. See QC Table for acceptance limits and corrective actions.

9.7 METHOD DETECTION LIMIT (MDL) STUDY
The MDL study shall consist of the analysis of a minimum of seven replicate analyses for a target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at a minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

10.1 This SOP meets the requirements of SW8270D. SW8270D does not require that CCC or SPCC compounds (as defined in SW8270C), be monitored. Paragon, however, continues to monitor these compounds routinely.

10.2 Compounds may utilize primary ions other than those listed in Table 2 of this SOP and Table 1 of the Method, if co-elution problems exist. Because the elution pattern will differ from instrument to instrument, changes may be instrument specific.

10.3 EPA METHOD 625
The items contained in this Section describe differences between Method 8270D and Method 625.

10.3.1 Method 625 prescribes different surrogates than Method 8270D. It may be permissible to use the same surrogates specified in Method 8270D, but only with approval from the QA Manager and the Project Manager. See Table 8 of Method 625 for a complete list of surrogates.

10.3.2 Surrogate concentration in Method 625 is 100ug/L. Paragon typically spikes samples to have a final concentration of 75ug/L for acid surrogate compounds and 50ug/L for base/neutral surrogate compounds.

10.3.3 Method 625 lists specific chromatographic columns and conditions (i.e., use of a packed column, and scan parameters tailored to the use of a packed column) to be used in the execution of the method. Some of these materials, apparatus, and conditions have been eclipsed by technology as described in this SOP. Section 8.1.2 of Method 625

states that technological advances are recognized and allows for use provided the precision and accuracy requirements put forth by the method can be achieved.

10.3.4 Initial Calibration - Although Method 625 permits as few as three points in the initial curve, Paragon will quantify from a 5-point curve (minimum) to meet compliance requirements for 8270D. This approach is compliant with Method 625.

10.3.5 Method 625 states that if the linearity of a compound is less than 35%RSD, an average response factor may be used. Otherwise, construct a linear curve with a correlation coefficient greater than 0.995.

10.3.6 Method 625 specifies that the DFTPP tune period is 24 hours. Method 8270D specifies DFTPP be passed every 12 hours.

10.3.7 Method 625 specifies that a continuing calibration verification (CCV) must be performed every working day (every 24 hours) rather than every 12 hours. The response for any parameter must not vary from the predicted response by more than 20%.

10.3.8 Method 625 specifies that a matrix spike and laboratory control spike must be performed on every 20 samples. The sample only needs to be spiked once; a matrix spike duplicate is not required. Also, all matrix spikes and blank spikes must contain every analyte of interest and be from a standard source independent of the calibration standard.

10.3.9 Method 625 states that a set of 4 QC Check samples must be analyzed by an analyst before any samples are processed to demonstrate the ability to perform the method. The concentrations of each compound must be 100µg/L. The results must fall within the acceptance criteria specified in Table 6 of EPA Method 625.

10.3.10 Method 625 states that the matrix spikes and blank spikes must meet the acceptance criteria listed in Table 6 from Method 625. Note that not all compounds have acceptance limits in this Table. For these compounds, the recovery must be reported; however, corrective actions based on those results are not required. Paragon will follow QC limits prescribed by our clients if requested.

11. REFERENCES

11.1 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 625," October 26, 1984.

11.2 US EPA SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, "Method 8270D", Revision 4, January 1998.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

12.1.2 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

12.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.5 All flammable compounds must be kept away from ignition sources.

12.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

12.1.7 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

12.1.8 Food and drink are prohibited in all lab areas

12.2 WASTE DISPOSAL

Refer to Paragon Analytics SOPs 003 and 015 for proper methods of waste disposal. The waste streams associated with this procedure are halogenated organic solvents, non-halogenated organic solvents, discarded extract vials and contact waste.

DOCUMENT REVISION HISTORY

4/10/06: References to LIMS Program Specifications added. Content updated to reflect SW8270D criteria (updated from 8270C). SIM discussion augmented. DOCUMENT REVISION HISTORY added.

3/1/07: Primarily minor format changes and clarifications. Section 9 QUALITY CONTROL and QC Table revamped for consistency with similar SOPs. CCC and SPCC comment was added to DEVIATIONS Section.

TABLE 2
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Suggested)

COMPOUND	PRIMARY ION	SECONDARY ION
pyridine	79	52
N-nitrosodimethylamine	74	42
aniline	93	66, 65
phenol	94	65, 66
bis(2-chloroethyl)ether	93	63, 95
2-chlorophenol	128	64, 130
1,3-dichlorobenzene	146	148, 111
1,4-dichlorobenzene	146	148, 111
1,2-dichlorobenzene	146	148, 111
benzyl alcohol	108	79, 77
bis(2-chloroisopropyl)ether	45	77, 121
2-methylphenol	107	108, 77, 79
N-nitroso-di-n-propylamine	70	42, 101, 130
3-methylphenol	108	107, 77, 79
4-methylphenol	108	107, 77, 79
hexachloroethane	117	201, 199
nitrobenzene	123	77, 51
isophorone	82	95, 138
2-nitrophenol	139	109, 65
2,4-dimethylphenol	107	122, 121
bis(2-choloroethoxy)methane	93	95, 123
2,4-dichlorophenol	162	164, 98
benzoic acid	105	122, 77
1,2,4-trichlorobenzene	180	182, 145
naphthalene	128	129, 127
4-chloroaniline	127	129, 65, 92
hexachlorobutadiene	225	223, 227
4-chloro-3-methylphenol	107	144, 142
2-methylnaphthalene	142	141, 115
hexachlorocyclopentadiene	237	235, 272
2,4,6-trichlorophenol	196	198, 97, 132
2,4,5-trichlorophenol	196	198, 97, 132
2-chloronaphthalene	162	127, 164
2-nitroaniline	65	92, 138
dimethyl phthalate	163	194, 164
2,6-dinitrotoluene	165	63, 89
acenaphthylene	152	151, 153, 76
3-nitroaniline	138	108, 92
acenaphthene	154	153, 152
2,4-dinitrophenol	184	63, 154
4-nitrophenol	109	139, 65
dibenzofuran	168	139
2,4-dinitrotoluene	165	63.89
2,3,4,6-tetrachlorophenol	232	230, 131, 61
diethyl phthalate	149	177, 150
fluorene	166	165, 167
4-chlorophenyl phenyl ether	204	206, 141

TABLE 2
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Suggested)

COMPOUND	PRIMARY ION	SECONDARY ION
4-nitroaniline	138	65, 108, 92
azobenzene	77	51, 182, 105
4,6-dinitro-2-methylphenol	198	51, 105
N-nitrosodiphenylamine	169	168, 167
4-bromophenyl phenyl ether	248	250, 141
hexachlorobenzene	284	142, 249
pentachlorophenol	266	264, 268
phenanthrene	178	179, 176
anthracene	178	176, 179
carbazole	167	139, 140
di-n-butyl phthalate	149	150, 104
fluoranthene	202	101, 203, 100
benzidine	184	92, 185
pyrene	202	200, 203, 101
butyl benzyl phthalate	149	91, 206
benzo(a)anthracene	228	229, 226
3,3'-dichlorobenzidine	252	254, 126
chrysene	228	226, 229
bis(2-ethylhexyl)phthalate	149	167, 279
di-n-octyl phthalate	149	167, 43
benzo(b)fluoranthene	252	253, 125
benzo(k)fluoranthene	252	253, 125
benzo(a)pyrene	252	253, 125
indeno(1,2,3-CD)pyrene	276	138, 277
dibenzo(a,h)anthracene	278	139, 279
benzo(g,h,i)perylene	276	138, 277
benzaldehyde	77	105, 106, 51
acetophenone	105	77, 120, 51
caprolactam	113	55, 85, 56
1,1'-biphenyl	154	153, 76
atrazine	215	200, 202
N,N-dimethylaniline	120	121, 77, 51
N-ethylaniline	106	121, 77
N-methylaniline	106	107, 77
tetramethylurea	72	44, 116
2-acetylaminofluorene	181	180, 223, 152
4-aminobiphenyl	169	115, 141
aramite	191	185, 319, 334
chlorobenzilate	251	253, 139, 111
disulfoton	88	89, 97, 274
diallate	234	236, 86
2,6-dichlorophenol	162	164, 63, 126
dimethoate	87	93, 125
4-dimethylaminoazobenzene	225	120, 77, 42
famphur	218	93, 125
4-nitroquinoline-n-oxide	160	89, 75, 190
N-nitrosodi-n-butylamine	116	158, 57, 99
N-nitrosodiethylamine	102	44, 42, 56
7,12-dimethylbenz(a)anthracene	256	241, 239

TABLE 2
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Suggested)

COMPOUND	PRIMARY ION	SECONDARY ION
3,3'-dimethylbenzidine	212	213, 211
ά,ά-dimethylphenethylamine	58	91, 134, 65
1,3-dinitrobenzene	168	76, 75, 122
ethyl methanesulfonate	79	109, 97
phorate	260	231, 97
pronamide	173	175, 145
safrole	162	104, 131, 77
isosafrole	104	162, 131, 77
methapyrilene	97	58, 261
3-methylcholanthrene	268	252, 253, 126
methyl methanesulfonate	80	65, 95
1,4-naphthoquinone	158	104, 130, 76
1-naphthylamine	143	115
2-naphthylamine	143	115
N-nitrosomethylethylamine	88	42, 56
N-nitrosomorpholine	56	116, 86
N-nitrosopiperidine	114	42, 55
N-nitrosopyrrolidine	100	41, 42
5-nitro-o-toluidine	152	106, 77, 79
pentachlorobenzene	250	248, 252, 215
pentachloroethane	117	119, 167, 165
pentachloronitrobenzene	237	295, 214
phenacetin	108	109, 179, 137
2-picoline	93	66, 39
1,2,4,5-tetrachlorobenzene	216	214, 218, 108
sulfotepp	322	202, 266, 238
o,o,o-triethylphosphorothioate	198	121, 93, 65
1,3,5-trinitrobenzene	213	120, 167
hexachloropropene	213	211, 117, 141
4-phenylenediamine	108	80, 107
2-toluidine	107	106, 77
thionazin	107	96, 248
bis(2-ethylhexyl)adipate	129	57, 71, 70
1,2-dinitrobenzene	168	50, 63, 76
1,4-dinitrobenzene	168	50, 75, 76
1-methylnaphthalene	142	141, 115
2,3,5,6-tetrachlorophenol	232	230, 131, 166
1-chloronaphthalene	162	164, 127
isodrin	193	195, 263, 66
kepone	272	274, 237
methyl parathion	263	125, 109
ethyl parathion	291	109, 97, 139
dibenz(a,j)acridine	279	280, 277
ADDITIONAL COMPOUNDS		
1,4-dioxane	88	58, 43
ethyl methacrylate	69	41, 86, 114
diphenyl ether	170	51, 77, 141
hydroquinone	110	81, 55

TABLE 2
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Suggested)

COMPOUND	PRIMARY ION	SECONDARY ION
hydroquinone-d_6 (surr)	114	
quinone	108	54, 82
SURROGATES		
1,2-dichlorobenzene-d_4	152	150, 115
2,4,6-tribromophenol	330	332, 141
2-chlorophenol-d_4	132	68, 134
2-fluorobiphenyl	172	171
2-fluorophenol	112	64
phenol-d_6 (d_5)	99	42, 71
terphenyl-d_{14}	244	122, 212
nitrobenzene-d_5	82	128, 54
INTERNAL STANDARDS		
acenapthene-d_{10}	164	162, 160
1,4-dichlorobenzene-d_4	152	
chrysene-d_{12}	240	120, 236
naphthalene-d_8	136	68, 108
perylene-d_{12}	264	260, 265
phenanthrene-d_{10}	188	94, 80

TABLE 3

DFTPP KEY ION ABUNDANCE CRITERIA

MASS	ION ABUNDANCE CRITERIA
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	40-110% of mass 198
443	17-23% of mass 442

TABLE 4

SYSTEM PERFORMANCE CHECK COMPOUNDS (SPCCs)

N-nitroso-di-n-propylamine
hexachlorocyclopentadiene
2,4-dinitrophenol
4-nitrophenol

TABLE 5

CALIBRATION CHECK COMPOUNDS (CCCs)

BASE/NEUTRAL FRACTION	ACID FRACTION
acenapthene	4-chloro-3-methyl phenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlobutadiene	2-nitrophenol
diphenylamine	phenol
di-n-octylphthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo(a)pyrene	

TABLE 6

TYPICAL SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-dichlorobenzene-d_8	naphthalene-d_8	acenapthene-d_{10}
aniline	benzoic acid	acenapthene
benzyl alcohol	bis(2-chloroethoxy)methane	acenapthylene
bis(2-chloroethyl) ether	4-chloroaniline	1-chloronapthalene
bis(2-chloroisopropyl) ether	4-chloro-3-methylphenol	2-chloronapthalene
2-chlorophenol	2,4-dichlorophenol	4-chlorophenyl phenyl ether
1,3-dichlorobenzene	2,4-dimethylphenol	dibenzofuran
1,4-dichlorobenzene	hexachlorobutadiene	diethyl phthalate
1,2-dichlorobenzene	isophorone	2,4-dinitrophenol
2-fluorophenol (surr)	2-methylnapthalene	2,4-dinitrotoluene
hexachloroethane	naphthalene	2,6-dinitrotoluene
2-methylphenol	nitrobenzene	fluorene
4-methylphenol	nitrobenzene-d_8 (surr)	2-fluorobiphenyl (surr)
N-nitrosodimethylamine	2-nitrophenol	hexachlorocyclopentadiene
N-nitrosodi-n-propylamine	1,2,4-trichlorobenzene	2-nitroaniline
phenol		3-nitroaniline
phenol-d_6 (surr)		4-nitroaniline
		4-nitrophenol
phenanthrene-d_{10}	chrysene-d_{12}	2,4,6-tribromophenol (surr)
anthracene	benzidine	2,4,6-trichlorophenol
4-bromophenyl phenyl ether	benzo(a)anthracene	2,4,5-trichlorophenol
di-n-butyl phthalate	bis(2-ethylhexyl)phthalate	
4,6-dinitro-2-methyl-phenol	butyl benzyl phthalate	perylene-d_{12}
diphenylamine	chrysene	benzo(b)fluoranthene
fluoranthene	3-3'-dichlorobenzidine	benzo(k)fluoranthene
hexachlorobenzene	pyrene	benzo(g,h,i)perylene
N-nitrosodiphenylamine	terphenyl-d_{14} (surr)	benzo(a)pyrene
pentachlorophenol	di-n-octyl phthalate	dibenz(a,h)anthracene
phenanthrene		indeno(1,2,3-cd)pyrene

Analytical Method: SW8270D; EPA 625	**Parameter:** Semivolatile Organic Compounds by GC/MS		**Summary of Internal Quality Control (QC) Procedures and Corrective Action**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Tuning Criteria	Every 12 hour period	DFTPP ion ratio criteria (Table 2) PCP Tailing <5 Benzidine Tailing <3 DDT degradation ≤20%	Retune. Do not proceed with analysis until tune meets criteria. Perform injection port and column maintenance. Do not proceed until tune meets criteria
Initial Calibration (ICAL)	Following major instrument maintenance; when CCCs and/or SPCCs in the daily calibration do not meet criteria	CCC: ≤30% RSD non-CCC: ≤15% RSD SPCC: ≥0.05 RF Linear regression, $r^2 \geq 0.990$ Quadratic fit, COD ≥ 0.990	For CCC and SPCC, evaluate/correct instrument malfunction as needed; reanalyze ICAL to obtain curve that meets criteria.
Initial Calibration Verification (ICV); independent source from ICAL	Following every ICAL	Measured concentrations of all compounds should be within ±25% of expected concentrations; up to 4 results may be accepted for individual analytes with values ≤50% D	Evaluate/correct instrument malfunction as needed, prepare new standard if suspect. Reanalyze ICV. If still out, perform new ICAL
Continuing Calibration Verification (CCV); at or near mid-point	Every 12-hour period following tune, if ICAL not performed	CCC: <20 %D SPCC: >0.05 RF Measured concentrations of non-CCCs should be within ±20% of expected concentrations; up to 4 results may be accepted for individual analytes with values ≤40% D	Re-analyze the daily standard. If failure repeats, evaluate/correct instrument malfunction; perform a new ICAL NOTE: Recoveries that are high and outside of the stated acceptance criteria may be acceptable in some programs if the analyte that is high was not detected in the associated samples.
Instrument Blank	Every 12-hour period After each calibration An extraction method blank may be used. The extraction method blank should be analyzed with the associated samples.	< ½ RL for all target compounds, or as otherwise specified in applicable LIMS program specification.	Reanalyze to determine if instrument contamination was the cause. If the instrument blank is still non-compliant, correct the problem before analysis of samples.
Extraction Method Blank	One per extraction batch of ≤20samples of similar matrix.	< ½ RL for all target compounds, or as otherwise specified in applicable LIMS program specification.	Re-analyze to determine if instrument contamination was the cause. If MB is still non-compliant, correct the problem and obtain a successful MB analysis before resuming analysis of samples. Samples associated with the failed MB may need to be reanalyzed. NOTE: If problem is isolated to the method blank (associated samples meet all IS and SS criteria and no target compounds are detected above limits), report and complete a non-conformance report (SOP 928).
Surrogate Spikes (SS)	Every standard, client and QC sample	See laboratory or client-specified limits; recoveries should be	If non-compliant, check calculations and spike preparation for documentable errors.

Analytical Method: SW8270D; EPA 625	**Parameter:** Semivolatile Organic Compounds by GC/MS		**Summary of Internal Quality Control (QC) Procedures and Corrective Action**
QC Check	Frequency	Acceptance Criteria	Corrective Action
		within acceptance limits. Surrogates will be considered diluted out, if the dilution of the extract is ≥ 10X.	Reanalyze sample once (re-analysis requirements may be fulfilled by existing multiple extractions, e.g., MS, MSD, REP). If still out, report results and note in narrative. Note: Because of the number of surrogates used by this method, the laboratory will allow for samples to have one acid and one base/neutral surrogate outside limits if the remaining surrogates suggest the problem is matrix related and that there were no problems with laboratory performance during the extraction and analysis. At the client's discretion, the sample may be Submitted for re-extraction.
Internal Standard (IS)	Every standard, client and QC sample	EICP area within -50% to +100% of previous daily calibration check standard.	Inspect instrument for malfunction; correct identified malfunctions, then reanalyze samples. If no instrument malfunction is identified, reanalyze. If analysis of sample extract is still out, report results and note in narrative. Re-analysis requirements may be fulfilled by existing multiple analyses (e.g., MS, MSD, REP, sample dilutions)
Matrix Spike & Matrix Spike Duplicate (MS/MSD)	One per extraction batch of ≤20samples of similar matrix.	See laboratory or client-specified limits; recoveries should be within advisory limits. RPDs for the spiked compounds should also be within advisory limits	If non-compliant, check calculations and spike preparation for errors; correct as needed. If no errors are found, and the associated LCS is within control limits, then sample matrix effects are the most likely cause. Narrate. If significant differences (>15%) exist between the MS and MSD (or between duplicates) reanalysis of the sample and spikes may be necessary.
Laboratory Control Spike & Laboratory Control Spike Duplicates (LCS/LCSD)	One per extraction batch of ≤20samples of similar matrix; typically the LCSD is analyzed only when matrix spikes are not performed	See laboratory or client-specified limits; recoveries must be within acceptance limits. When the full list of compounds is spiked, the laboratory will accept a small number of sporadic marginal exceedances, based on the probability that a certain number of compounds will exceed their control limits. Systematic or	If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze LCS to determine if instrumental conditions or extraction preparation was the cause. Notify the Supervisor and initiate corrective action (NCR). Re-analyze associated samples, if appropriate. Note: recoveries that are high and outside of acceptance criteria may be acceptable, when the same target

Analytical Method: SW8270D; EPA 625	**Parameter:** Semivolatile Organic Compounds by GC/MS		**Summary of Internal Quality Control (QC) Procedures and Corrective Action**
QC Check	Frequency	Acceptance Criteria	Corrective Action
		gross failures shall not be accepted.	compound is not detected in any sample in the batch. Narrate.
Retention Time Shift (RT)	Every sample, standard, and blank	RT shift <30 seconds compared to daily standard Relative retention time (RRT) of sample must be ± 0.06 RRT units of daily calibration check.	Inspect chromatographic system for malfunction; correct identified malfunctions, then reanalyze sample.
Method Detection Limit (MDL) Study	At minimum, annually	Value must be < RL.	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria Consult with Quality Assurance Manager; RL may be adjusted if needed.

Must Discard 30 Days from _____ (date printed)

Amended (see red text below) to further highlight other client criteria.
12/27/07 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 511 REVISION 8

TITLE: **VOLATILES REAGENT WATER PREPARATION AND BLANK ANALYSIS**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1-8-07
QUALITY ASSURANCE MANAGER _____ DATE 1/8/07
LABORATORY MANAGER _____ DATE 1-8-07

HISTORY: Rev0, 4/5/93; Rev1, PCN #96, 12/20/93; Reviewed, no revisions, 1/13/95; Rev2, 1/13/99; Rev3, 7/9/99; Rev4, 3/26/02; Rev5, 3/14/03; Rev6, 2/13/04 & 3/10/05 (updated format); Rev7, 7/24/06; Rev8, 1/5/07.

1. SCOPE AND APPLICATION

Volatiles reagent water is prepared water that is made in the GC/MS-VOAs Lab. This reagent water is then used to make working calibration standards, dilute samples, etc. It is also used to make blanks (e.g., refrigerator, trip, method reagent) that are used in volatiles analyses. The water must be purged and heated so that no contaminants or interferences are present that could compromise the quality of volatiles sample results. This type of care must be taken for volatiles analyses so that the level of common laboratory contaminants (e.g., methylene chloride, acetone, 2-butanone) is minimized. Typical analytical methods (SW8260, SW8021) allow these common laboratory contaminants to be present at levels as high as five or ten times the analyte reporting limit (RL), contingent upon the specific contaminant, while any other target compound detected, must be at a concentration less than the analyte RL.

Note that other acceptance criteria, such as <RL common contaminants, <½ RL all other targets (DOD LIMS program specification), may apply.

2. SUMMARY

A volume of water to be prepared is collected in a glass container, purged with nitrogen gas, and heated while purging continues. The purging also continues while the processed water is allowed to cool. The prepared water is then stored in the preparation container, tightly sealed, until aliquotted for use.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to carryout these procedures as discussed in this SOP and to complete all documentation required for review.

3.2 Any personnel who note anomalies or out-of-control events associated with these procedures, or the analysis of the resultant blanks, must document the problem and take corrective action.

4. APPARATUS AND MATERIALS

4.1 hot plate

4.2 glass container, 4L or similar size, an Erlenmeyer flask is typically used

4.3 Millipore, or equivalent, benchtop water purification system. Capable of producing ultra-high purity (i.e., ASTM Type I or better) water.

5. REAGENTS

5.1 ASTM Type I Water. Although the water obtained from Paragon's laboratory deionized (DI) water system meets ASTM Type I criteria, further finished water obtained by running laboratory DI water through the benchtop Millipore purification system, is used as the source water for preparing volatiles reagent water.

5.2 Nitrogen gas, ultra pure

6. PROCEDURE

6.1 REAGENT WATER PREPARATION

6.1.1 A volume of Millipore water to be prepared is collected. Typically a 4L Erlenmeyer flask is used.

6.1.2 The container is placed on a hot plate, and the contents are purged at a moderate rate with nitrogen gas.

6.1.3 While purging continues, the container is then heated until the water boils, after which the heat is turned off.

6.1.4 The purging continues, as the prepared water cools, for at least 4-6 hours.

6.1.5 The prepared water is stored, tightly sealed, in the preparation container, until aliquotted for use.

6.2 BLANK ANALYSES

6.2.1 Refer to SOP 512 for the analysis and evaluation of refrigerator blanks. Refer to the appropriate determinative SOP (e.g., SOP 424, 525) for the analysis and evaluation of trip or method reagent blanks.

6.2.2 Per the above SOPs, the blank analysis data are documented in the instrument daily raw data files.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

Personal protective equipment (PPE) shall consist of safety glasses, a lab coat, and gloves, and must be worn at all times.

7.2 WASTE DISPOSAL

Unused prepared water may be discarded down the laboratory's drain.

8. REFERENCES

8.1 Standard Operating Procedure (SOP) 425, current iteration, "Determination of Aromatic Volatile Organics by Gas Chromatography - Methods SW8021B and EPA 602", Paragon Analytics.

8.2 Standard Operating Procedure (SOP) 525, current iteration, "Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry -- Methods SW8260B and EPA 624", Paragon Analytics.

DOCUMENT REVISION HISTORY

7/24/06: Added DOCUMENT REVISION HISTORY section; incorporated Form.

1/5/07: Changed Title. Standardized format (Sections 1, 2, 4, 5), added Millipore unit to Section 4. Updated format, Section 6; updated use of Millipore water as source water and method of data retention. Updated Waste Disposal, Section 7.2. Removed references to SOP 526 (EPA 524.2) as this SOP has been retired. Removed Form (relevant to SOP 512 only).

Must Discard 30 Days from _____ (date printed)

Amended (see red text Section 6) to further highlight other client criteria that may apply. 12/27/07 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 512 REVISION 10

TITLE: **REFRIGERATOR BLANK PREPARATION AND ANALYSIS**

FORMS: **342** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1-5-07

QUALITY ASSURANCE MANAGER _____ DATE 1/5/07

LABORATORY MANAGER _____ DATE 1-8-07

HISTORY: Rev0, 12/20/93; Rev1, PCN #321, 1/13/95; Rev2, 12/29/96; Rev3, 1/11/99; Rev4, 7/9/99; Rev5, 1/10/00; Rev6, 3/26/02; Rev7, 3/14/03; Rev8, 2/13/04 and 3/10/05 (updated format); Rev9, 7/24/06; Rev10, 1/5/07.

1. SCOPE AND APPLICATION

Refrigerator blanks (storage blanks) for all refrigerators that house volatile samples, including temporary storage provided by the Sample Control walk-in cooler RU #20, are analyzed weekly per the applicable analysis method, to establish that the refrigeration units used for volatiles sample storage are contaminant-free. Documentation of refrigerator blank results is maintained for traceability purposes.

2. SUMMARY

A suite of six (6) 40mL VOA vials for each volatile sample storage unit are prepared as refrigerator storage blanks prior to the beginning of each month. The storage blank vial preparation and placement must occur 1-2 weeks prior to the beginning of each month, so that the vials are in contact with the refrigerator's environment long enough to pick up any contaminants that may be present. Reagent water (prepared per SOP 511) is used as the source water for these blanks. The blanks are stored in the appropriate storage areas, with one vial analyzed weekly (i.e., every 7 days±1 day), per the applicable Method (SW8260, SW8021). Results from the volatiles storage blank analyses are evaluated promptly to determine if contamination has occurred that may affect volatiles sample integrity.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to carryout the procedures as discussed in this SOP and to complete all documentation required for review.

3.2 Any personnel who note anomalies or out-of-control events associated with the analysis of these samples must document the problem and take corrective action.

4. APPARATUS AND MATERIALS

4.1 VOA vials, 40mL, septum-seal, certified 'clean'

NOTE: Bottle lot numbers and manufacturer's lot analysis information are

retained on file by the Sample Control Department.

4.2 granulated activated carbon, laboratory grade

5. REAGENTS

Reagent water, prepared per SOP 511

6. PROCEDURE

6.1 STORAGE BLANK PREPARATION

6.1.1 Fill six (6) 40mL VOA vials per each volatile sample storage unit with freshly prepared reagent water (SOP 511). Cap each vial and invert to ensure that it is headspace free. **Note that six vials are prepared to ensure that one vial is available for each week of the month, plus an extra vial(s) to assist in confirmation and corrective action if needed.** Document preparation on Form 342.

6.1.2 Date and initial each vial. Also label each vial as a refrigerator blank with a Departmental/location designation (e.g., "SC" for Sample Control, etc.). Place all six vials in the appropriate sample storage refrigerator. **Note that the storage blank vial preparation and placement must occur 1-2 weeks prior to the beginning of each month, so that the vials are in contact with the refrigerator's environment long enough to pick up any contaminants that may be present.**

6.2 ANALYSIS

6.2.1 One storage blank is to be analyzed weekly (i.e., every 7 days±1 day), for every refrigerator that houses volatiles samples. The storage blanks are analyzed per the applicable Method (SW8260, SW8021), and must be analyzed within the 12-hour tune for GC/MS Volatiles, and within a closing Continuing Calibration Verification (CCV) for GC Fuels. Archive the refrigerator blank analysis data along with the instrument daily raw data files.

6.2.2 Results from the storage blank analysis are to be evaluated promptly. **Target compounds -- including common laboratory contaminants (e.g., methylene chloride, acetone, 2-butanone) -- detected at or above the reporting limit (RL) are considered to be a warning of potential contamination problems and require corrective action.** If contamination at levels at or above the RL is identified, analyze another storage blank vial (i.e., one of the "extra" vials prepared) to confirm the results.

NOTE: Other acceptance criteria, such as <RL common contaminants, <½ RL all other targets (e.g., DOD LIMS program specification), may apply.

or per other applicable criteria

6.2.3 If contamination at levels at or above the RL is confirmed, proceed with corrective actions. **A Nonconformance Report (NCR), Form 313, must be processed immediately per procedures outlined in**

SOP 928.

6.3 CORRECTIVE ACTIONS

6.3.1 Corrective action shall include locating and resolving the source of contamination (e.g., leaking VOA vial, highly contaminated samples). The source can be isolated by placing it, in its original container, inside another, larger, sealed container, into which a small amount of GAC (granulated activated carbon) is placed.

6.3.2 Prepare four or more additional storage blanks per Section 6.1 of this SOP, and place them in the affected storage unit. Analyze one of the blanks daily until the contamination is less than the RL. **or per other applicable criteria**

6.3.3 Repeat Steps 6.3.1 and 6.3.2 as necessary until the contamination problem is resolved.

6.3.4 Data generated from samples stored in a refrigeration unit where refrigerator blank contamination has been confirmed shall be considered suspect and shall be documented as nonconforming data. In the event of confirmed contamination, an NCR form shall be completed and included with the data report to document and communicate the potential cross-contamination of all samples stored in the refrigerator at the time of contamination.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

Personal protective equipment (PPE) shall consist of safety glasses, a lab coat, and gloves, and must be worn at all times.

7.2 WASTE DISPOSAL

Aqueous purge and trap waste shall be disposed of in the aqueous laboratory waste stream. A satellite waste collection vessel may be obtained from the Waste Compliance Officer.

8. REFERENCES

8.1 Standard Operating Procedure (SOP) 425, current iteration, “Determination of Aromatic Volatile Organics by Gas Chromatography - Methods SW8021B and EPA 602”, Paragon Analytics.

8.2 Standard Operating Procedure (SOP) 525, current iteration, “Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry -- Methods SW8260B and EPA 624”, Paragon Analytics..

DOCUMENT REVISION HISTORY

7/24/06: Added DOCUMENT REVISION HISTORY section; incorporated Form.

1/5/07: Changed Title. Standardized format (Sections 4, 5). Updated format, Section 6; updated how analysis data are retained. Referenced determinative SOPs in Section 8.

Paragon Analytics.

REFRIGERATOR BLANK PREPARATION

Prep. Date	For Month / Year of	No. Vials Prepared	Preparer's Initials

REFRIGERATOR BLANK ANALYSIS

Date of Analysis	For Month / Year of	Vial Designation	Analyst	Results (< RL) Yes or No	Comments

Reviewed by _____ Date _____

Form 342r0.frm (9/29/99)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 525 REVISION 12

TITLE: **DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY – METHODS SW8260B AND EPA 624**

FORMS: **NONE** **(instrument printout used as run log)**

APPROVED BY:

TECHNICAL MANAGER Steven Ayer DATE 2/9/07

QUALITY ASSURANCE MANAGER [signature] DATE 2/8/07

LABORATORY MANAGER [signature] DATE 2-9-07

HISTORY: Rev0, 3/21/96; Rev1, 6/10/96; Rev2, 5/5/97; Rev3, 4/13/98; Rev4, 2/15/99; Rev5, 9/26/01; Rev6, 1/23/02; Rev7, 3/26/02; Rev8, 10/28/02; Rev9, 4/24/04; Rev10, 11/22/04; Rev11, 2/27/06; Rev12, 2/8/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- SW-846 methods 5030C, 5035A and 8260B -- are used to determine volatile organic compounds in a variety of matrices. This SOP is applicable to nearly all types of samples, regardless of water content, including: groundwater, aqueous sludges, caustic or acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons or catalysts, soils, and sediments. The following compounds are presently being analyzed using this SOP. Other compounds can be analyzed after successful demonstration of capability (DOC) and method detection limits study (MDL). Analytes in the Table below are listed in typical elution order. Analytes that are part of Paragon's standard reporting list are depicted in bold.

Parameter	CAS No[b]	Purge & Trap
dichlorodifluoromethane	75-71-8	A
chloromethane	74-87-3	A
vinyl chloride	75-01-4	A
bromomethane	74-83-9	A
chloroethane	75-00-3	A
trichlorofluoromethane	75-69-4	A
acrolein	107-02-8	A
1,1-dichloroethene	75-35-4	A
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	A
acetone	67-64-1	PP

Parameter	CAS No[b]	Purge & Trap
iodomethane	74-88-4	A
carbon disulfide	75-15-0	PP
methylene chloride	75-09-2	A
trans-1,2-dichloroethene	156-60-5	A
methyl tertiary butyl ether	1634-04-4	A
acrylonitrile	107-13-1	A
1,1-dichloroethane	75-34-3	A
vinyl acetate	108-05-4	A
cis-1,2-dichloroethene	156-59-2	A
2-butanone	78-93-3	PP
bromochloromethane	74-97-5	A
chloroform	67-66-3	A
1,1,1-trichloroethane	71-55-6	A
2,2-dichloropropane	594-20-7	A
carbon tetrachloride	56-23-5	A
1,1-dichloropropene	563-58-6	A
1,2-dichloroethane	107-06-2	A
benzene	71-43-2	A
trichloroethene	79-01-6	A
1,2-dichloropropane	78-87-5	A
dibromomethane	74-95-3	A
bromodichloromethane	75-27-4	A
2-chloroethyl vinyl ether	110-75-8	A
cis-1,3-dichloropropene	10061-01-5	A
4-methyl-2-pentanone	108-10-1	PP
toluene	108-88-3	A
trans-1,3-dichloropropene	10061-02-6	A
1,1,2-trichloroethane	79-00-5	A
2-hexanone	591-78-6	PP
tetrachloroethene	127-18-4	A
1,3-dichloropropane	142-28-9	A
dibromochloromethane	124-48-1	A
1,2-dibromoethane	106-93-4	A
1-chlorohexane	544-10-5	A

Parameter	CAS No[b]	Purge & Trap
chlorobenzene	108-90-7	A
1,1,1,2-tetrachloroethane	630-20-6	A
ethylbenzene	100-41-4	A
m- and p-xylene	108-38-3/106-42-3	A
o-xylene	95-47-6	A
styrene	100-42-5	A
bromoform	75-25-2	A
isopropylbenzene	98-82-8	A
1,2,3-trichloropropane	96-18-4	A
1,1,2,2-tetrachloroethane	79-34-5	A
bromobenzene	108-86-1	A
n-propylbenzene	103-65-1	A
2-chlorotoluene	95-49-8	A
1,3,5-trimethylbenzene	108-67-8	A
4-chlorotoluene	106-43-4	A
tert-butylbenzene	98-06-6	A
1,2,4-trimethylbenzene	95-63-6	A
sec-butylbenzene	135-98-8	A
1,3-dichlorobenzene	541-73-1	A
p-isopropyltoluene	99-87-6	A
1,4-dichlorobenzene	106-46-7	A
n-butylbenzene	104-51-8	A
1,2-dichlorobenzene	95-50-1	A
1,2-dibromo-3-chloropropane	96-12-8	PP
1,2,4-trichlorobenzene	120-82-1	A
hexachlorobutadiene	87-68-3	A
naphthalene	91-20-3	A
1,2,3-trichlorobenzene	87-61-6	A
trans-1,4-dichloro-2-butene	110-57-6	PP
acetonitrile	75-05-8	PP
allyl chloride	107-05-1	A
chloroprene	126-99-8	A
1,4-dioxane	123-91-1	PP
ethanol	64-17-5	PP

Parameter	CAS No[b]	Purge & Trap
ethyl methacrylate	97-63-2	A
ethyl-tert-butyl ether	637-92-3	n/a
hexachloroethane	67-72-1	PP
isobutyl alcohol	78-83-1	PP
isopropyl ether	108-20-3	n/a
methacrylonitrile	126-98-7	PP
methyl methacrylate	80-62-6	A
propionitrile	107-12-0	PP
tert-amyl methyl ether	994-05-8	n/a
tert-butanol	75-65-0	n/a

A	Adequate response by this technique.
b	Chemical Abstract Services Registry Number.
PP	Poor purging efficiency resulting in high EQLs.
n/a	Not applicable; not designated in method.

This SOP describes purge & trap GC/MS procedures that can be used to identify and quantify most organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. However, for the more soluble compounds, quantification limits are approximately five to ten times higher because of poor purging efficiency. Ketones, alcohols and aldehydes are typical of classes of compounds that may have elevated reporting limits due to their high degree of water solubility.

Note that the body of this SOP specifies the procedures to be used for Method SW8260B. Any additional or contradictory requirements for EPA Method 624 are addressed in Section 10.

2. SUMMARY

Volatile compounds are introduced into the gas chromatograph (GC) by purge & trap. Purged sample components are trapped in a tube containing suitable sorbents in accord with Methods SW5030C or 5035A. When purging is complete, the sorbent tube is heated rapidly and back-flushed with helium to desorb trapped sample components. The analytes are desorbed directly onto a narrow-bore capillary column for analysis. The column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph.

As analytes elute from the capillary column, they are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantification) ion relative to an internal standard with the response factor or calibration equation generated

from a multi-point calibration curve using average response factors or regression equations.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Analyst to perform the analyses according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Paragon Project Manager is responsible for directing a chlorine residual check to be performed just prior to analysis as applicable.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the review sheet indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to correct any errors found during the review.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks and the above sources are suspected, the analyst should change the purge gas source and

regenerate the molecular sieve purge gas filter and/or sorbent trap. Many trace impurities in the purge (carrier) gas are removed by passing the He through a heated catalyst bed that is capable of removing hydrocarbons and oxygen.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing the purge needle or apparatus and sample syringes with three portions of organic-free reagent water between samples. Sample tubes are only reused if washed and baked before the next use. After analysis of a sample containing high concentrations of volatile organic compounds, one or more reagent blanks should be analyzed to check for cross-contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purge needle or apparatus with methanol and then rinse it thoroughly with organic-free reagent water. In extreme situations, the entire sample pathway of the purge & trap may require dismantling and cleaning or replacement.

4.2.1 The relatively low purging efficiency of many analytes from a large volume sample (e.g., 10mL, 25mL) often results in significant concentrations remaining in the sample purge tube after analysis. Archon autosamplers use the same purge vessel repetitively for water analysis, but rinse the purge vessel with He and water between samples

4.2.2 If carryover contamination is suspected, (this is likely when a sample containing high concentration levels of volatile compounds is followed by a sample containing low levels of the same volatile compounds), all samples that may have been affected must be re-analyzed. Sample analysis may continue if a cleanup blank or sample following the high concentration sample is free (below the reporting limit) from compounds present over the calibration range in the high level sample. Analyst experience should be used to determine which compounds tend to carryover and at what levels.

4.2.3 Annotations made to instrument run logs should indicate if a sample contains possible carryover contamination. If the subsequent rerun of the sample confirms the presence and level of the volatile compounds, either analysis may be used. If, however, the rerun shows that the presence of the compounds was carryover contamination, only the rerun should be used. The original analysis should be considered non-usable data for the analytes that may have carried over.

4.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric

sources of methylene chloride, or random background levels will result. Because methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean because clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

4.4 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling and handling protocol serves as a check on such contamination. To check for cross-contamination during sample storage, the laboratory periodically analyzes sample storage refrigerator blanks (SOP 512).

5. APPARATUS AND MATERIALS

5.1 PURGE & TRAP AUTOSAMPLER DEVICE
Autosampler - OI 4552/Archon, Varian Archon, or equivalent
Sample concentrator - Tekmar LSC 2000, Tekmar LSC 3000 or OI 4560 Liquid Sample Concentrator equipped with VO-Carb 3000 (or OI #10) adsorbent trap, or equivalents

5.2 GAS CHROMATOGRAPH (GC), DETECTOR AND MASS SPECTRAL LIBRARY
Hewlett Packard (HP) Model 5890A or 6890 GC capable of splitless or split/splitless injection or direct interface to a purge & trap apparatus. Equipped with variable constant differential flow controllers (so that the column flow rate will remain constant throughout desorption) and a temperature-programmable oven or equivalents. Also equipped with a HP5971, 5972 or 5973 mass spectrometer detector, capable of scanning from 35 to 300amu every 2sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for p-bromofluorobenzene (BFB) which meets all of the criteria in Table 1 (shown subsequently) when 50ng or less of the GC/MS tune standard is introduced through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC. The NBS/EPA/NIST mass spectral library (library may vary with instrument) is also used to identify non-target compounds generally known as tentatively identified compounds (TICs).

GC/MS interface to the mass spectrometer: Direct coupling by inserting the column into the mass spectrometer is generally used for 0.18 to 0.32mm-ID columns. Any enrichment device or transfer line can be used if all of the performance specifications described in this SOP (including tuning) can be achieved.

5.3 DATA ACQUISITION AND PROCESSING SYSTEM

A computer system that facilitates continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass, and plotting such ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits.

5.4 COLUMNS - Equivalent columns/guard columns may also be used

Column 1 - 60m x 0.25mm ID capillary column with RTX-624 stationary phase (Restek), 1.4µm film thickness, or equivalent

Column 2 - 60m x 0.25mm ID capillary column with RTX-VMS (Restek), 1.4µm film thickness, or equivalent

5.5 GASES- **only high purity or higher grade gases may be used!**

Helium: purge & trap and carrier gas

5.6 MEASURING DEVICES

microsyringes - 5, 10, 25, 50, 100, 250, 500, and 1,000µL

syringes - 5, 10, or 30mL, glass

syringe valve, two-way with Luer ends (three each), if applicable to the purging device

laboratory balance, 0.01g sensitivity (used for weighing solid samples)

5.7 CONSUMABLE SUPPLIES

- Compact Vespel/Graphite Ferrule, Restek #20264 or equivalent
- Graphite Ferrules, various sizes
- glass scintillation vials, 20mL and 40mL, with Teflon™/-lined/low-level siloxane screw-caps, or, glass culture tubes with Teflon™-lined screw-caps
- vials, 2mL, with Teflon™-lined screw-caps
- Pasteur pipettes, 5 ¾" and 5mL, disposable
- volumetric pipettes, 10mL, Class A, disposable
- volumetric flasks, Class A - 5mL, 50mL, and 100mL, with ground-glass stoppers
- spatula, stainless steel
- pH paper, acidic narrow range and wide range
- PTFE-coated magnetic stir bars, for use in soils purged with the Archon autosamplers (SW5035, SW5035A)
- Mininert™ or CERTAN™ vials or equivalent

6. REAGENTS - At minimum, reagent grade chemicals shall be used in all tests.

6.1 Organic-free reagent water (SOP 511)

6.2 Methanol (CH_3OH), purge & trap quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents. J.T. Baker #907702 or equivalent

6.3 Pre-conditioned Ottawa sand (for use as clean matrix for method blank (MB) and laboratory control sample (LCS) analyses associated with solid matrix sample analyses): Pre-condition by drying in an oven set at 105°C or greater overnight. EMD #SX0075-3 or equivalent

6.4 STANDARDS

NOTE: Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards in methanol be stored at –10°C to –20°C in Mininert™ or CERTAN™ vials with Teflon™-lined screw-caps. Stock standards that are not accessed as part of routine operations may be stored in 2mL glass vials with Teflon™-lined caps (i.e. Mininert™ vials are not required for rarely utilized stock standards).

6.4.1 All standards are maintained per PAR SOP 300. Two independent sources of commercial target analyte stock standards, in methanol, are required. The stock standards are purchased as certified solutions from suitable vendors. Typically, concentrations of stock solutions vary from 1,000-10,000µg/mL.

6.4.2 Unopened stock standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules, if recommended by the manufacturer. Standards for this procedure must be equilibrated to ˉ10-ˉ20°C (stored in freezer) before opening and protect from light. After opening/initial use, transfer remaining stock standard to a suitable vial (Mininert™ or CERTAN™ vial with a Teflon™-lined screw-cap) with minimal headspace, and store in a freezer (ˉ10-ˉ20°C). All opened stock standards must be replaced after 3 months from date opened, or sooner, if comparisons with laboratory control samples indicate a problem.

6.4.3 ***Gas stock solutions expire one week*** after the ampule has been opened and transferred to a Teflon™-lined screw cap vial or equivalent. ***Other calibration stock solutions expire three months*** after the ampule has been opened and transferred to a Mininert™ or CERTAN™ screw cap vial or equivalent. ***See SOP 300 for additional information on standards expiration.***

6.4.4 First source materials are used to create calibration and continuing calibration verification (CCV) standards. Second source materials are

used to create the initial calibration verification (ICV) solution. Laboratory control and matrix spike standards may be from either source (the second source is most commonly used for spiking).

Non-target analyte internal standard (IS) and surrogate (SS) stock standards are also purchased. The IS is used to quantitate analytes detected in samples. The SS is used to monitor system performance and method effectiveness with each sample matrix. The internal standards (ISs) used for this method are: fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected. Prepare IS stock and intermediate standards in methanol using the procedures described above. It is recommended that the intermediate standard be prepared at a concentration of 50µg/mL of each internal standard compound. Typically, addition of 5µL of this standard to 5.0mL (or 5g) of sample, calibration standard, or quality control (QC) sample would be the equivalent of 50µg/L (50µg/kg). The surrogates currently utilized are: toluene-d_8, 4-bromofluoro-benzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate standard in methanol, typically at a concentration of 2,000µg/mL, should be purchased as a certified solution and stored as described above. An intermediate surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250µg/mL in methanol. Each standard, sample or QC sample undergoing analysis must be spiked with the surrogate spiking solution prior to analysis. Typically, 5µL of solution containing surrogate standards and internal standards (IS), is added to every 5mL sample. Surrogates are spiked independently of ISs during preparation of initial calibration standards. Section 9 of this SOP gives definitions and uses of surrogates and QC (i.e., LCS/LCSD, MS/MSD) samples.

Prepare intermediate QC spike standards, in methanol, from volatile organic compounds that will be representative of the compounds being investigated. At a minimum, the matrix spike will include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene, typically at a concentration of 50µg/mL for each analyte.

6.4.5 An appropriate volume of target analyte stock standard is diluted, with methanol, to a specific volume to create intermediate standards. The intermediate standard may contain the compounds of interest singly or mixed together. Intermediate standards must be stored with minimal headspace and should be checked frequently for signs of degradation, especially just prior to preparing working calibration standards from

them. Store standards in an appropriate vial with minimal headspace; the standards may be retained as prescribed in SOP 300. All dilutions should be performed using syringes, and purge & trap grade MeOH.

6.4.6 4-bromofluorobenzene (BFB) tune standard: A standard solution containing 50ng/µL of BFB in methanol is prepared.

NOTE: If using a system with automated introduction of standards, such as the O-I Archon autosampler, an equipment validation study must be performed to determine the actual volume of standard delivered. The concentration of standard may be adjusted accordingly for the actual volume delivered at the 1µL setting. For example: (1.135µL actual delivery)(441µg/mL IS/SS spiking solution)/5mL = 100µg/L.

6.4.7 Target analyte calibration (working) standards: Calibration standards at a minimum of five concentrations should be prepared from the intermediate standards. Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration less than or equal to the reporting limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. The laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s). **Aqueous calibration (working) standards are not stable and must be prepared on the day of loading on the autosampler.**

To prepare a target analyte calibration standard for purge & trap, add an appropriate volume of an intermediate standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the capped flask three times only. Transfer 5.0mL (10mL or 25mL if lower detection limits are required) of each standard to a gas-tight syringe along with 5µL of internal standard (for 5mL samples). Archon autosamplers add the internal standard and surrogates when programmed to do so. Then transfer the contents to a purging device or syringe. Perform purge & trap or direct injection as outlined in Methods SW5030C or SW5035A. It is also acceptable to add the appropriate amount of standard directly to a gas-tight syringe containing 5.0mL (10mL or 25mL) of organic-free reagent water.

6.4.8 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials and of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 Samples from chlorinated water sources should be dechlorinated with sodium thiosulfate ($Na_2S_2O_3$) in the field at the time of collection. These samples should then be acidified with hydrochloric acid (HCl) following dechlorination. Based upon project knowledge provided by the client, where applicable, Paragon's Project Manager may instruct the volatiles analysts to test for chlorine residual just prior to preparation for analysis. A chlorine residual test kit, obtainable from the Sample Receiving Department, is used to check for chlorine residual. Notify the Project Manager immediately if residual chlorine is present.

7.3 Volatile organic analysis of water and soil samples extracted by Methods SW5030C or SW5035A must be performed within 14 days of collection unless otherwise specified by the client. Water samples are usually preserved by adding approximately four (4) drops of concentrated hydrochloric acid (HCl) to each 40mL VOA vial. The purpose of the hydrochloric acid is to prevent microbial degradation of target compounds. If the water sample is unpreserved, the holding time may be shortened to seven (7) days from the date of collection. Volatile organic analysis of soil samples received in EnCore™ samplers to be extracted by Method SW5035A shall be frozen upon receipt and analyzed within 14 days of collection. Other types of collection and preservation techniques may be required by Method SW5035A and should be evaluated according to the specific needs of the client. Other means of preservation for samples to be prepared for analysis by Method SW5035A include freezing soil in a 40mL vial after addition of water and a stir bar, as well as addition of sodium bisulfate solution ($NaHSO_4$) and a stir bar. Method SW5035A also allows preservation with methanol for solid samples with expected higher concentrations of target analytes. Preservation of samples for subsequent analysis via Methods SW5035A/8260B may be required within 48hrs after time of collection.

7.4 Just prior to preparation for analysis, obtain a small aliquot of each aqueous sample to be analyzed and using pH paper, measure the pH of each sample; record the result next to the sample's identity on the previously prepared daily sequence log. If the pH of a preserved sample is >2, immediately notify the appropriate Project Manager and discuss the pH excursion in the data package

case narrative. Aqueous samples that are intentionally not preserved at the time of collection do not require Project Management notification.

7.5 Samples to be prepared by Method SW5030C must be collected in glass containers with minimal headspace and stored at 4±2°C. Samples to be prepared by Method SW5035A should be collected in EnCore™ sampling devices and stored at <-7°C, but no less than -20°C. Other types of collection and preservation techniques may be required by Method SW5035A and should be evaluated according to the specific needs of the client.

7.6 To prevent loss of volatile organic compounds, samples must not be opened until the time of analysis.

8. PROCEDURE

Three alternate methods are provided for sample introduction. All internal standards, surrogates, and matrix spikes (when applicable) must be added to samples before purging commences:

- Purge & trap per Method SW5030C (aqueous samples)
- Purge & trap per Method SW5030C (for dilution of solid or waste liquid samples via methanol extraction described in SW5035A)
- Purge & trap per Method SW5035A for solid samples collected in a manner consistent with the method or modification thereof (for samples submitted as samples that must be transferred by laboratory personnel to a purge vessel from containers submitted by the client)

8.1 TYPICAL PURGE & TRAP DEVICE SETTINGS

Instrument conditions may be varied as needed, however, the instrument conditions employed during initial calibration (ICAL) must be used for all subsequent sample analyses that are quantitated using the initial calibration. If operating conditions are altered, a new calibration must be prepared.

<u>Purge & trap settings for OI 4560A purge & trap device:</u>
purge time = 7-11 minutes
desorb temperature = 190°C
desorb time = at least 1.0 minute
trap bake = at least 4 minutes at 210°C
(or according to manufacturer's recommendation for all parameters above)

<u>Purge & trap settings for Tekmar LSC 2000 or 3000 purge & trap device:</u>
purge time = 7-11 minutes
desorb temperature = 250°C
desorb time = at least 1.0 minute
trap bake = at least 4 minutes at 260°C
(or according to manufacturer's recommendation for all parameters above)

8.2 TYPICAL GAS CHROMATOGRAPH SETTINGS

initial temperature = 60°C
initial time = 0.1 minute
temperature ramp A = 10°C/minute
temperature ramp B = 25°C/minute
final temperature A = 105°C
final temperature B = 220°C
final hold time A = 0 minutes
final hold time B = until all compounds elute
P&T transfer line temperature = 120°C
GC/MS transfer line temperature = 280°C
injection temperature = 150°C
electron energy = 70eV (nominal)
mass range = 35-300amu
scan time = 0.6-2 seconds per scan

8.3 AUTOSAMPLER CLEANING

After use, each purge tube is removed from the autosampler, washed and regenerated per SOP 334. Additionally, each purge needle is flushed with organic-free DI water (note that the purge tube is rinsed in place, as part of the system program, if using the OI Archon autosampler), then the exterior is wiped with a KimWipe™ and MeOH.

8.4 CHROMATOGRAPHIC MAINTENANCE

8.4.1 Bake out the trap and column. Extra blanks may be necessary to achieve an adequate baseline if carryover is observed. Replace trap if performance problems are demonstrated and cannot be alleviated by routine maintenance.

8.4.2 If trap and front end are not clean and functioning properly, clip a loop from the column or replace as necessary.

8.4.3 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperatures. Oxygen may enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Oxidized columns will exhibit baselines that rise rapidly during temperature programming. If a column is oxidized, replacement may be necessary.

8.5 INITIAL CALIBRATION (ICAL)

Instrument conditions may be varied as needed; however, the instrument conditions employed during initial calibration must be used for all subsequent sample analyses that are quantitated using that initial calibration. If operating conditions are altered, a new calibration must be prepared.

8.5.1 Each GC/MS system must be hardware-tuned to meet Method criteria (see Table 1 below) for a 5-to-50ng injection or purging of 4-bromofluorobenzene (BFB). A BFB tune is performed prior to analysis to demonstrate the ability of the system to separate ions and assign proper ratios to fragments. Analyses must not begin until these criteria are met. Typically, 1µL of a 50ng/µL BFB tune solution is analyzed by direct injection.

TABLE 1

BFB MASS INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)*

MASS	INTENSITY REQUIRED (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

* Alternate tuning criteria may be used (e.g., CLP, EPA Method 524.2, or manufacturers' instructions), provided that method performance is not adversely affected.

8.5.2 Set up the purge & trap system as outlined in Method SW5030C, or Method SW5035A if closed system purge & trap analysis is to be utilized. A set of at least five calibration standards containing all of the target analytes and surrogates is needed. The calibration must contain a standard at or below the reporting limit for each compound, the other calibration standards should contain analytes at concentrations that define the range of the method, but do not exceed the linear range of the instrument. Due to the varying reporting limit requirements of the laboratory's clientele and the varying instrument response of the target compounds, seven levels are typically analyzed. Below is a list of typical calibration levels used during ICAL. Project requirements and instrument performance may require modifications to the levels listed.

Final Concentration (µg/L of 5mL and 5g purges)	Internal Standard (µg/L of 10mL purges)	Final Concentration (µg/L of 10mL purges)
100	25	50
75	25	35
50	25	20
20	25	10
10	25	2
5	25	1
2	25	0.5
50 CCV level	25	20 CCV level
20 ICV level	25	10 ICV level

8.5.3 Calibration must be accomplished using the sample introduction technique that will be used for sample analysis. The purging efficiency for 5mL of water is greater than that for 10mL or 25mL. Therefore, develop the standard curve using the volume of sample to be analyzed. Prepare working calibration standards as described in Section 6.

8.5.4 Tabulate the area response of the characteristic ions (see Table 2 at end of SOP) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = (A_x C_{IS})/(A_{IS}C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{IS} = Area of the characteristic ion for the specific internal standard.

C_{IS} = Concentration of the specific internal standard.

C_x = Concentration of the compound being measured.

The average RF must be calculated and recorded for each compound using at least five RF values calculated for each compound from the initial calibration curve. System performance criteria must be met before this calibration curve can be used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average relative response factor (RRF). These compounds are chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene.

The minimum RRFs for volatile SPCCs are as follows:

Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	0.1
Chlorobenzene	0.3
1,1,2,2-Tetrachloroethane	0.3

The SPCCs are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantification ion (m/z 173) is directly affected by tuning BFB at ions m/z 174/176. Increasing the m/z 175/176 ratio relative to m/z 95 may improve bromoform response.

Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge & trap systems and/or active sites in trapping materials.

8.5.5 Using the RFs from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. The percent RSD is calculated as follows:

$$\%RSD = \frac{SD}{\overline{RF_X}} x100\%$$

where:

RSD = Relative standard deviation

RF_x = Mean of 5 initial RFs for a compound

SD = Standard deviation of the initial RFs for a compound

$$SD = \sqrt{\sum_{i=1}^{n} \frac{(RF_i - \overline{RF})^2}{n-1}}$$

where:

RF_i = RF for each of the 5 calibration levels

n = number of RF values (i.e., 5)

8.5.6 In general, the %RSD for GC/MS systems should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) must be equal to or less than 30%. The CCCs are:

1,1-dichloroethene
chloroform
1,2-dichloropropane
toluene
ethylbenzene
vinyl chloride

If the %RSD is >30% for any CCC, the initial calibration is not acceptable and can not be used for sample analysis. Corrective action is required to eliminate the source of the problem (i.e., system leak and/or column active sites) and a new ICAL must be performed and meet the CCC criteria before sample analysis can continue. Client calibration requirements may also be prescribed in the LIMS program specification.

8.5.7 LINEARITY

If the %RSD of any compound is <15%, then the compound's response is assumed to be constant over the calibration range, and the average relative response factor may be used for quantification.

If the %RSD of any compound is >15%, a calibration curve of area ratio (A/A_{is}) versus concentration ratio (C/C_{is}), using first or second order regression fit of the five or more calibration points, may be constructed.

The type of curve fit applied should be chosen to best represent the data.

The use of calibration curves is a recommended alternative to average response factor calibration and is a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system. The coefficient of determination (COD, r^2 value) of the linear

or higher order regression used to define the calibration curve, is an expression of "goodness of fit", and must be ≥0.99. Quadratic regressions may be used with a minimum of 6 calibration points, and must yield a COD (r^2 value) of ≥0.99. A quadratic regression should not be used to compensate for detector saturation.

8.5.8 Calibration curves are verified each 12-hour shift by purging a continuing calibration verification standard (CCV). Recalibration is required only if calibration and on-going performance criteria cannot be met.

8.6 INITIAL CALIBRATION VERIFICATION (ICV)

A second source ICV standard is analyzed after the ICAL to independently verify the accuracy of the calibration. The concentration of the ICV should be different from that of the CCV and varied over time. If the control criteria are not met, the ICV shall be remade and analyzed to verify true concentration. If the ICV still fails, a new initial calibration must be generated.

It is recommended that the difference between the measured and expected concentrations be less than 25%. Due to the large number of analytes determined simultaneously using this procedure, it is considered likely that there may be sporadic failures of the <25% criteria. Consequently, it is permitted for the difference between expected and measured concentrations for 3 compounds out of 70 to be as high as 50% difference between measured and expected.

The second source check can also serve as the laboratory control sample (LCS) for samples analyzed in the same 12h shift as the ICAL. The LCS criteria may be different than the ICV criteria described above.

8.7 CONTINUING CALIBRATION VERIFICATION (CCV)

Performed at the beginning of each 12-hour sequence when initial calibration is not performed.

8.7.1 Prior to the analysis of samples, inject or purge 5 to 50ng of the 4-bromofluorobenzene standard following Method SW5030C or Method SW5035A. The resultant mass spectra for the BFB must meet all of the criteria given in Table 1 (shown previously) before sample analysis begins. These criteria must be met at the start of each 12-hour shift.

8.7.2 The ICAL curve for each compound of interest must be checked and verified once every 12 hours during analysis with the introduction technique used for samples. This is accomplished by analyzing a calibration standard that is at or near the midpoint concentration for the working range of the GC/MS. The SPCC compounds are checked, then the CCC compounds are checked. Then the %Ds for all target compounds are evaluated against the initial calibration.

8.7.3 SYSTEM PERFORMANCE CHECK COMPOUNDS (SPCCs)
A system performance check must be made each 12 hours. This is the same check that is applied during the initial calibration except that the daily response factor is evaluated against the criteria given previously. The SPCC criteria must be met before analysis can continue. If the minimum RRFs are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are: standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

8.7.4 CALIBRATION CHECK COMPOUNDS (CCCs)
After the system performance check is met, the CCCs are used to check the validity of the ICAL. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = (RF - RF_1)/RF \times 100$$

where:

RF_1 = Calibration Check Compound standard response factor
RF = Average response factor (system performance check)

If the %D for each CCC is $\leq$20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% difference) for any one CCC, corrective action must be taken. Problems similar to those discussed under SPCCs could affect this criterion. If the source of the problem cannot be determined after corrective action has been taken, a new multi-point calibration must be generated. The CCC criterion MUST be met before quantitative sample analysis begins. If the CCCs are not required analytes for all of the samples analyzed on one 12-hour shift, then all required analytes must meet the 20%D criterion.

The difference (for average RF) or drift (for regressions) for each target analyte is also evaluated against the ICAL. If a higher order equation is being utilized, the compound should be evaluated using the % drift calculation shown below:

$$\% \text{ drift} = [(\text{calc. conc.} - \text{theoretical conc.})/\text{theoretical conc.}](100\%)$$

The %D (drift or difference depending on calibration process) is evaluated for all target analytes and should be ≤20% for each target analyte, or data may need to be qualified depending on client or program specifications.

8.7.5 RETENTION TIME REPRODUCIBILITY

The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the midpoint standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrections must be made as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from that in the midpoint standard level of the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. Samples should not be analyzed and reported if the criteria described above are not met.

8.8 SAMPLE ANALYSIS

BFB tuning criteria and calibration verification criteria (discussed above) must be met before analyzing samples. All samples and working standard solutions must be allowed to warm to ambient temperature before analysis. Set up the purge & trap system as outlined in Method SW5030C, or Method SW5035A if closed system purge & trap introduction will be used.

8.8.1 PURGE TEMPERATURE

8.8.1.1 For soil analysis, the ICAL, all CCVs, and all field and QC samples shall be heated to 40°C during the purge.

8.8.1.2 For aqueous analysis, a heated purge is not required. The same purge conditions used for soil analysis may be used for aqueous analysis, however, if the ICAL, all CCVs, and all field and QC samples are heated to 40°C during the purge.

It is recommended that purge volumes of 10 to 25mL should not use a heated purge due to the amount of water vapor that may be introduced into the purge & trap system. The ICAL, all CCVs, and all field and QC samples should be left at ambient temperature during the purge.

8.8.2 AQUEOUS ANALYSIS

8.8.2.1 The process of taking an aliquot destroys the validity of aqueous samples for future analysis; therefore, if there is only one VOA vial, the analyst should prepare a second aliquot for analysis concurrently to protect against possible loss of sample integrity, or transfer the remaining sample to a 20mL VOA vial (without headspace) and refrigerate. This second sample is maintained only until such time when the

analyst has determined that the first sample has been analyzed properly.

8.8.2.2 Remove the plunger from a 5mL leur-lock syringe. If lower detection limits are required, use a 10-to-25mL leur-lock syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger, compress the sample and vent any residual air, while adjusting the sample volume to 5.0mL (10mL or 25mL).

8.8.2.3 Manually add 5µL (or appropriate volume) of the intermediate surrogate and internal standards to each sample (if not using an autosampler such as Archon, that adds the surrogates and/or ISs as part of the process). The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 5µL of the surrogate and internal standard spiking solution to 5mL of sample is equivalent to a concentration of 50µg/L of each standard.

8.8.2.4 For matrix spike analysis, add 2µL (or appropriate volume) of the intermediate matrix spike solution to the 5mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 20µg/L of each matrix spike standard.

8.8.2.5 The sample is placed in a purge tube on the autosampler. Proceed with purge & trap analysis by Method SW5030C. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the calibrated range of the instrument, the sample must be reanalyzed at a higher dilution.

Secondary ion quantification is allowed only when there are sample interferences with the primary ion.

When a sample is analyzed that has saturated ions from a high concentration compound, this analysis must be followed by an organic-free reagent water blank analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences (refer to Section 4 for further details).

8.8.2.6 It should be noted that most aqueous analyses (10mL and 25mL) that are performed with the use of the OI 4552/Archon or Varian Archon autosamplers undergo a different aliquotting procedure. All working standards and some sample dilutions are prepared in a 50mL volumetric flask, spiked accordingly, then are transferred to a 40mL VOA vial (without headspace). The vial is placed in the autosampler tray, where internal standards and surrogates are added automatically (if needed) and purge & trap analysis is then performed.

8.8.2.7 The following procedure is appropriate for diluting aqueous purgeable samples. Sample dilution is based on analyte concentration, non-target compound concentration, or the presence of surfactants (foaming samples). All steps must be performed without delay until the diluted sample is in a gas-tight syringe. If usable data has not been generated for a less diluted analysis, the dilution should keep the response of the major constituents (previously saturated peaks) in the upper portion of the linear range to generate the lowest reporting limits possible.

- Dilutions may be made in volumetric flasks (10 to 100mL) or gas-tight syringes (5mL or 30mL). Select the volumetric flask or syringe that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

- Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

- Inject the proper aliquot of sample from the syringe into the flask. Dilute the sample to the mark with organic-free reagent water. Cap the flask and invert three times. Repeat above procedure for additional dilutions.

- Fill a 5mL (or 30mL) syringe with the diluted sample. An alternative method is to inject the proper aliquot of sample directly into the 5mL or 30mL syringe filled with organic-free reagent water.

- Add 5µL (or appropriate volume) of the intermediate surrogate and internal standards to each sample. The surrogates and internal standards may be mixed and added as a single spiking solution. The addition of 5µL of the surrogates and internal standard spiking solution to 5mL of sample is equivalent to a concentration of 50µg/L of each standard.

8.8.2.8 The following procedure can be used to composite aqueous samples prior to GC/MS analysis:

- Add 5mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.

- The samples must be cooled at 4+2°C during this step to minimize volatilization losses.

- Mix well and draw out a 5mL aliquot for analysis.

- Follow sample introduction, purging, and desorption steps described in Method SW5030C.

- If less than five samples are used for compositing, a proportionately smaller syringe may be used unless a 25mL sample is to be purged.

- Add 5µL (or appropriate volume) of the intermediate surrogates and internal standards to each sample. The surrogates and internal standards may be mixed and added as a single spiking solution. The addition of 5µL of the surrogates and internal standard spiking solution to 5mL of sample is equivalent to a concentration of 50µg/L of each standard.

8.8.3 SOIL SAMPLE ANALYSIS BY METHOD SW5035Amod

8.8.3.1 Homogenize the sample well, taking care to minimize the loss of volatile constituents.

8.8.3.2 Weigh 5g of soil into an appropriate purge vessel; place the sample on the autosampler. For method blanks and LCSs, 5g of Ottawa sand should be added to the purge vessel.

8.8.3.3 Add 5mL of organic-free water to the sample. In the case of LCS or MS samples, the associated spike is added with this aliquot.

8.8.3.4 The Archon autosampler adds a total of 5mL of water to each sample. The Archon autosampler also adds an appropriate amount of the intermediate surrogates and internal standard solution to the reagent water, which is then added to the sample. For matrix spike analysis, add the appropriate volume (e.g., 2µL) of the matrix spike solution with the reagent water.

8.8.3.5 The following procedure is appropriate for diluting soil purgeable samples. Soil sample dilution is based on analyte concentration or unknown compound concentration. If usable data has not been generated for a less diluted analysis, the dilution should keep the response of the major constituents (previously saturated peaks) in the upper portion of the linear range to generate the lowest reporting limits.

- Soil dilutions are made by weighing an aliquot of less than 5g of sample into the purge tube. To ensure a representative sample aliquot, no less than 0.5g of soil should be purged. For reporting purposes, a nominal amount of 5g will be considered the purge amount, and amounts less than this will be treated as dilutions. If a dilution greater than can be obtained by 0.5g of soil is required, a medium level extraction must be performed (see Section 8.8.4 below).

8.8.4 MEDIUM LEVEL SOIL SAMPLES (METHANOL-EXTRACTION)
Methanolic extraction /analysis is used for high concentration solid samples requiring dilutions greater than that which can be soundly achieved using smaller sample volume, or for samples that are difficult to homogenize.

8.8.4.1 Homogenize the sample as well as possible, taking care to minimize the loss of volatile constituents.

8.8.4.2 Weigh approximately 5g (record actual weight to 0.01g) of sample into a labeled, tared 20mL VOA vial. Clean the outer lip of the vial with a Kimwipes™ before obtaining the final weight. In some instances, such as low density soils or odd matrices, an aliquot of less than 5g may be necessary.

8.8.4.3 Add 5mL of methanol, cap and shake vigorously for 2 minutes. Allow solid and methanol to separate for at least 10 minutes. Note that alternate soil weights and methanol volumes may be used depending upon the level of sample dilution required. Enough methanol must be added to the vial to completely cover the soil aliquot.

8.8.4.4 Calculate the volume of the methanol extract that when brought to a final volume of 5mL in water, will bring the dilution concentration into the upper portion of the instrument calibration (factor in any dilution that may have been made by the initial extraction of the sample with methanol). To protect the system from trap or column overload, a maximum of 100µL of extract may be used. The dilution is prepared in the syringe used to transfer the sample to the purge vessel. Proceed with the analysis as discussed for aqueous samples above (Section 8.8.2).

8.8.4.5 A medium level blank should be prepared in the same manner using 5.0g of Ottawa sand and 5mL of methanol. 100µL of this methanol extract injected into 5mL of water is to be analyzed before the sample extract, to ensure no methanol contamination.

8.8.5 SOIL SAMPLE ANALYSIS BY METHOD 5035A

8.8.5.1 Transfer the contents of an EnCore™ soil sampler to a 40mL VOA vial containing a magnetic stir bar.

8.8.5.2 Use 5g of Ottawa sand in a 40mL VOA vial as the matrix basis for method blanks (MBs)and LCSs.

8.8.5.3 Add 5mL of organic-free water to the vial.

8.8.5.4 For matrix spikes, add 2µL (or appropriate amount) of intermediate spiking solution.

8.8.5.5 Samples may be submitted by clients in 40mL vials which already contain water, preservative ($NaHSO_4$) and stir bar or water and stir bar only. Samples submitted in vials are analyzed in the vials without opening the vial.

8.8.5.6 Place vial on the autosampler.

8.8.5.7 The Archon is used to add internal standards and surrogates solution and 5mL of organic-free water to the purge vessel bringing the final liquid purge volume to 10mL.

8.8.5.8 Place the VOA vial in the Archon autosampler which will automatically inject 1µL of surrogates and internal standards (if appropriate) prior to purging. Note: The 1µL volume is approximated; as instructed by the instrument manufacturer, the internal loop used to deliver the standard is calibrated for each autosampler to determine the absolute volume being delivered. The autosampler will stir and heat the contents of the VOA vial during the purge process.

8.8.5.9 Soil dilutions are made by weighing an aliquot of less than 5g from the Encore™ into the VOA vial. To ensure a representative sample aliquot, no less than 0.5g of soil should be purged. For reporting purposes, a nominal amount of 5g will be considered the purge amount, and amounts less than this will be treated as dilutions. If a dilution greater than can be obtained by 0.5g of soil is required, a medium level extraction must be preformed by extracting the contents of the EnCore™ as described in Section 8.8.4 above.

8.9 DATA INTERPRETATION

8.9.1 QUALITATIVE ANALYSIS

8.9.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of the method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met:

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

- The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of

the standard component. (RRT = RT of the analyte/ RT of the internal standard).

- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.

- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulders or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

- Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes co-elute (i.e., only one total ion current chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound. Analyst experience and judgment is important when evaluating co-eluting compounds.

8.9.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

- The relative intensities of the major ions should agree within ±20%. Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.

- Molecular ions present in the reference spectrum should be present in the sample spectrum.

- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

- Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the analyst assign a tentative identification.

8.9.2 QUANTITATIVE ANALYSIS

8.9.2.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The IS used shall be the one nearest the retention time of that of a given analyte.

8.9.2.2 When the detector response is linear and passes through the origin, calculate the concentration of each identified analyte in the sample as follows:

WATER:

$$Concentration(\mu g / L) = \frac{(A_x)(I_s)}{(A_{IS})(\overline{RF})(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured

I_s = Amount of internal standard injected (ng)

A_{IS} = Area of characteristic ion for the internal standard

$\overline{RF}$ = Mean relative response factor for compound being measured

V_o = Volume of water purged (mL), taking into consideration any dilutions made

SEDIMENT/SOIL SLUDGE (on a dry-weight basis) & WASTE (normally on a wet-weight basis):

$$Concentration(\mu g / kg) = \frac{(A_x)(I_s)V_t)}{(A_{is})(\overline{RF})(V_i)(W_s)(D)}$$

where:

A_x, I_s, A_{is}, $\overline{RF}$ = Same as for water.

V_t = Volume of total extract (µL) (Use 10,000µL or a factor of this when dilutions are made)

Vi = Volume of extract added (µL) for purging

WS = Weight of sample extracted or purged (g)

D = % dry weight of sample/100, or 1 for a wet-weight basis

8.9.2.3 Where requested by the client, an estimate of concentration for non-calibrated components in the sample may be made. The formulae given above should be used with the following modifications: The areas A_x and A_{IS} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. The chromatographic data system calculates the concentration and reports which IS was used in the calculation. Use the nearest IS free of interferences. Upon request, Paragon will report the top 10 non-calibrated

components (Tentatively Identified Compounds, TICs) with total ion areas > 10% of the total ion area of the nearest internal standard. Identification of TICs with less than 10% relative abundance is difficult at best, and generally should not be attempted. Some clients may request the reporting of more compounds or compounds with lower areas relative to the closest IS. Consult LIMS program specification for further direction.

8.9.2.4 Alternatively, the regression line fitted to the initial calibration may be used for determination of analyte concentration.

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

For this method, an analysis batch is defined as a group of 20 or fewer field samples that is associated with one unique set of batch QC samples. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS), and duplicate (field sample, LCS or MS). All quality control samples must be carried through all stages of the sample preparation and measurement steps. In addition, batch QC samples should be analyzed on the same instrument as the samples in the batch. Consult LIMS program specification for additional or alternative requirements.

9.2 BLANK ANALYSIS

A method (reagent) blank (MB) must be analyzed for each 12-hour BFB tune and per batch of 20 or fewer field samples of similar matrix. Target compounds may not be detected above one-half the reporting limit (RL). Common laboratory contaminants (e.g., acetone, 2-butanone, methylene chloride) are allowed at levels as high as the RL. Occurrence of these common laboratory contaminants should be considered a warning and must be reported in the data package case narrative. See QC Table for further details.

9.3 SURROGATES

Surrogate recovery is monitored to assess method performance of the particular matrix. Surrogates are added to all standards, blanks, samples and QC samples prior to analysis. See QC Table for acceptance limits and corrective actions.

9.4 INTERNAL STANDARDS

Internal standards are added to all standards, field and quality control samples analyzed. Retention times and responses are evaluated for internal standards. See QC Table for acceptance limits and corrective actions.

9.5 LABORATORY CONTROL SAMPLES

A matrix-specific laboratory control sample (LCS) is analyzed per batch of 20 field samples. It is Paragon's practice to also analyze a laboratory control sample

duplicate (LCSD) per batch of 20 field samples. LCS (LCSD) samples are analyzed to evaluate the efficiency of the method performed. See QC Table for acceptance limits and corrective actions.

9.6 MATRIX SPIKE(S)
A matrix spike (MS) and matrix spike duplicate (MSD) sample are analyzed to evaluate the effect of the matrix. Additional sample volume of client samples is needed to perform these analyses. The frequency of the MS/MSD shall be one pair per batch of 20 field samples, assuming adequate volume has been provided. See QC Table for acceptance limits and corrective actions.

9.7 METHOD DETECTION LIMIT (MDL) STUDY
The MDL study shall consist of the analysis of a minimum of seven replicate analyses for a target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at a minimum, annually, following the guidance of SOP 329.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW8260B. Alternate quantitation ions may be used to limit or eliminate common interferences caused by co-elution of standards or matrix contributions.

EPA METHOD 624 REQUIREMENTS
Suggested surrogates and internal standards are listed in EPA 624, Table 3. Paragon uses the same surrogates and internal standards for both Methods SW8260B and EPA 624 as follows: ISs - fluorobenzene, chlorobenzene-d_5, 1,4-dichlorobenzene-d_4; SSs - toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4 and dibromofluoromethane. Two of each of the SSs and ISs listed above are included in EPA 624, Table 3.

Method EPA 624 states that the concentration of the surrogate spike used should be 30µg/L; Paragon typically uses a 50µg/L concentration surrogate spike.

EPA 624 states specific adsorbent trap and purge & trap conditions, and chromatographic columns and conditions, as well as mass spectrometer conditions to be used in the execution of the method (i.e., specific purge time, use of a packed column, and scanning conditions tailored for packed column use). Some of these materials, apparatus, and conditions have been eclipsed by technology as described in this SOP. Note that Section 8.1.2 of Method EPA 624 provides for the use of technological advances so long as the precision and accuracy requirements put forth by the Method can be achieved.

Method EPA 624 requires at least three points in the ICAL; Paragon quantitates from a 5-to-7-point curve to meet compliance requirements for Method SW8260B. This approach also meets compliance requirements for EPA 624, as more than three points are used to calibrate.

Method EPA 624 states that if the %RSD of the average response factor is less than 35%, then an average response factor may be used. Otherwise, construct a linear curve with a correlation coefficient greater than 0.995. Paragon follows the calibration criteria discussed previously in the SOP.

EPA 624 specifies that the BFB tune period is 24 hours. Paragon follows the procedure as discussed in SW8260B, which specifies that BFB criteria must be passed every 12 hours.

Method 624 states that a continuing calibration verification (CCV) must be performed every working day (i.e., every 24 hours). Paragon observes a criterion that a CCV must be performed every 12 hours. Method 624 also requires that the results of the CCV must meet the requirements set forth in Table 5 of the Method, and that any compounds without limits in this Table must have their recovery reported, but corrective actions are not required.

EPA 624 states that a matrix spike (MS) and laboratory control spike (LCS) must be performed per every 20 samples. The native sample only needs to be spiked once; a matrix spike duplicate (MSD) sample is not required. EPA 624 also states that the matrix spikes and laboratory control (blank) spikes must meet the acceptance criteria listed in Table 5 of the Method (note that not all compounds have acceptance limits in this Table; for these compounds, the recovery must be reported, however, corrective actions based on those results are not required). Furthermore, EPA 624 discusses matching each compound's spike amount with the amount of the compound in the samples chosen for spiking, and also matching the spike amount to the appropriate regulatory level for each compound. Because samples from several sites are usually batched together, it is Paragon's practice to use only one spiking level is for each compound.

Method EPA 624 states that a set of 4 QC Check samples must be analyzed by an analyst before any samples are processed to demonstrate the ability to perform the method. The concentrations of each compound must be 20µg/L, and the results must fall within the acceptance criteria specified in Table 5 of the method. Paragon does observe Demonstration of Capability (DOC) requirements, but at the spike levels presented in the SOP and requiring that the results must meet the laboratory's LCS criteria established for the procedure (based on SW-846 guidance).

11. REFERENCES

11.1 Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water, Method 524.2, USEPA, Office of Research Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.

11.2 40 CFR, Part 136, Appendix A, 7-1-86 Edition, Method 624.

11.3 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry", Revision 2, December 1996.

11.4 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Method 5030C, "Purge And Trap For Aqueous Samples", Revision 3, May 2003.

11.5 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Method 5035A, "Closed System Purge And Trap And Extraction For Volatile Organics in Soil And Waste Samples", Revision 1, July 2002.

11.6 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Method 8000C, "Determinative Chromatographic Separations", Revision 3, March 2003.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

12.1.2 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

12.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.5 All flammable compounds must be kept away from ignition sources.

12.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

12.1.7 All compressed gas cylinders must be secured at all times a regulator is in place. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

12.1.8 Food and drink are prohibited in all lab areas

12.2 WASTE DISPOSAL

12.2.1 The aqueous phase of the purge & trap waste shall be disposed of in the aqueous lab waste stream. A satellite waste collection vessel may be obtained from the Waste Manager.

12.2.2 The solid phase of the purge & trap waste shall be disposed of in the contaminated soils and solids waste stream. A satellite waste collection vessel may be obtained from the Waste Manager.

12.2.3 Solvent wastes must be disposed of in the appropriate waste containers.

12.2.4 Any rinse waters used for rinsing syringes or other devices prior to sample contact may be disposed of as Aqueous Lab Waste.

12.2.5 Any methanol, hexane or other non-halogenated organic solvents that has not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Non-halogenated Waste.

12.2.6 All empty solvent bottles are disposed of according to the appropriate SOPs (003, 015). Please note that all labels and markings must be defaced prior to disposal.

DOCUMENT REVISION HISTORY

2/8/07: Reference to instrument printout used as run log included in HEADER. SECTION 3 LIMS program specification language strengthened. Reorganized STANDARDS and ANALYSIS Sections, updated format, method quantitation ions defined as guidelines. Revamped QC Section and Table. Expanded SAFETY, HAZARDS & WASTE DISPOSAL Section. Added DOCUMENT REVISION HISTORY Section.

TABLE 2

CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

TARGET ANALYTE	PRIMARY CHARACTERISTIC ION(S)	SECONDARY CHARACTERISTIC ION(S)
dichlorodifluoromethane	85	87
chloromethane	50	52
vinyl chloride	62	64
bromomethane	96	94
chloroethane	64	66
trichlorofluoromethane	101	151, 153
acrolein	56	55, 58
1,1-dichloroethene	96	53, 61
1,1,2-trichloro-1,2,2-trifluoroethane	101	103, 151, 153
acetone	58	43
iodomethane	142	127, 141
carbon disulfide	76	78
methylene chloride	84	86, 49
trans-1,2-dichloroethene	96	61, 98
methyl tertiary butyl ether	73	57
acrylonitrile	53	52, 51
1,1-dichloroethane	63	65, 83
vinyl acetate	43	86
cis-1,2-dichloroethene	96	61, 98
2-butanone	43	72
bromochloromethane	128	49, 130
chloroform	83	85
1,1,1-trichloroethane	97	99, 61
2,2-dichloropropane	77	97
carbon tetrachloride	117	119
1,1-dichloropropene	75	110, 77
1,2-dichloroethane	62	98
benzene	78	52, 77
trichloroethene	95	97, 130, 132
1,2-dichloropropane	63	112
dibromomethane	93	95, 174
bromodichloromethane	83	85, 127
2-chloroethyl vinyl ether	63	65, 106
cis-1,3-dichloropropene	75	77, 39
4-methyl-2-pentanone	43	58, 85, 100
toluene	91	92
trans-1,3-dichloropropene	75	77, 39

TABLE 2

CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

TARGET ANALYTE	PRIMARY CHARACTERISTIC ION(S)	SECONDARY CHARACTERISTIC ION(S)
1,1,2-trichloroethane	83	85, 97
2-hexanone	43	58, 57, 100
tetrachloroethene	164	129, 131, 166
1,3-dichloropropane	76	78
dibromochloromethane	129	127
1,2-dibromoethane	107	109, 188
1-chlorohexane	91	55, 93
chlorobenzene	112	77, 114
1,1,1,2-tetrachloroethane	131	133, 119
ethylbenzene	91	106
m- + p-xylene	106	91
o-xylene	106	91
styrene	104	78
bromoform	173	175, 254
isopropylbenzene	105	120
1,2,3-trichloropropane	110	75, 77
1,1,2,2-tetrachloroethane	83	131, 85
bromobenzene	156	77, 158
n-propylbenzene	91	120
2-chlorotoluene	91	126
1,3,5-trimethylbenzene	105	120
4-chlorotoluene	91	126
tert-butylbenzene	119	91, 134
1,2,4-trimethylbenzene	105	120
sec-butylbenzene	105	134
1,3-dichlorobenzene	146	111, 148
p-isopropyltoluene	119	134, 91
1,4-dichlorobenzene	146	111, 148
n-butylbenzene	91	92, 134
1,2-dichlorobenzene	146	111, 148
1,2-dibromo-3-chloropropane	75	155, 157
1,2,4-trichlorobenzene	180	182, 145
hexachlorobutadiene	225	223, 227
naphthalene	128	
1,2,3-trichlorobenzene	180	182, 145
trans-1,4-Dichloro-2-butene	53	88, 75
1,1,1,2-tetrachlorobenzene	131	133, 119
1,4-dioxane	88	58, 43, 57

TABLE 2

CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

TARGET ANALYTE	PRIMARY CHARACTERISTIC ION(S)	SECONDARY CHARACTERISTIC ION(S)
acetonitrile	41	40, 39
allyl chloride	76	41, 39, 78
chloroprene	53	88, 90, 50
cis-1,4-dichloro-2-butene	75	53, 77, 124
ethanol	45	46, 43
ethyl methacrylate	69	41, 99, 86
ethyl-tert-butyl ether	59	87, 57, 41
hexachloroethane	201	166, 199, 203
isobutyl alcohol	43	41, 42, 74
isopropyl ether	45	43, 87, 59
methacrylonitrile	41	67, 39, 52
methyl methacrylate	69	41, 100, 39
pentachloroethane	167	130, 132, 165
propionitrile	54	52, 55, 40
tert-amyl methyl ether	73	87, 55, 71
tert-butanol	59	41, 57, 43
1,2-dichloroethane-d_4 (SUR)	65	
toluene-d8 (SUR)	98	
4-bromofluorobenzene (SUR)	95	174, 176
dibromofluorobenzene (SUR)	113	
chlorobenzene-d_5 (IS)	82	117
1,4-dichlorobenzene-d_4 (IS)	152	115,150
1,4-difluorobenzene (IS)	114	
fluorobenzene (IS)	96	70

Analytical Method: 8260B, EPA 624	**Parameter:** Volatile Organic Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
Tuning Criteria	Every 12 hour period	BFB abundance criteria (Table 1) must be met	Re-tune. Do not proceed with analysis until tune meets criteria.
Initial Calibration (ICAL)	When CCCs and/or SPCCs in the daily calibration do not meet criteria or following major instrument maintenance	CCC: ≤30% RSD; SPCC RFs ≥0.10: chloromethane, 1,1-DCA, bromoform SPCC RFs ≥0.30: chlorobenzene, 1,1,2,2-tetrachloroethane Ave RF may be used if: non-CCC s are ≤15% RSD r^2 for regression (or quadratic) curve fit must be ≥0.99; a quadratic curve may be used if 6 or more data points are used	For CCCs and SPCCs, evaluate/correct instrument malfunction (if any), reanalyze ICAL
Initial Calibration Verification (ICV): different source than that of ICAL standards	Following every ICAL	Measured concentrations of all analytes should be within 25% of expected concentrations. Sporadic failures of up to 50% allowed for up to three analytes IS retention times <30 seconds drift from mid-point in most recent ICAL IS areas –50 to +100% of corresponding internal standard area in the mid-point of the most recent ICAL	Re-analyze ICV. If still out, evaluate/correct instrument malfunction as needed; perform a new ICAL
Continuing Calibration Verification (CCV); at or near mid-point	Every 12-hour period following tune, if ICAL not performed. Required for quantitating all samples analyzed during the 12 hour sequence	CCC: ±20 %D SPCC: same requirements ICAL Measured concentrations of all non-CCC analytes should be within 20% of expected concentrations. Sporadic failures of up to 50% allowed for up to three analytes IS retention times <30 seconds drift from mid-point in most recent ICAL IS areas –50 to +100% of corresponding internal standard areas in the mid-point of the most recent ICAL	Re-analyze the daily standard. If failure repeats, evaluate/correct instrument malfunction; perform a new ICAL NOTE: Recoveries that are high and outside of the stated acceptance criteria may be acceptable in some programs if the analyte that is high was not detected in the associated samples.

Analytical Method: 8260B, EPA 624	**Parameter:** Volatile Organic Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
Method Blank (MB)	Every 12-hour period; after each calibration/check and 1 per batch of 20 samples of like matrix	< ½ RL for all target compounds, except common laboratory contaminants (e.g., acetone, 2-butanone, methylene chloride), which are allowable to the RL	Re-analyze to determine if instrument contamination was the cause. If MB is still non-compliant, correct the problem and obtain a successful MB analysis before resuming analysis of samples. NOTE: Reporting of samples associated with MBs that yield contaminants may permitted by some program specifications or at the client's discretion. Example: Toluene in MB at RL but not detected in any sample above the MDL. In this case, document occurrence and resolution using a Nonconformance Report (NCR), SOP 928.
Surrogates (SS)	Every standard, client sample and QC sample	See laboratory or other applicable limits; recoveries should be within these limits	If non-compliant, check calculations and spike preparation for errors; correct as needed. If no errors are found, sample may be reanalyzed once (note that reanalysis may be fulfilled by existing multiple analyses - e.g., duplicate, spike duplicate, dilution). If still non-compliant, report results and narrate. NOTE: Per program specifications, surrogate recovery that is high and outside of acceptance criteria, with no associated target compounds detected, may not require reanalysis.
Internal Standard (IS)	Every standard, client sample and QC sample	Average area within -50% to +100% window of corresponding daily calibration verification standard area RT shift <30 seconds compared to daily standard (STD50); relative retention time (RRT) of sample must be ± 0.06 RRT units of standard	Inspect instrument for malfunction, correct. Sample may be reanalyzed (note that reanalysis may be fulfilled by existing multiple analyses - e.g., duplicate, spike duplicate, dilution). If out-of-limit areas are explained by the sample matrix (e.g., high hydrocarbon content contributes to IS areas), reanalysis is not required. Narrate.
Matrix Spike (MS)	1 per batch of 20 samples of like matrix	See laboratory or other applicable limits; recoveries for the spiked compounds should be within these advisory limits	If non-compliant, check calculations and spike preparation for errors; correct as needed. If no errors are found, and the associated LCS is within control limits, then sample matrix effects are the most likely cause. Narrate.
Matrix Spike Duplicate (MSD) or Duplicate	1 per batch of 20 samples of like matrix	See laboratory or other applicable limits; recoveries for the spiked compounds should be within these advisory limits	If non-compliant, check calculations for errors. If significant differences exist between the duplicate results, consult with Department Manager (reanalysis of the sample and spikes may be

Analytical Method: 8260B, EPA 624	**Parameter:** Volatile Organic Compounds		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
		RPDs for the spiked compounds should also be within advisory limits	necessary, or sample inhomogeniety may be the likely cause).
Laboratory Control Sample (LCS) or Duplicate	1 per batch of 20 samples of like matrix; typically the LCSD is analyzed when matrix spikes are not performed	See laboratory or other applicable limits; recoveries for the spiked compounds should be within these limits NOTE: When the full list of compounds is spiked, the laboratory will accept a small number of sporadic marginal exceedances, based on the probability that a certain number of compounds will exceed their control limits. Exceedances must be sporadic and marginal, systematic or gross failures shall not be accepted.	If non-compliant, check calculations and spike preparation for documentable errors; correct as needed. If no errors are found, then re-analyze to determine if instrumental conditions was the cause. Notify the Supervisor and initiate corrective action (NCR). Re-analyze associated samples, if appropriate. Note that recoveries that are high and outside of acceptance criteria may be acceptable, when the same target compound is not detected in any sample in the batch. Narrate.
Method Detection Limit (MDL) Study	At minimum, annually	Value must be < reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. Consult with Quality Assurance Manager - reporting limit may be adjusted if needed.

Must Discard 30 Days from _____ (date printed)

ALS LABORATORY GROUP - FORT COLLINS
STANDARD OPERATING PROCEDURE 603 REVISION 11

TITLE: **EXTRACTION OF HYDROCARBONS FROM SOIL AND WATER SAMPLES**

FORMS: **602** (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2.12.09

QUALITY ASSURANCE MANAGER _____ DATE 2/12/09

LABORATORY MANAGER _____ for KDC DATE 2/12/09

HISTORY: Rev0, 1/7/92; Rev1, 2/12/93; Rev2, PCN #74, 1/6/94; Rev3, 2/17/95; Rev4, 6/10/96; Rev5, 10/15/01; Rev6, 3/1/02; Rev7, 3/19/03; Rev8, 5/28/04; Rev9, 2/27/06; Rev10, 11/20/07; Rev11, 2/12/09.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes ALSLG-FC's in-house procedures used to extract Diesel Range Organics (DRO) and other extractable organic matter, from aqueous and solid matrices. Environmental samples prepared by this procedure may be subsequently analyzed via SW-846 Method 8015 or other State-specific procedure. Per SW-846 Method 3580A, high concentration organic liquid samples may be diluted (i.e., not extracted) then analyzed.

NOTE: Where DRO preparation and analysis are specified via California-LUFT (Cal Luft) procedures, this SOP is not relevant. For water samples extracted per Cal Luft field manual procedures, refer to SOP 626, Separatory Funnel Extraction. Soil samples for Cal Luft are extracted per the procedure in the field manual.

2. SUMMARY

Environmental and laboratory quality control (QC) samples are extracted with hexane. A methanol-water solution is used as a wetting agent to assist in the extraction of solid matrix samples. Solid samples are prepared by tumbling using a TCLP-type rotary tumbler, followed by centrifuging. Aqueous samples are prepared by manual shaking, followed by settling. Sodium sulfate is dissolved in all aqueous samples to help salt-out target compounds. The hexane layer, which rises to the top of each prepared sample, is drawn off and placed in a labeled extract vial. The extracts are delivered to the Fuels Group and stored in the designated refrigerator.

3. RESPONSIBILITIES

3.1 It is the responsibility of the individual performing this procedure to prepare the samples according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing

these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 ALSLG-FC's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALSLG-FC's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors, and documentation of measures taken to correct these errors.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the preparation or analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences upon analysis. Only scrupulously cleaned glassware and reagent grade (or better) chemicals and pesticide grade (or better) solvents may be used. These materials and the analytical system must be demonstrated to be free from interferences by the preparation and analysis of method blanks.

5. APPARATUS AND MATERIALS

5.1 sample vials with screw-tops, 40mL or other suitable size, glass, disposable

5.2 volumetric flasks, 100-200mL, glass, dedicated for petroleum hydrocarbon (DRO) preparation and kilned

5.3 solvent dispensers, pump-style or equivalent

5.4 laboratory balance capable of weighing to 0.01g, and verified per SOP 305

5.5 syringes, plastic, 60mL, disposable

5.6 syringes, glass, 1.0mL or equivalent

5.7 Pasteur pipets, glass, disposable

5.8 centrifuge

5.9 rotary tumbler, TCLP-type or equivalent

5.10 metal spatulas, kilned

6. SOLVENTS AND REAGENTS - Only reagent grade (or better) chemicals and pesticide residue grade (or better) solvents shall be used.

6.1 organic-free deionized (DI) water, obtainable from the laboratory's DI water system

6.2 hexane (C_6H_{14})

6.3 methanol (CH_3OH)

6.4 acetone (CH_3COCH_3)

6.5 sodium sulfate (Na_2SO_4), kilned

6.6 Ottawa sand, or equivalent, kilned

6.7 methanol:water solution (80/20 $^{v}/_{v}$): Prepare by mixing 4 parts methanol with 1 part DI water.

6.8 surrogate and spiking solutions: Prepared by the Fuels Group. See SOPs 406 and 300 for preparation, handling, storage and documentation details. These solutions are prepared in acetone.

NOTE: Allow all surrogate and spiking solutions to come to room temperature before use.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 All samples should be collected using an appropriate sampling plan.

7.2 Samples should be collected in glass containers with Teflon-lined lids.

7.3 Unpreserved water samples must be extracted within 7 days of collection. Usually, a 7-day holding time is observed for aqueous samples preserved with hydrochloric acid (HCl). However, some State programs may allow a 14-day to extraction holding time.

7.4 Solid matrix samples must be extracted within 14 days of collection (sooner if client specifications dictate).

8. PROCEDURES

NOTE: All abnormal conditions or odors **must** be noted on the benchsheet (Form 602). Examples of notable items include: extremely wet or rocky samples, large amounts of solids in water samples, presence of free product, hydrocarbon odor, and formation of emulsions during extraction. **Consult**

the Department Manager regarding difficult, unusual matrices.

8.1 EXTRACTION OF SOLID SAMPLES

8.1.1 Decant and discard any water layer. Mix sample thoroughly, especially composited samples. Discard any foreign objects (e.g., sticks, leaves, rocks) or any portion of the sample that appears to *not* be representative of the sample. The sample must be well-mixed to ensure that a representative sub-sample is obtained.

8.1.2 For each environmental sample, weigh approximately 20g of representative sample into a labeled 40mL glass vial with a screw-top cap. Record the weight on the benchsheet (Form 602). If sufficient sample volume was provided, choose one sample (per batch of twenty or fewer client samples) and measure a total volume of three aliquots, subdividing this volume into three labeled 40mL glass vials to serve as the sample and MS/MSD pair. This technique will help to ensure sample homogeneity.

8.1.3 For each batch of twenty (or fewer) client samples processed, prepare one solid matrix method blank (MB), and a solid matrix laboratory control sample (LCS). Note that ALSLF-FC typically also prepares a laboratory control sample duplicate (LCSD) per batch. For each of these QC samples, measure approximately 20g of kilned Ottawa sand into a 40mL glass vial with a screw-top cap. Label the vials as the MB, LCS, and LCSD.

8.1.4 Add the appropriate amount of surrogate solution (typically 1.0mL) to each prepared vial of environmental and QC sample.

NOTE: Use acetone as the solvent rinse for the syringe.

8.1.5 Add the appropriate amount of petroleum hydrocarbon (DRO) spiking solution (typically 1.0mL) to each of the LCS, LCSD, MS and MSD samples.

8.1.6 Add 20mL methanol:water solution to each environmental and QC sample.

8.1.7 Add 5.0mL of hexane to each environmental and QC sample.

8.1.8 Tightly cap each prepared sample vial and pack (with cushioning) into large plastic containers for rotary tumbling. Tumble for about 45 minutes.

8.1.9 Remove the sample vials from the tumbler and centrifuge for 4-10 minutes to separate the phases. To ensure vial integrity, the centrifuge speed must not exceed 1400 RPM – centrifuging at higher speeds risks

breakage.

If the phases do not separate, then centrifuge in subsequent 4-10 minute intervals until separation does occur, or use other mechanical or physical techniques to break the emulsion. Adding sodium sulfate to the top of the emulsion and subsequently centrifuging the sample will frequently break the emulsion as the sodium sulfate is "pulled through" it. Other approaches include freezing the emulsion or filtering through glass wool or sodium sulfate. Consult with Department Supervisor.

8.1.10 For each sample, use a clean disposable glass pipet to carefully transfer most of the top hexane layer into an appropriately labeled extract vial. Avoid transferring any solid material. **Total recovery of the hexane layer is not required because the concentration of target and surrogate compounds is assumed to be consistent throughout the hexane layer.** Cap the extract vial tightly.

8.1.11 Observing internal chain-of-custody procedures (SOP 318), deliver the extractable petroleum hydrocarbon extracts to the Fuels Group for storage and analysis.

8.2 EXTRACTION OF AQUEOUS SAMPLES

8.2.1 Kilned, dedicated volumetric flasks are used for extraction of aqueous petroleum hydrocarbon (DRO) samples. Note that because a plastic syringe is used for quantitative measurement of the sample aliquot, these flasks are *not* used in a volumetric capacity.

Assemble a sufficient number of flasks and cover the bottom of each with a layer of kilned sodium sulfate (Na_2SO_4). Label each flask with the appropriate sample number.

8.2.2 Mixing each aqueous sample prior to taking an aliquot is necessary in order to ensure that the aliquot is representative. For each client sample, use a clean 60mL plastic syringe to deliver 160mL of representative sample into the flask designated for that sample. If sufficient sample volume is present, choose one sample (per batch of twenty or fewer client samples) and measure two additional aliquots of sample (one each) into two labeled flasks to serve as the MS/MSD pair.

8.2.3 For each batch of twenty (or fewer) client samples processed, prepare one aqueous matrix method blank (MB) and an aqueous matrix laboratory control sample (LCS). Note that ALSLG-FC typically also prepares a laboratory control sample duplicate (LCSD) per batch. Use a (single) clean 60mL plastic syringe to measure a total volume of 160mL DI water into each volumetric flasks labeled as the MB, LCS and LCSD.

8.2.4 Add the appropriate amount (typically 0.8mL) of surrogate solution to each prepared flask of environmental or QC sample.

NOTE: Use acetone as the solvent rinse for the syringe.

8.2.5 Add the appropriate amount (typically 0.8mL) of petroleum hydrocarbon (DRO) spiking solution to each of the LCS, LCSD, MS and MSD samples.

8.2.6 Add 4.0mL of hexane to each environmental and QC sample.

8.2.7 Tightly cap each prepared sample flask and manually shake each one for two minutes. Allow the contents to settle. If an emulsion forms, transfer the sample to a suitable labeled vial and centrifuge. Addition of more sodium sulfate may help to break the emulsion.

8.2.8 If necessary, add enough DI water to bring the hexane layer to an accessible position in the neck of each flask.

8.2.9 For each sample, use a clean disposable glass pipet to carefully transfer most of the hexane layer from the neck of the flask into an appropriately labeled extract vial. Avoid transferring any of the aqueous layer. **Total recovery of the hexane layer is not required because the concentration of target analyte is assumed to be consistent throughout the hexane layer**.

8.2.10 Cap each extract vial tightly. Observing internal chain-of-custody procedures (SOP 318), deliver the petroleum hydrocarbon extracts to the Fuels Group for storage and analysis.

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

For this method, a preparation batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the MB, LCS, MS and laboratory duplicate (an LCSD or MSD, r both, can serve as the laboratory duplicate). All QC samples must be carried through all stages of the sample preparation and measurement steps.

9.2 METHOD BLANK

MBs are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. For this procedure, the solid matrix method blank consists of 20g of kilned Ottawa sand, and the aqueous method blank consists of 160mL organic-free DI water. See QC Table of SOP 406 for acceptance limits.

9.3 LABORATORY CONTROL SAMPLE

The LCS is analyzed to measure the accuracy of the method in a controlled matrix. A known amount of analyte is prepared and analyzed. For this method, 20g of kilned Ottawa sand (solid matrix) and 160mL organic-free DI water (aqueous matrix) are used for the LCS. See QC Table of SOP 406 for acceptance limits.

9.4 MATRIX SPIKE SAMPLE

The MS sample is analyzed to assess the effect of matrix interferences upon the sample analysis. A known amount of analyte is spiked into a replicate aliquot of a selected sample and analyzed. See QC Table of SOP 406 for acceptance limits.

9.5 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. The LCS, MS, or both may be analyzed in duplicate to serve this purpose. Precision is expressed as Relative Percent Difference (RPD). RPD calculations are discussed in SOP 406. See QC Table of SOP 406 for acceptance limits.

10. DEVIATIONS FROM THE METHOD

The extraction procedures documented in the SOP have been developed in-house and are not based on a particular published method. There are, therefore, no deviations from a promulgated method.

11. HEALTH, SAFETY, AND WASTE DISPOSAL

11.1 HEALTH AND SAFETY

11.1.1 Read the appropriate MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). **As hexane has a TLV ≤ 50ppm, the preparation steps in this procedure which require addition of hexane must be carried out in an adequately ventilated fume hood.**

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name; NFPA Health, Flammability and Reactivity ratings; and date.

11.2 WASTE DISPOSAL

11.2.1 Hexane may be disposed of in the Acetonitrile/Non-halogenated Waste

stream.

11.2.2 Aqueous sample waste shall be disposed of in one of the Aqueous Lab Waste streams (radioactive or non-radioactive, as appropriate).

11.2.3 Solid sample waste shall be air-dried and disposed of in one of the Contaminated Soils and Solids waste streams (radioactive or non-radioactive, as appropriate).

11.2.4 Extract vials and associated extracts are disposed of by the analytical group into the appropriate extract and vial waste container.

11.2.5 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 USEPA, SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Method 8015B, December 1996.

12.2 USEPA, SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, Method 8015D, June 2003.

DOCUMENT REVISION HISTORY

11/20/07: Updated LIMS program specification language Section 3.3. Revised Section 6.7 Surrogate and Spiking Solutions (removed detail and referenced SOPs 406 and 300 instead). Minor clarifications made to Section 8. Removed acceptance limits from Section 9 and referenced QC Table of SOP 406 instead. Added DOCUMENT REVISION HISTORY and Form.

2/12/09: Updated laboratory references to ALSLG-FC. Changed Title, and made DRO references more generic to accommodate alternate use of State-specific protocols. Listed acetone in reagents, and identified use of acetone for syringe rinse. Amended hexane volumes added in Section 8. Added Appendix A – FL-PRO.

APPENDIX A

HYDROCARBON EXTRACTION VIA THE FL-PRO METHOD

1. SCOPE AND APPLICATION

The procedural particulars given in this Appendix supercede the guidance given in the main body of SOP 603. The procedures depicted in this Appendix are applicable to the preparation of aqueous and solid matrix samples to be subsequently analyzed by the Florida Residual Petroleum Organic Method (FL-PRO).

2. SUMMARY

The FL-PRO Method is designed to measure concentrations of extractable petroleum hydrocarbons in water and soil in the alkane range of C_8-C_{40}. The method is based on solvent extraction, followed by GC-FID analysis. Other organic compounds, including chlorinated hydrocarbons, phenols, and phthalate esters, are measurable by this procedure, thus the resultant EPH results include these compounds.

A volume of sample is spiked with two surrogates then extracted using Methylene Chloride. The extract is concentrated, then treated with silica gel. The silica gel cleanup is a mandatory part of the procedure, designed to remove potential interferences from animal and vegetable oil, and grease and biogenic terpenes.

3. RESPONSIBILITIES
INTERFERENCES
APPARATUS AND MATERIALS
SOLVENTS AND REAGENTS

Refer to SOP 603 main text.

4. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Certain sampling considerations apply, refer to Method for more details.
Water samples must be acidified to pH<2 with HCl or H_2SO_4.
All samples must be stored at 4±2°C until extraction.
Extraction must be performed within 7 days of collection for aqueous samples, and within 14 days of collection for solid samples.
All analyses must be performed within 40 days of extraction.

5. STANDARDS

Both surrogate and spike standard is specific to this test:

5.1 Surrogate standard contains o-terphenyl at 100ug/mL, and nonatriacontane at 600ug/mL (in acetone). Note: These concentrations are 2X those specified in the Method (Section 7.4.1), which says to add 2mL of surrogate solution. ALSLG-FC will add 1mL, therefore the doubling in concentration.

5.2 Spike contains even-numbered straight-chain alkanes from C_8 to C_{40}. The water spiking solution should be 5000ug/mL Total PHS, and the soil spike should be 3000ug/mL Total PHS (Petroleum Hydrocarbon Standard). 1mL of spike will give the required concentrations in the sample.(Method Section 7.4.3, 7.4.4).

6. PROCEDURES

6.1 EXTRACTION OF SOLID SAMPLES
10g of sample is extracted by Soxhlet (SOP 625) for 18-24 hours. (Method Section 9.1.5).

6.2 EXTRACTION OF AQUEOUS SAMPLES
1L of sample is extracted with dichloromethane by CLLE (SOP 617) for 18-24 hours. (Method Section 9.1.3).

6.3 EXTRACT CONCENTRATION
Dry and concentrate the samples using KD apparatus (SOP 607) to a final volume of 2.0mL. N-Evap (SOP637) may also be used to achieve final volume of 2.0mL. If the extract is highly colored or a precipitate forms during concentration, the final volume should be higher (5-10mL)(Method Section 9.1.2.10 thru 10.1.2.16)

6.4 SILICA GEL CLEANUP
Silica gel cleanup is mandatory for this procedure. Add 0.3g of loose silica gel to the extract and shake the mixture for 5 minutes, or pass the extract through a silica gel solid-phase extraction cartridge that has been conditioned with 5mL of dichloromethane. (Method Section 9.1.6.1)

6.5 Observing internal chain-of-custody procedures (SOP 318), deliver the petroleum hydrocarbon extracts to the Fuels Group for storage and analysis.

7. QUALITY CONTROL

See SOP 603 main text.

8. DEVIATIONS FROM THE METHOD

No technical deviations.

9. HEALTH, SAFETY, AND WASTE DISPOSAL

See SOP 603 main text.

10. REFERENCES

"Method for Determination of Petroleum Range Organics (FL-PRO)", Revision 1. Florida Department of Environmental Protection. November, 1995.

DOCUMENT REVISION HISTORY

2/12/09: New

Paragon Analytics

DIESEL RANGE ORGANICS (DRO) -- EXTRACTION BENCHSHEET

WO #s _____ **Matrix:** AQ SO _____ **Batch #** _____ **Surrogate Code** _____ **M Spike Code** _____ **Initials** ___ **Balance ID** ___

Extr. Start Date/Time _____ **Stop Date/Time** _____ **Ext Code** 8015M Cal Luft **Method** 8015M Cal Luft **SOP** _____ **Rev** __ **Reviewed by / Date** _____

SAMPLE							EXTRACT		
Sample Number	Amount (g / mL)	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Extract Solvent	Solvent Volume (mL)	Final Volume (mL)	**Date Vialed**	**Comments**

Reagents: MeOH DCM 80% MeOH / 20% H_2O Prep ID/ Date Hexane Na_2SO_4 Form 602r10.doc (7/20/05)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 604 REVISION 8

TITLE: SILICA GEL CLEANUP -- METHOD SW3630C

FORMS: 605, 609 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-14-07

QUALITY ASSURANCE MANAGER _____ DATE 11/13/07

LABORATORY MANAGER _____ DATE 11-14-07

HISTORY: Rev0, 12/12/91; Rev1, PCN #75, 1/6/94; Rev2, PCN #361, 2/17/95; Rev3, 7/15/99; Rev4, 11/18/99; Rev5, 4/9/02; Rev6, 2/13/04; Rev7, 2/27/06; Rev8, 11/12/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes procedures for the cleanup of polar interferences from extracts. This procedure is adapted from SW-846 Method 3630C. This procedure is primarily used to clean up extracts intended for analysis of Polynuclear Aromatic Hydrocarbons (PAHs).

2. SUMMARY

The extract from a sample is brought to a known volume and exchanged into the appropriate solvent (see SOPs 607 and 637). The extract is eluted through a column (or cartridge) of silica gel to remove interfering contaminants. The volume of the processed extract is then reduced using Kuderna Danish apparatus, after which the extract is exchanged into appropriate solvent and/or blown down to volume. The extract is then submitted for analysis. For extract volumes of 2mL or more, only an aliquot of the extract is cleaned up, with the remainder of the extract being reserved in the event of problems occurring during the cleanup stage.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all benchsheets or other documentation required for review.

3.2 These procedures are performed in the laboratory by personnel who have demonstrated the ability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the processing of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Method SW3630B states that phthalate esters have been detected in extracts processed with solid phase extraction cartridges. Phthalate esters are not typically analyzed as part of the process described here. However, phthalate esters may interfere with subsequent analysis by UV or other detectors. A method blank shall be prepared and analyzed with each sample set to monitor this potential interference.

5. APPARATUS AND MATERIALS

5.1 buret or chromatography column with Teflon™ stopcock, 250mm length, 10mm ID, or as suitable

5.2 Erlenmeyer flasks, various sizes

5.3 beakers, various sizes

5.4 graduated cylinders, 25 and 50mL

5.5 Pasteur pipettes, glass

5.6 buret clamps or wooden funnel racks

5.7 ring stands

5.8 wooden spatula handle or equivalent (for tapping column)

5.9 top loading balance, 0.01g sensitivity

5.10 glass wool

5.11 syringes, 5mL or as needed

5.12 vacuum manifold - VacElute Manifold SPS-24 (Analytichem International) or equivalent, consisting of glass vacuum basin, collection rack, and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500mL sidearm flask fitted with a one-hole stopper and glass tubing.

6. REAGENTS - Only reagent grade or better chemicals shall be used.

6.1 silica gel cartridges, commercially prepared, Burdick and Jackson #7058G, 1g or equivalent

6.2 silica gel, 100/200 mesh, EM #SX01436-1 or equivalent
Activate in a foil-covered glass beaker at approximately 130°C for about 16hrs prior to use. Store in approximate 130°C oven when not in use.

6.3 sodium sulfate (Na_2SO_4), anhydrous, ACS granular. Purify by heating at approximately 400°C (kiln) for 2-6 hours.

6.4 SOLVENTS – **use only pesticide or HPLC grade.**

hexane	C_6H_{14}
acetone	CH_3COCH_3
methanol	CH_3OH
methylene chloride	CH_2Cl_2

7. COLUMN PROCEDURE

7.1 Collect apparatus and reagents for silica gel cleanup prior to beginning the solvent exchange (methylene chloride to hexane) process.

7.2 The solvent exchange process is described in SOP 607. Follow solvent exchange procedure, and adjust the extract volume to 2.0mL for silica gel cleanup. Decreased or increased final volume may be necessary for some extracts.

7.3 **This process must be performed in a fume hood. The dry silica gel is very fine-grained and can become airborne if not handled carefully. If inhaled, the fine particles pose a health risk.** Set up the chromatography columns as follows:

7.3.1 Plug the column with glass wool and rinse column thoroughly with methylene chloride. Leave column full and receiver 1/4 full with methylene chloride.

7.3.2 Tare a 150mL beaker on a top loading balance. Add approximately 10g of silica gel to the tared beaker. When the gel has settled in the beaker, check the weight. Add (or remove) gel to reach 10g.

7.3.3 A slurry of silica gel and methylene chloride can be made in the beaker to assist transfer to the column. Slowly pour the 10g of slurry from the beaker into the chromatography column. Rinse the beaker and column with enough methylene chloride to wash any remaining silica gel slurry into the column.

7.3.4 Place a beaker below the column. Open the stopcock on the column. Using a wooden spatula, gently tap the column to settle the silica gel slurry and remove all air. Rinse the reservoir to help settle the gel. Collect the eluting methylene chloride in a waste beaker.

7.3.5 After the silica gel slurry has settled completely, add a layer of sodium sulfate (1-2 cm thick) to the top of the column. Continue eluting the methylene chloride until the meniscus is just above the sodium sulfate layer.

7.3.6 GENERAL COMMENTS ON COLUMN LOADING AND ELUTING

- It is acceptable to stop the column flow at any time.
- It is not advisable to load and elute more than 5 samples at one time.
- If at any point during elution, the column virtually or actually stops dripping, poke the Na_2SO_4 at the top of the column with a long tipped pipette.
- All elution rates should be approximately 2 mL/min or less.
- Do not let the silica gel go dry after the rinse described in Step 7.4 below, until all eluent is collected at the end (i.e., Step 7.10).

7.4 Elute each column with 40mL hexane. Collect the eluent in a waste beaker and discard. Stop the elution when the meniscus of the hexane is just above the sodium sulfate layer.

7.5 Add the extract to the column. When the meniscus of sample is just above the sodium sulfate layer, rinse the concentrator tube with 2mL of hexane and add the rinsate to the column. Continue elution, collecting the eluent in a waste beaker.

7.6 Just prior to exposure of sodium sulfate, add 25mL hexane and continue elution.

7.7 Just prior to exposure of sodium sulfate, close stopcock to stop flow.

7.8 Position a 50mL Erlenmeyer flask beneath the column. Add 25mL of 90/10 hexane/methylene chloride and elute at a rate up to 2mL/min.

7.9 When the meniscus reaches the sodium sulfate, add 35mL of 60/40 (3:2) hexane/methylene chloride, and restart elution at a rate of up to 2mL/min.

7.10 When the column has stopped dripping, the collected fraction of the extract is concentrated to final volume as well as changed over to the final solvent per SOPs 607 and 637.

7.11 Complete benchsheets and observe proper internal chain-of-custody procedures (SOP 318) to deliver the extracts to the appropriate analytical area.

8. CARTRIDGE PROCEDURE

8.1 Place cartridge on the manifold. Condition the cartridge by eluting 5mL of methylene chloride at less than 2mL/min. flow rate into a waste tube. **Do not pull air through the cartridge after the conditioning has started, until Step 8.3 (elution) is complete.** The 2nd conditioning step is to elute 5mL hexane at less than a 2mL/min flow rate. **Do not let the silica gel in the cartridge go dry.**

8.2 Replace waste tube with a clean collection tube. Load entire extract (assuming 1 or 2mL volume) onto cartridge after exchange to hexane (described in Step 7.2). Just before the top of the cartridge goes dry, go to Step 8.3 below to elute targets.

8.3 To elute targets, add 4-5mL of 10/90 methylene chloride/hexane. When only a few millimeters of this eluting solvent remains above the gel, add 4-5mL more of 10/90 methylene chloride/hexane. When the 2nd portion of elution solvent has passed through the cartridge, the collection tube contains the cleaned up extract.

8.4 Bring the cleaned up extract to a final volume and appropriate solvent per SOPs 607 and 637.

8.5 Complete benchsheets and observe proper internal chain-of-custody procedures (SOP 318) to deliver the extracts to the appropriate analytical area.

8.6 Note that the cartridge procedure has less capacity to clean up interferences than the column procedure described in Section 7, because the cartridges contain less adsorbent material (1g versus 10g).

9. QUALITY ASSURANCE

The quality control (QC) samples associated with the sample extracts that are cleaned up using this procedure *must also* be processed through this cleanup method.

10. DEVIATIONS FROM THE METHOD

10.1 The extract is exchanged into hexane instead of cyclohexane prior to loading onto column or cartridge.

10.2 Hexane is used instead of pentane wherever referenced in SW3630. Pentane boils at very close to room temperature at Paragon's elevation.

11. SAFETY, HAZARDS AND WASTE

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 The silica gel and/or cartridges are disposed of in the Contaminated Soils and Solids waste.

11.2.2 Any hexane, acetonitrile, or other nonhalogenated organic solvents may be disposed of in the acetonitrile/Nonhalogenated waste.

11.2.3 Any methylene chloride waste may be disposed of in the halogenated solvent waste.

11.2.4 Empty solvent bottles are to be properly disposed. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, "Method 3630C", December 1996.

DOCUMENT REVISION HISTORY

11/12/07: Removed reference to SW8310 in SCOPE AND APPLICATION (Paragon no longer supports this procedure). General word-smithing and clarification. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) -- EXTRACTION & CLEANUP WORKSHEET

WO #s _____ **Matrix** AQ SO Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____ **Balance ID** ___

Ext Code 8310 E610 **Meth** (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)W Dilute **SOP** (617)CLE (647)SONC (625)SOX (626)SEP **Rev** ___ **Initials** ____

Ext Start Date _____ **Time** _____ **End Date** _____ **Time** _____ **Cleanup** (3630C) Silica Gel **SOP 604 Rev** ___ **Date** _____ **Time** _____ **Initials** ____

SAMPLE						EXTRACT / CLEANUP							
Sample No.	Amount (g /mL)	**pH**	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hexane Exchange	Date KD (Final)	Date Methanol Exchange	**A-Disk Size**	Final Volume (mL)	Vialed Date	**Comments**

Reagent Lots: MeCl, _____ Hexane _____ Methanol _____ Silica Gel _____ Na_2SO_4 _____ Reviewed by / Date _____

Form 605r5.frm (8/10/2001)

Form 609r12.doc (7/7//05)

Paragon Analytics

SEMIVOLATILES EXTRACTION / CLEANUP WORKSHEET

WO #s _____ **Matrix** ___ **Batch ID** _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** __ **Extr SOP/Rev** __ **Extr Code:** 8270C CLP SOW E625

Extr Method: (3520C)CLE (3550C)SONC (3540C)SOX (3510C)SEP (3580A)Waste Dilution **Initials** _____ **Extr Start Date/Time** _____ **Extr Stop Date/Time** _____

Cleanup Code: (3620B) Florisil (3640A) GPC (See other forms) Silica Gel **Cleanup SOP/Rev** ____ **Date/Time** _____ **Initials** _____ **Reviewed by / date** _____

SAMPLE								EXTRACT / CLEANUP					
Sample No.	Amount (g / mL)	Initial pH	**pH** (≤ 2)	**pH** (11-13)	Surrogate (mL)	Matrix Spike (mL)	Sur / Matrix Spike Witnessed	Date KD (Initial)	Cleanup Date	Date KD (Final)	Final Volume (mL)	Date Vialed	Comments

Steam bath _____ °C.

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Silica Gel _____ (See other GPC forms) H_2SO_4 _____ NaOH _____ Na_2SO_4 _____

Must Discard 30 Days from _____ (date printed)

Amended 3/17/08 to include Steam Generator Operator's Aid. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 607 REVISION 9

TITLE: **EXTRACT CONCENTRATION USING KUDERNA-DANISH APPARATUS**

~~FORMS:~~ **~~602, 604, 605, 609, 616~~ (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-12-07

QUALITY ASSURANCE MANAGER _____ DATE 11/12/07

LABORATORY MANAGER _____ DATE 11-12-07

HISTORY: Rev0, 2/13/92; Rev1, PCN #100, 1/20/94; Rev2, PCN #371, 2/17/94; Rev3, 2/18/99; Rev4, 10/25/99; Rev5, 4/6/02; Rev6, 12/5/02; Rev7, 3/6/04; Rev8, 2/27/06; Rev9, 11/12/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the drying of extracts followed by concentration using a Kuderna-Danish (K-D) apparatus and a steam bath or water bath. This procedure can also be used to exchange the extract from one solvent to another (e.g., methylene chloride to hexane).

2. SUMMARY

Extraction of samples is described in SOP 617 (Method SW3520C), SOP 625 (Method SW3540C), SOP 626 (Method SW3510C), and SOP 664 (Method SW8151A). These processes extract the water-insoluble and slightly water-soluble organic compounds from aqueous and solid samples in preparation for analysis by various determinative chromatographic procedures.

This SOP addresses the drying and concentration of extracts using a Kuderna-Danish apparatus over a steam or water bath. The extracts are dried by passing them through a column of anhydrous sodium sulfate as they are loaded into the K-D apparatus. Concentration is accomplished by using the K-D apparatus to reflux the solvent at a temperature high enough to cause excess solvent to evaporate, while collecting the organic compounds of interest in the concentrator tube attached to the bottom of the apparatus.

Final concentration of the extract using the nitrogen blowdown technique is described in SOP 637. An alternative solvent exchange procedure is also discussed in SOP 637.

3. RESPONSIBILITIES

3.1. It is the responsibility of the analyst to perform the procedure according to this SOP and to complete all benchsheets or other documentation required for review.

3.2. Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training

review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3. Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4. The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of the measures taken to correct the errors.

3.5. All personnel who work with samples involving this method have a responsibility to note any anomalies or out-of-control events associated with the processing of the samples. Any anomalies or discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1. Solvents, reagents, glassware and other hardware used in this procedure may yield artifacts and/or interferences to sample analysis. Refer to SOP 334 for guidance on glassware cleaning.

4.2. Phthalate esters are present in many types of products commonly found in the laboratory. In particular, samples and sample extracts must not be allowed to come into contact with plastics and latex products, as phthalates are easily extracted from these materials. Phthalate contamination may result if such contact occurs.

5. APPARATUS AND MATERIALS

5.1. Kuderna-Danish (K-D) apparatus consisting of the following:

concentrator tube, graduated, 10mL or other appropriate size

evaporation flask, attached to concentrator tube with a clip, 500mL or other appropriate size

macro Snyder column, 3-ball

5.2. funnels, steel or borosilicate glass

5.3. glass wool, solvent-rinsed

5.4. boiling chips, Teflon™ or silicon carbide, solvent-rinsed, approximately 10/40 mesh

5.5. Pasteur pipets, borosilicate glass, disposable

5.6. steam bath, Organomation S-Evap Model 120 or equivalent

5.7. steam generator, Chromalox Model CM13-9 or equivalent

5.8. glass syringes, 1mL or as appropriate

5.9. vials, glass, with PTFE-lined caps of appropriate size

6. REAGENTS - Only reagent grade or better chemicals shall be used.

6.1. Sodium sulfate (Na_2SO_4), granular. Purified at approximately 400 °C (kilned) for 2-4 hours in a shallow tray. The sodium sulfate and scoop are kept in a closed container to prevent contamination.

NOTE: Take care to check specific tests being performed. Some extraction processes require use of acidified sodium sulfate to avoid loss of target analytes. Examples are Methods SW8151A, EPA 615 or EPA 515.1.

6.2. SOLVENTS - **All solvents must be pesticide residue grade or equivalent**

methylene chloride (CH_2Cl_2)

hexane (C_6H_{14})

acetonitrile (CH_3CN)

methanol (CH_3OH)

7. PROCEDURE

7.1 Assemble a Kuderna-Danish concentrator by attaching a 10mL concentrator tube to a 500mL evaporative flask with a clip. Drop one or two prepared boiling chips into the concentrator tube. Boiling chips are necessary to keep the solvent from "bumping".

7.2 Prepare a drying column for each extract by placing a plug of prepared glass wool in the neck of a funnel. Pour a layer of prepared sodium sulfate on top of the glass wool so that the funnel is approximately ½ full.

7.3 Rinse the sodium sulfate drying column thoroughly with methylene chloride (or the appropriate extraction solvent, if other) and discard this rinse. Three rinses with 20-30mL of solvent are typical of this process.

7.4 Prior to pouring the sample through the drying column, look for the presence of water in the round bottom flask containing the extract. If it appears that there is water in the extract, add more sodium sulfate to the funnel and swirl prior to pouring the extract through the column.

7.5 Place a rinsed drying column into the upper opening of the K-D setup and slowly pour the extract through the sodium sulfate. After all of the extract is poured through the drying column, rinse the round bottom flask or other glassware containing the extract three times with 5-10mL methylene chloride (or other appropriate extraction solvent), and pour these rinses through the drying column. The three rinses are to ensure quantitative transfer of the extract to the Kuderna-Danish apparatus. Rinse the funnel with additional methylene chloride (or other appropriate solvent) and pass the rinse through the drying column.

NOTE: During this process, monitor the condition of the sodium sulfate to determine that the bed of sodium sulfate is not solidifying and exceeding its drying capacity. If the sodium sulfate bed can be stirred and is still free flowing, effective moisture removal from the extracts is occurring. If the sodium sulfate bed has begun to "cake", do not add more extract. Prepare another drying column as described above, re-dry the contents of the K-D flask, and continue drying the extracts.

7.6 Remove the funnel, pour the sodium sulfate contents onto a piece of foil located in a fume hood, and allow to dry.

7.7 Wet a 3-ball Snyder column with 1-2mL methylene chloride (or other appropriate solvent) poured through the top of the column. Repeat the rinse. Attach the 3-ball Snyder column to the K-D apparatus.

7.8 Place the K-D apparatus on the S-Evap so that the concentrator tube is completely in the S-Evap and the entire rounded lower surface is bathed with hot vapor from the steam generator.

7.9 Adjust the steam per manufacturer settings so that the proper rate of distillation is achieved. At the proper rate of distillation, the balls in the column will actively chatter, but the chambers will not flood.

7.10 When the apparent volume of the extract reaches 4-5mL, and if no solvent changeover is needed, remove the K-D apparatus from the S-Evap and allow it to drain and cool for at least 10 minutes with the 3-ball Snyder column in place.

NOTE: If extract volume cannot be reduced to an apparent volume of 4-5mL in a reasonable amount of time, the K-D procedure should be stopped as little or no solvent is likely remaining in the K-D apparatus. Target compounds may be lost if continued heating takes place and no solvent is left in the apparatus. A final volume of 10mL or greater is likely to be necessary if this occurs. Record on the benchsheet why the extract could not be further concentrated. Consult with the Extractions Group Leader or the Department Manager if other questions arise.

7.11 If solvent exchange is required at this point, dispense 20-50mL of the exchange solvent (5-10 times the volume of the extract in the concentrator tube is required for a successful exchange) through the Snyder column while the concentrator remains on the bath. Again concentrate the extract, raising the temperature of the S-Evap, if necessary, to maintain proper distillation. Exchange solvents that are typically used are listed in **Table 1**. Remove the K-D apparatus from the S-EVAP and allow to drain and cool for 10 minutes with the Snyder column in place.

7.12 After cooling, wipe any water remaining around the lower joint using an absorbent towel or Kim-Wipe™. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2mL of methylene chloride or other appropriate solvent to ensure quantitative transfer of the material from the flask to the concentrator tube. Remove the plastic clip and detach the concentrator tube.

7.13 If a desired final volume below 5-10mL is needed, proceed using the nitrogen blowdown procedure (SOP 637). Nitrogen blowdown is generally not needed for methods where final extract volume is 10mL, (e.g., Methods SW8081 and SW8082). For these methods, the extract is brought to final volume during the quantitative transfer to a glass vial, which is then capped with a PTFE-lined screw cap. The extracts are then delivered to the appropriate analytical group for refrigerated storage. Internal chain of custody procedures (SOP 318) must be observed.

8. QUALITY ASSURANCE

8.1 All sample extracts and associated quality control sample extracts must be processed in the same manner using this procedure.

8.2 Re-extraction of the sample may be warranted if any of the following should occur:

The extract is concentrated to dryness.

The extract is found to contain both water and the extraction solvent after concentrating due to a loose connection between the concentrator tube and the K-D flask.

The extract is concentrated too rapidly (excessively high temperature). This may cause target analyte loss.

More than 1% of the extract is spilled while pouring through sodium sulfate.

8.3 If re-extraction is not possible due to extenuating circumstances (i.e., no sample remaining, past holding time), the extract should be kept and the benchsheet noted accordingly. Notify the Department Manager and the Project Manager so that the client can be apprised of the situation immediately, and initiate a Non-Conformance Report (NCR) per SOP 928 immediately.

9. DEVIATIONS FROM THE METHOD

This SOP meets the requirements of SW-846 Chapter 4 methods. There are no known deviations from the methods referenced in this procedure (SW3510C, SW3520C, SW3540C, SW8151A).

10. SAFETY, HAZARDS AND WASTE DISPOSAL

10.1 SAFETY AND HAZARDS

10.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

10.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

10.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). **Since methylene chloride, hexane and acetonitrile have TLVs ≤ 50ppm; the work described in this procedure must be carried out within an adequately ventilated fume hood.**

10.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

10.1.5 High-pressure steam presents severe burn hazards to humans. If it comes into contact with human tissue, the steam will rapidly cool and condense and in the process will deposit 550 calories of heat per gram of steam into the tissue. This can result in a very severe burn. **Use extreme care around sources of steam to prevent a steam burn.**

10.2 WASTE DISPOSAL

10.2.1 Hexane, acetone, or other nonhalogenated organic solvents may be disposed of in the Acetonitrile/Nonhalogenated Waste.

10.2.2 Dichloromethane (methylene chloride) is disposed of in the Halogenated Organic Waste satellite collection vessel.

10.2.3 Disposal of sample wastes are discussed in the appropriate extraction SOP.

10.2.4 The analytical groups responsible for analysis of the extracts shall dispose of the extracts and extract vials via the appropriate waste streams.

10.2.5 All empty solvent bottles shall be disposed of appropriately. Note that all labels and markings on solvent bottles must be defaced prior to disposal.

10.2.6 Dried sodium sulfate and glass wool are disposed of in the contaminated

soils and solids satellite area bucket.

11. REFERENCES

11.1 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3510C.

11.2 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3520C.

11.3 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3540C.

11.4 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 8151A.

DOCUMENT REVISION HISTORY

11/12/07: Minor clarifications. Updated LIMS program specification language Section 3.3. Added DOCUMENT REVISION HISTORY and Forms.

Table 1
Typical Extraction and Exchange Solvents

Analytical Method	Extraction Solvent	Exchange Solvent for Cleanup	Exchange Solvent for Analysis
8015 (CaLuft)	methylene chloride	methylene chloride for Paragon Si-Gel	methylene chloride
8081	methylene chloride	methylene chloride for SW 3640 GPC hexane for SW 3630 florisil	hexane
8082	methylene chloride	hexane for SW 3665 Sulfuric Acid	hexane
8141	methylene chloride	methylene chloride for SW 3640 GPC	hexane
8151	diethyl ether		hexane or diethyl ether
8270	methylene chloride	methylene chloride for SW 3640 GPC methylene chloride for Paragon Si-gel	methylene chloride
8310	methylene chloride	hexane for SW 3630 Si-gel methylene chloride for Paragon Si-gel	acetonitrile or methanol

Paragon Analytics

DIESEL RANGE ORGANICS (DRO) -- EXTRACTION BENCHSHEET

WO #s _____ **Matrix:** AQ SO _____ **Batch #** _____ **Surrogate Code** _____ **M Spike Code** _____ **Initials** ___ **Balance ID** ___

Extr. Start Date/Time _____ **Stop Date/Time** _____ **Ext Code** 8015M Cal Luft **Method** 8015M Cal Luft **SOP** _____ **Rev** __ **Reviewed by / Date** _____

SAMPLE							EXTRACT		
Sample Number	Amount (g / mL)	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Extract Solvent	Solvent Volume (mL)	Final Volume (mL)	**Date Vialed**	**Comments**

Reagents: MeOH DCM 80% MeOH / 20% H2O Prep ID/ Date Hexane Na2SO4 Form 602r10.doc (7/20/05)

Paragon Analytics

HERBICIDE EXTRACTION / CLEANUP BENCHSHEET

WO #s _____ **Matrix** AQ Solid Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____

Extraction: Code 8151A E615 E515 **Method** (3540C)SOX (3510C)SEP (3580A)WDilute **SOP** ___ **Rev** ___ **Initials** _____ **Was glass wool & Na_2SO_4 acidified?** Y N

Balance ID ____ **Cleanup Code** (3640A)GPC (see other forms) (3620B)Florisil **SOP** 641(GPC) 648(Florisil) **Rev** ___ **Florisil Lot No.** _____ **Initials** _____

Extraction Start Date _____ **Time** _____ **Extraction End Date** _____ **Time** _____ **Reviewed by / date** _____

$MeCl_2$ _____ **Hexane** _____ **NaCl** _____ **Acidified Na_2SO_4** _____ **H_2SO_4** _____ **Form 604r9.frm (12/7/2002)**

NaOH _____ **KOH** _____ **Diazald** _____ **Carbitol** _____ **Diethyl Ether** _____ **HCl** _____

SAMPLE							EXTRACT							
Sample No.	Amount (g / mL)	pH (≥ 12)	pH (≤ 2)	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hydrolysis (SO only)	Date KD (Final)	Date Partitioning (SO only)	Date Hexane Exchange	Final Volume (mL)	Date Vialed	Type of Cleanup

Comments:

Paragon Analytics

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) -- EXTRACTION & CLEANUP WORKSHEET

WO #s _____ **Matrix** AQ SO Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____ **Balance ID** ___

Ext Code 8310 E610 **Meth** (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)W Dilute **SOP** (617)CLE (647)SONC (625)SOX (626)SEP **Rev** ___ **Initials** ____

Ext Start Date _____ **Time** _____ **End Date** _____ **Time** _____ **Cleanup** (3630C) Silica Gel **SOP 604 Rev** ___ **Date** _____ **Time** _____ **Initials** ____

SAMPLE						EXTRACT / CLEANUP							
Sample No.	Amount (g / mL)	**pH**	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hexane Exchange	Date KD (Final)	Date Methanol Exchange	**A-Disk Size**	Final Volume (mL)	Vialed Date	**Comments**

Reagent Lots: $MeCl_2$ _____ Hexane _____ Methanol _____ Silica Gel _____ Na_2SO_4 _____ Reviewed by / Date _____

Form 605r5.frm (8/10/2001)

Form 609r12.doc (7/7//05)

Paragon Analytics

SEMIVOLATILES EXTRACTION / CLEANUP WORKSHEET

WO #s _____ **Matrix** ___ **Batch ID** _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** __ **Extr SOP/Rev** __ **Extr Code:** 8270C CLP SOW E625

Extr Method: (3520C)CLE (3550C)SONC (3540C)SOX (3510C)SEP (3580A)Waste Dilution **Initials** _____ **Extr Start Date/Time** _____ **Extr Stop Date/Time** _____

Cleanup Code: (3620B) Florisil (3640A) GPC (See other forms) Silica Gel **Cleanup SOP/Rev** ___ **Date/Time** _____ **Initials** _____ **Reviewed by / date** _____

SAMPLE								EXTRACT / CLEANUP					
Sample No.	Amount (g / mL)	Initial pH	**pH** (≤ 2)	**pH** (11-13)	Surrogate (mL)	Matrix Spike (mL)	Sur / Matrix Spike Witnessed	Date KD (Initial)	Cleanup Date	Date KD (Final)	Final Volume (mL)	Date Vialed	Comments

Steam bath _____ °C.

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Silica Gel _____ (See other GPC forms) H_2SO_4 _____ NaOH _____ Na_2SO_4 _____

_____ A

PESTICIDES / PCBs -- EXTRACTION WORKSHEET

Paragon Analytics

WO #s _____ **Batch ID** _____ **Surr Code** _____ **Matrix Spike Code** _____
Ex Date/Time _____ (start) _____ (stop) **Matrix** Aq Solid Other _____ **Balance ID** _____ **Ex SOP** ____ **Rev**___ **Initials** ____
Ex Method: (3520C) CLE (3550B) SONC (3540C) SOX (3510) SEP (3580) Wdilute (SOP 673) Wipes **EX Code:** 8081B (pest) 8082 (PCB) 608 (pest) 8081B (TCLP pest)

Sample No.	Amount (g / mL)	pH	Surr. Spike Amt. (mL)	Matrix Spike Amt. (mL)	Spike Analyst / Witness	Date KD / Analyst	Final Solvent	Final Vol. (mL)	Cleanup Req. (y / n)	Comments
					/	/				
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Lots: $MeCl_2$ _____ Hexane _____ Na_2SO_4 _____

Form 616r13.xls (3/29/05)

_____ B

PESTICIDES / PCBs -- CLEANUP WORKSHEET

Paragon Analytics

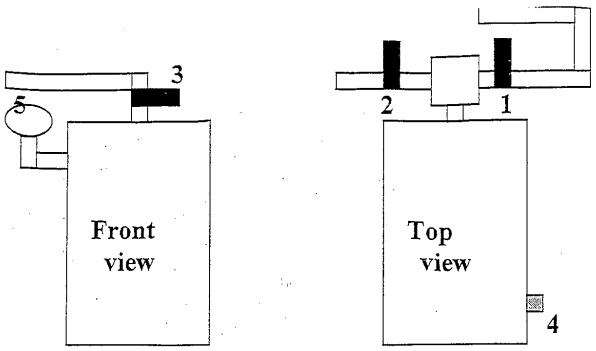
WO #s _____ **Batch ID** _____ **Cleanup SOP** _____ **Rev**____ **Initials** _____

Cleanup Method: (3620B) Florisil (3665A) Sulfuric (3640A) GPC (See additional forms) Other _____

FLORISIL: Has lot check been done? y/n _____ **GPC** (Note: half the extract is lost during cleanup) **SULFURIC ACID**

Sample No.	Amount Extract (mL)/ Solvent	Date Cleanup / Analyst	Final volume (mL) / Solvent	**Date Vialed / Analyst**	Amount Extract (mL) / Solvent	**Date Cleanup / Analyst**	Date KD / Analyst	Final volume (mL) / Solvent	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Comments

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Sulfuric acid _____ Na_2SO_4_____ **Reviewed by / date** _____



1. **Water inlet valve**
2. **Steam blowout valve**
3. **Steam valve**
4. **Boiler switch knob**
5. **Steam pressure gauge**

Steam Generator Start up

1. Check to see if steam blowout valve[2] is closed. (perpendicular to pipe) If not close it.
2. Open water inlet valve[1]. (parallel to pipe)
3. Turn boiler switch knob[4] on to 250. If boiler switch light does not come on re-check in five minutes. Light should be on. If light is not coming on contact supervisor.
4. After approximately 30 minutes Steam pressure gauge[5] should read between 20-60 psi. If not, wait until desired pressure is reached.
5. Open steam valve[3]. (parallel to pipe)

Steam Generator Shutdown

Caution: Pipes and Generator will be hot!

1. Turn boiler switch knob[4] to OFF
2. Close water inlet valve[1]. (perpendicular to pipe)
3. Close steam valve[3]. (perpendicular to pipe)
4. SLOWLY* open steam blowout valve[2]. (parallel to pipe)

**Caution: Do not open blowout valve fully until a majority of the steam is released. The tubing carrying the steam outside may come out of the wall.*

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 608 REVISION 12

TITLE: **METHOD FOR TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) EXTRACTION OF WASTES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOCs) BY ZERO HEADSPACE EXTRACTION (ZHE) -- METHOD SW1311**

FORMS: **608, 646, 825, 345** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3-4-08

QUALITY ASSURANCE MANAGER Deb Schad DATE 3/4/08

LABORATORY MANAGER _____ DATE 3-4-08

HISTORY: Rev0, 4/8/92; Rev1, 7/18/92; Rev2, 3/1/93; Rev3, PCN #101, 1/21/94; Rev4, 9/18/94; Rev5, 3/15/96; Rev6, 3/1/99; Rev7, 10/25/99; Rev8, 10/25/01; Rev9, 3/6/03; Rev10, 5/12/04; Rev11, 3/9/06; Rev12, 3/4/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW-846 Method 1311 -- are designed to determine the mobility of volatile organic compounds (VOCs) present in liquids, soils, and wastes (including multiphasic samples). Application of these procedures to matrices other than those specified will be handled individually to simulate the leaching procedure as best as possible.

2. SUMMARY OF METHOD

For liquid wastes (i.e., those containing less than 0.5% dry solid material) the waste, following filtration through a 0.6 to 0.8µm glass fiber filter, is defined as the ZHE extract (leachate).

For wastes containing greater than or equal to 0.5% solids, the particle size of the waste solid phase is reduced when necessary. The liquid, if any, is separated from the solid phase in order to determine the percent solids in the sample. The solid phase is then extracted with an amount of extraction fluid equal to twenty (20) times the weight of the solid phase. For volatiles analysis only Fluid #1 is used. A special extractor vessel for volatile compounds is used in this procedure. Following extraction, the liquid extract (leachate) is separated from the solid phase by filtration through a 0.6 to 0.8µm filter.

If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is typically added back to the solid phase prior to addition of Fluid #1 and leaching. If incompatible, the initial liquid phase is analyzed separately from the leachate and the results are mathematically combined to yield a volume-weighted average concentration.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the logbooks, analytical review sheets or case narratives indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work and documentation of the measures taken to remedy any errors found in the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Major contaminant sources are volatile materials in the laboratory. Analyses of reagent blanks provide information about the presence of these contaminants. The ZHE vessels are thoroughly cleaned between uses. The vessel number used for each sample or blank is recorded in the logbook. The same vessel is not to be used repeatedly for the blank - all vessels must be used for the blank on a rotating basis.

5. APPARATUS AND MATERIALS

5.1 **Zero-Headspace Extraction vessel (ZHE),** ADAM 3745 ZHE or equivalent. These devices are used when the mobility of VOCs are of concern. The ZHE allows for liquid-solid separation (within the device), extraction, and final extract filtration without opening the vessel. Thus, headspace and potential loss of volatiles from this closed system is effectively precluded. The ZHE have an

internal volume of 500-600mL and are equipped to accommodate a 90-100mm diameter filter. The devices utilize Viton™ o-rings to form a seal. These o-rings should be inspected before each use and may need to be replaced if they show signs of wear or damage.

For the ZHE vessel to be acceptable for use, the piston within the ZHE should be mobile with approximately 15psi or less (it is helpful to first moisten the piston o-rings slightly with extraction fluid). If it takes more pressure to move the piston, the o-rings in the device should be replaced. If replacing the o-rings does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted for re-machining.

Each ZHE device contains a built-in pressure gauge. The gauge should be frequently monitored to ensure that the ZHE is free of leaks throughout the extraction process. If the gauge indicates that the ZHE is not holding pressure correctly, or if the device shows other signs of a leak, pressurize the device to 50psi, allow it to stand unattended for 1 hour, and recheck the pressure. The ZHE can also be submerged in water after pressurization to check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace o-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted. If new ZHE are purchased, they must successfully pass this pressurization test prior to being used for sample analysis.

The ZHE vessel is used for filtration of the final ZHE extract. The ZHE vessel must be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50psi). When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE vessel.

5.2 **Pressure filtration device**, Associated Design and Manufacturing Model 3750-LHWF or equivalent. A.K.A. “lunar lander”.

5.3 pH meter, accurate to $\pm$0.05 pH units @ 25°C.
Meter must be calibrated prior to use (see Form 825).

5.4 **Fiber filter**, borosilicate glass, free of binder materials, 0.6 to 0.8µm particle size. *Pre-filters must not be used.* Glass fiber filters are fragile and should be handled with care. Use Gelman #66256, 90mm or equivalent, and/or Whatman #6890-2507, 25mm or equivalent.

5.5 VOA vials, 20mL or 40mL, septum seal, certified ‘clean’.

5.6 laboratory balance, accurate to ±0.01g.

5.7 centrifuge, Fisher Scientific Marathon 10k or equivalent.

5.8 drying oven, capable of maintaining 100±20°C.

5.9 apparatus for pressurizing ZHE's: Ultra high-purity Nitrogen tank, regulator (set to around 60psi), hose, and adapter for attachment to ZHE and pressure filtration device ("lunar lander").

5.10 rotary tumbler with 30±2rpm capability, Associated Design and Manufacturing Model 3740 or equivalent.

5.11 **ZHE Extract Collection Devices**, used to collect the initial liquid phase and the final extract of the waste. Plastic gas-tight syringes (50-60mL with Luer-Lok® fitting) or TEDLAR® bags may be used. Following collection, the extract is filtered during transfer to a 'VOA' vial (20 or 40mL volume) to meet the method requirements for storage in minimal headspace conditions until time of analysis. The devices listed are recommended for use under the following conditions:

5.11.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), a syringe should be used to collect and combine the initial liquid and solid extract.

5.11.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

5.11.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5mL of liquid expressed from the device. The remaining aliquots are used for analysis.

6. REAGENTS - Only reagent grade or better chemicals shall be used.

6.1 **reagent water**: defined as water in which an interferent is not observed at or above the method's detection limit of the analyte(s) of interest.

6.2 **glacial acetic acid (HOAc)**

6.3 **sodium hydroxide (NaOH), 12M**: Add 480g NaOH to 1000mL reagent water; mix thoroughly.

6.4 **Extraction Fluid #1**: Add several liters reagent water to a 22L container. Add 125mL HOAc and 140mL 12M NaOH. Bring final volume to 22L with reagent water. Mix thoroughly. pH must be 4.93±0.05.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 All samples should be collected using an appropriate sampling plan.

7.2 There may be requirements on the minimal size of the field sample, depending upon the physical state of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of percent solids and particle size. Another aliquot may be needed to actually conduct the nonvolatile extraction. An additional aliquot is needed for the volatile organics extraction. Quality control (QC) samples may require additional aliquots. Further, it is wise to collect additional sample in case something goes wrong with the initial attempt to conduct the test.

7.3 Preservatives shall not be added to samples before extraction.

7.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

7.5 Because the samples are to be analyzed for volatiles, care shall be taken to minimize their loss; samples shall be collected and stored accordingly. Samples should be collected in glass jars with Teflon®-lined lids and stored at 4±2°C. (although EnCore® samplers may also be used for sample collection, their limited sampling capacity makes them less desireable for this procedure). Samples should only be opened immediately prior to extraction.

7.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Maximum hold times are:

Sample Holding Times [days]

	Time from field collection to TCLP leaching	Time from ZHE-TCLP leaching to determinative analysis
Volatiles	14 days	14 days

8. PROCEDURES

8.1 PRELIMINARY EVALUATION

Preliminary evaluation includes: (1) determination of percent solids; (2) determination of whether or not the waste contains insignificant solids and is, therefore, its own extract after filtration; and (3) determination of whether or not the solid portion of the waste requires particle size reduction (if required, procedure is described in SOP 609).

NOTE: Even if only the volatile TCLP extraction is being done, it is often useful to perform the (initial) phase separation in order to determine the optimum sample aliquot with which to charge the ZHE. The experienced prep analyst may, however, choose to forego this procedure, as percent solids determination is also conducted as part of the procedure in determining the amount of extraction fluid to add (Steps 8.2.3 through 8.2.5).

Select samples and record on benchsheet. Perform preliminary TCLP evaluations on a minimum 100g aliquot of waste (if there is insufficient sample or it is impractical to use 100g, notate on benchsheet).

8.1.1 DETERMINATION OF PERCENT SOLIDS
PHASE SEPARATION

8.1.1.1 **Percent solids** is defined as that fraction of a waste sample (as a percentage of the total sample), from which no liquid may be forced out by an applied pressure, as described below. Visual inspection may be sufficient for this determination.

If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids), then proceed to Section 8.1.3 - Particle Size Reduction Determination.

8.1.1.2 **Phase Separation**. If the sample is liquid or multiphasic, liquid/solid separation is required to make a preliminary determination of percent solids. This involves the filtration device described in Section 5.2, and performance of the procedures outlined below:

8.1.1.2.1 Pre-weigh the filter, spatula, and beaker that will receive the filtrate. Record the weights in the appropriate boxes on the TCLP % solid benchsheet (Form 608). Foil dishes may be used to collect solids from sample with very low solids content and the foil dish weight must be recorded before solids are placed on the foil.

8.1.1.2.2 Assemble the filtration device and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

8.1.1.2.3 Weigh out a subsample of the waste (100g minimum) and record the weight. If sufficient sample is not available, record such on benchsheet.

8.1.1.2.4 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

8.1.1.2.5 Quantitatively transfer the waste sample to the filtration device (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature before filtering.

8.1.1.2.6 After transferring the waste sample to the filtration device, place the spatula in the beaker, weigh, and record the initial sample weight on the TCLP % solids benchsheet.

8.1.1.2.7 Gradually apply gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If air or filtered liquid does not move through the filter at this range of pressures and if no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10psi increments to a maximum pressure of 50psi. **Note that instantaneous application of high pressure can rupture the glass fiber filter and may cause premature plugging.**

When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

8.1.1.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration as outlined above, this material may not filter. If this is the case, the material within the filtration device is defined as a solid as is carried though the TCLP extraction. **Do not replace the original filter with a fresh filter under any circumstances.** Use only one filter.

8.1.1.3 Determine the weight of the liquid phase by subtracting the weight of the empty beaker (8.1.1.2.1) from the total weight of the filtrate-filled beaker syringe; record weight on TCLP % solids benchsheet (Form 608).

Determine the weight of the solid phase (8.1.1.2.8) of the waste sample by subtracting the weight of the liquid phase (above) from the weight of the total waste sample (8.1.1.2.3); record weight on TCLP % solids benchsheet.

8.1.1.4 Calculate the percent solids as shown below:

$$\text{Percent Solids} = \frac{\text{Weight of solid (8.1.1.3)}}{\text{Total weight of waste (8.1.1.2.3)}} \times 100$$

8.1.2 DETERMINATION OF INSIGNIFICANT SOLIDS

If the percent solids as determined above (8.1.1.4) is equal to or greater than (≥) 0.5%, then proceed either to Section 8.1.3 (particle size reduction determination) or continue as outlined below (8.1.2.1), if it is noticed that a small amount of the filtrate is entrained in wetting of the filter.

If the percent solids determined (8.1.1.4) is less than (<) 0.5%, then proceed to Section 8.2 (ZHE procedure), with a fresh portion of the waste.

8.1.2.1 Remove the solid phase and filter from the filtration apparatus.

8.1.2.2 Dry the filter and solid phase at 100±20°C until two successive weighings yield the same value (±1%). Record the final weight on the benchsheet (Form 608).

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. If it is suspected that the material is flammable, drying in the hood overnight is recommended. When the filter paper is dry, re-weigh and calculate the % solids with the new value. This Step is performed when it is suspected that the weight from the moisture in the filter paper has caused the % solids value to rise above 0.5%. Perform this Step only in borderline cases.

8.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent Dry Solids} = \frac{\text{Wt dry sample + filter - Tared wt of filter}}{\text{Initial weight of sample (8.1.1.2.3)}} \times 100$$

8.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 8.2.

8.1.3 PARTICLE SIZE REDUCTION DETERMINATION

8.1.3.1 Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1cm^2, or is smaller than 1cm in its narrowest dimension (i.e., is capable of passing through a 9.5mm [0.375 inch] standard sieve). If the particle size is larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above.

8.1.3.2 Note that the surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

8.1.3.3 Safety concerns such as dust control may preclude the grinding of samples for particle size reduction. These safety concerns must *always* be addressed before

attempting to grind any sample. Generally due to health and safety concerns, grinding to reduce particle size is not practiced in the extractions area. Samples requiring particle size reduction have been sent to an appropriate facility before an extraction was performed.

8.1.3.4 Particle size reduction prior to leaching for volatile organics may lead to loss of target compounds, compromising the analytical results.

8.1.3.5 If a particle size reduction of the solid portion of the waste is required, continue as follows:

8.1.3.5.1 Prepare the waste for extraction by crushing, cutting or grinding the solid portion of the waste to a suitable surface area or particle size.

8.1.3.5.2 *Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4±2°C prior to particle size reduction.*

8.1.3.5.3 *The means used to effect particle size reduction must not generate heat in and of itself.*

8.1.3.5.4 *Work carefully and quickly, as exposure of the waste to the atmosphere should be avoided to the extent possible.*

8.1.3.5.5 **Note that sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth and similar) waste materials. Actual measurement of surface area is not recommended.**

8.1.3.5.6 When the surface area or particle size has been appropriately altered, proceed to Section 8.2.3 - Filtration.

8.2 ZHE PROCEDURE

Use the ZHE vessel to obtain TCLP extract for analysis of VOCs only. Leachates resulting from the use of the ZHE shall not be used to evaluate the mobility of

nonvolatile analytes (e.g., metals, pesticides, semivolatiles). The ZHE vessel has an internal capacity of 500-600mL, and can thus accommodate a maximum of approximately 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

8.2.1 EQUIPMENT SET-UP

8.2.1.1 Charge the ZHE vessel with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE vessel to obtain 25 grams of solid is not permitted.

8.2.1.2 **Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Manipulation of the sample to be leached should be done when cold (4±2°C) to minimize loss of volatiles. Leaching fluids are added at room temperature. After filtration, leachates should be cooled to 4±2°C by placing the 'VOA' vial into a suitable refrigeration unit as soon as practical.**

8.2.1.3 Pre-weigh the (evacuated) filtrate collection container (5.11) and set aside. If using a Tedlar™ bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis.

8.2.1.4 Place the ZHE piston within the body of the ZHE (it is helpful to first moisten the piston o-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move after the ZHE is charged with sample (based upon sample size requirements as discussed previously). Secure the gas inlet/outlet (bottom) flange (with the valve open) onto the ZHE body per the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set the liquid inlet/outlet flange (top flange) aside.

8.2.2 ALIQUOT DETERMINATIONS

8.2.2.1 If the sample is 100% solid (8.1.1.1), weigh out a subsample (25g maximum – care should be taken to choose a sample weight that will yield sufficient leachate to support the

analysis) of the waste, record weight (Form 608), and proceed to Step 8.2.3 - Filtration.

8.2.2.2 If the waste contains <0.5% dry solids (8.1.2.3), the liquid portion of waste, after filtration, is defined as the ZHE extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required (weigh out a 100-500g subsample, record weight). Proceed to Step 8.2.3 - Filtration.

8.2.2.3 If the waste contains ≥0.5% dry solids, use the percent solids information obtained in Step 8.1.1.4 to determine the optimum sample size to charge into the ZHE vessel as follows:

$$\text{Wt of waste to charge ZHE} = \frac{10}{\text{percent solids (8.1.1.4)}} \times 100$$

Weigh out the appropriate size of waste subsample as determined and record the weight on the ZHE benchsheet (Form 608).

8.2.3 FILTRATION

8.2.3.1 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

8.2.3.2 Quickly and quantitatively transfer the entire sample (liquid and solid phases) of the waste aliquot as prepared above to the ZHE vessel.

NOTE: If waste material (>1% of original subsample weight) has obviously adhered to the container used to transfer the sample to the ZHE vessel, determine the weight of this residue and subtract it from the sample weight (8.1.1.2.3) to determine the actual weight of the waste subsample that will be filtered. Record on benchsheet.

8.2.3.3 Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE vessel body in accordance with the manufacturer's instructions. Tighten all ZHE fittings, and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

8.2.3.4 Attach the gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10psi (or more if necessary) to force all headspace *slowly* out of the ZHE vessel.

At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4±2°C reduces the amount of expressed liquid beyond what would be expressed at room temperature, then allow the sample to warm to room temperature before filtering.

If the waste is 100% solid (8.1.1.1), slowly increase the pressure to a maximum of 50psi to force most of the headspace out of the device, then proceed to Section 8.2.6 - Extraction (Tumbling).

8.2.3.5 Attach the evacuated pre-weighed 60mL plastic Luer-Lok® syringe to the liquid inlet/outlet valve of the ZHE and open the valve. Begin applying gentle pressure of 1-10psi to force the liquid phase of the sample into the filtrate collection container. **Note that instantaneous application of high pressure can rupture the glass fiber filter and may cause premature plugging.**

If no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10psi increments (and waiting a 2-minute interval with no additional liquid passing) to a maximum of 50psi.

When liquid flow has ceased such that continued pressure filtration at 50psi does not result in any additional filtrate within a 2-minute period, stop the filtration.

8.2.3.6 Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container; record weight on ZHE benchsheet. Using the information recorded on the benchsheet, calculate the amount of solid waste left inside the ZHE.

8.2.4 PHASE DISCUSSION

The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase. Some wastes, such as oily wastes and some paint wastes, will obviously contain some material

that appears to be a liquid. Even after applying pressure filtration, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (8.1.2.3), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 8.2.7 - Preparation for Volatile Analysis.

The liquid phase may now be either analyzed immediately (8.2.7), stored at 4±2°C under minimal headspace conditions until time of analysis, or recombined (if miscible) with the sample prior to tumbling.

8.2.5 Determine the weight of Extraction Fluid # 1 to add to the ZHE vessel as follows (**Extraction Fluid # 1 is used in all cases)**:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (8.1.1.4)} \times \text{weight of waste filtered (i.e., the solid waste left inside the ZHE, 8.2.3.6)}}{100}$$

Record on benchsheet (Form 608).

8.2.6 EXTRACTION (TUMBLING)

8.2.6.1 Fill a clean beaker of appropriate volume with Extraction Fluid #1, then fill a clean 60mL gas-tight Luer-Lok® syringe from the beaker. Vent residual air from the syringe so that it only contains the measured amount of fluid.

With the ZHE vessel in the vertical position, attach the syringe to the liquid inlet/outlet valve. Release gas pressure on the ZHE piston (open the gas inlet/outlet valve), open the liquid inlet/outlet valve, and depress the syringe plunger to transfer extraction fluid into the ZHE vessel. Close the liquid inlet/outlet valve and remove the syringe.

Continue to add extraction fluid to the ZHE in this manner until the appropriate amount (8.2.5) has been introduced into the device.

8.2.6.2 After the extraction fluid has been added, immediately close both the liquid inlet/outlet valve and the gas inlet/outlet valve.

8.2.6.3 Reposition the ZHE vessel in the vertical position with the liquid inlet/outlet valve on top. Pressurize to 5-10psi and slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of extraction fluid. *This bleeding should be done quickly - stop at the first appearance of liquid from the valve.* Re-pressurize to 5-10psi and check all ZHE fittings to ensure that they are closed.

8.2.6.4 Place the ZHE in the rotary extractor apparatus and rotate at 30±2 rpm for 18±2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23±2°C during agitation. SOP 663 describes the procedures for monitoring tumbler revolutions and room temperature.

8.2.6.5 Following the 18±2 hour agitation period, check the pressure gauge on the ZHE vessel to see that pressure has been maintained. If the pressure has not been maintained, the device has leaked. Check the ZHE vessel for leaking as specified in Section 5.1, and correct the problem. Perform the extraction again with a new aliquot of waste sample.

8.2.6.6 If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases.

8.2.6.6.1 If the waste contained an initial liquid phase that has been stored, the leachate may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) that holds the initial liquid phase. *A separate filtrate collection container must be used if combining would create multiple phases, or if there is not enough volume left within the filtrate collection container.*

8.2.6.6.2 After attaching the filtrate collection container (TEDLAR® bag or clean syringe) slowly open the liquid inlet/outlet valve (top flange) to collect the filtered leachate. Note that an in-line glass fiber filter may be used to filter the material within the ZHE vessel if it is suspected that the internal glass fiber filter has ruptured. *All extract shall be filtered and collected if the*

TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase that was NOT recombined with solids prior to tumbling.

8.2.6.6.3 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 8.2.3 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 8.2.3 and the initial liquid phase (8.1.1.2) are collectively defined as the TCLP extract.

8.2.7 PREPARATION FOR VOLATILE ANALYSIS
Following collection of the TCLP extract, immediately prepare the extract for analysis (by transferring to a septum-sealed "VOA" vial) and store with minimal (preferably zero) headspace at 4±2°C until analyzed.

Analyze the TCLP extract according to the appropriate determinative method. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a volume-weighted average as shown below:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = volume of the first phases (L)

C_1 = concentration of target analyte in the first phase (mg/L)

V_2 = volume of the second phase (L)

C_2 = concentration of target analyte in the second phase (mg/L)

9. QUALITY CONTROL

9.1 A minimum of one method blank (MB) using the same extraction fluid as used for the samples (extraction fluid #1), must be analyzed for every 20 extractions that have been conducted in an extraction vessel. No more than 20 field samples may be included in a batch.

9.2 Matrix spike and laboratory control samples are prepared at the time of analysis by the volatiles analysis group.

10. DEVIATIONS FROM THE METHOD

This SOP meets the requirements of SW-846 Method 1311. There are no known deviations from this method.

It should be noted that, when only the volatile TCLP extraction is being done (i.e., no semivolatile or metals), the initial percent solids determination (using the "lunar lander") may be skipped, as the percent solids can be determined after the sample is loaded into the ZHE (Steps 8.2.3.4 through 8.2.3.6). Experience of the prep analyst weighs heavily here, as (in the case of a very wet sample matrix), too small of an aliquot into the ZHE may not yield an adequate volume of leachate for analysis.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses and a lab coat when working with chemical materials (e.g., standards, solvents, reagents, or samples).

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Glacial acetic acid has a TLV of 10ppm.

11.2 SAFETY AND HAZARDS

11.2.1 Unused sample leachate may be disposed of in the Aqueous Laboratory Waste.

11.2.2 Unused sample leachate solids may be disposed of in the Contaminated Soils and Solids Waste.

11.2.3 Waste from processing radioactive samples shall be disposed of in the appropriate radioactive waste stream.

11.2.4 All empty solvent bottles shall be disposed of according to the appropriate SOPs. All labels and markings must be defaced prior to disposal.

12. REFERENCES

Test Methods for Evaluating Solid Waste Physical/Chemical Methods, US EPA, Volume 1C, 3rd edition. Method SW 1311, Rev 0, July 1992.

DOCUMENT REVISION HISTORY

3/4/08: Minor clarifications throughout. Augmented LIMS program specification language Section 3.3. Added detail re: ZHE vessels Section 5.1. Reformatted Section 8, included temperature monitoring and SOP 663 reference. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

ZHE PERCENT SOLIDS DETERMINATION & TUMBLING

Work Order # _____	**(Start) Date** _____ **Time** _____	**(Run) Temp. (min/max)** _____/_____ **°C**
Batch # _____	**(Start) RPM** _____ **Temp.** _____ **°C** *(from min/max* SN 21251556)	**(Stop) Date** _____ **Time** _____
Method _____ **SOP 608 Rev** _____	**(Start) PSI** _____ **Analyst** _____ RESET MIN/MAX AFTER READING OBTAINED	**(Stop) RPM** _____ **Temp.** _____ **°C**
Leaching Fluid ID		**(Stop) PSI** **Analyst**
Filtration Date _____ **Time** _____ **Initials** _____		**Reviewed by date** _____

		Percent Solids Determination						ZHE Aliquot					
Sample Number	**Sample Matrix**	Free Liquid? Y / N *	Initial Sample Weight (g)	Filter Weight (g)	Beaker Weight (g)	Sample Dry Weight (g)	% Solid (DRY/TOT)	Tumbler Number	Aliquot (g)	Fluid Volume (mL)	**Final pH**	**Leachate Number**	**Comments**

* If "No", percent solids are 100% by visual inspection (test not performed). INTERNAL COC TRANSFER: Relinquished by _____ (initials) to _____ (RU # & Location) _____ (Date & Time)

Form 608r11.doc (10/25/07)

Paragon Analytics

LEACHING FLUIDS LOG

Lot Nos.: Sodium Hydroxide _____ Glacial Acetic Acid _____

Solution Name	Date Prepared	Initials	Volume NaOH Used (mL)	Volume Glacial Acetic Acid Used (mL)	Total Volume Made (mL)	Final pH	Comments

Reviewed by _____ Date _____

FORM 646r1.doc (4/17/02)

Paragon Analytics

Corning Model 320 pH Meter Calibration & Maintenance Log

Result Units = pH units

Date	Time	Analyst	4.01 Solution Lot No./ Result	10.01 Solution Lot No./ Result	% Slope	7.00 Solution Lot No./ Result	Check Solution Result
			/	/		/	
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Comments/Maintenance Notes:

Form 825r0.xls (4/18/2003)

Paragon Analytics

TEMPERATURE LOGBOOK

ORGANIC EXTRACTIONS - TCLP ROOM

Acceptable Range 23 ± 2 °C

A current temperature reading must be recorded at the onset of TCLP tumbling, and the min/max memory must be reset. DO NOT initiate tumbling if temperature is not within acceptable limits. The current temperature and min/max information must be recorded at the completion of tumbling. Both the Department and QA Managers must be notified in a timely manner if an excursion occurs.

		Thermometer: 41406316 (min/max)				
DATE	TIME	Current Temp. (°C)	Temp. Min (°C) Date/Time Occurred	Temp. Max (°C) Date/Time Occurred	INITIALS	COMMENTS

Reviewed by / date _____ **Form 345r1.doc (7/10/06)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 609 REVISION 12

TITLE: **METHOD FOR TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) OF WASTES AND SOILS FOR THE ANALYSIS OF METALS AND SEMIVOLATILE ORGANICS -- METHOD SW1311**

FORMS: **623, 646, 825, 345 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER_____ DATE 3.4.08

QUALITY ASSURANCE MANAGER_____ DATE 3/4/08

LABORATORY MANAGER_____ DATE 3-4-08

HISTORY: New, Rev0, 2/26/92; Rev1; 7/18/92; Rev2, 3/11/93; Rev3, PCN #102, 1/21/94; Rev4, PCN# 274, 9/22/94; Rev5; 2/27/96; Rev6, 2/12/99; Rev7, 3/14/00; Rev8, 3/14/02; Rev9, 4/3/03; Rev10, 4/16/04; Rev11, 3/9/06; Rev12, 3/4/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW-846 Method 1311 -- are designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. This procedure is performed to analyze the soluble metals and non-volatile organic compounds that could leach from a sample if it were in a landfill site. Application of these procedures to matrices other than those specified will be handled individually to simulate the leaching procedure as best as possible.

Procedures for ZHE TCLP extractions are described in SOP 608.

2. SUMMARY

For liquid wastes (i.e., <0.5% solids), the sample is filtered through a 0.7µm glass fiber filter, and the filtrate is defined as the TCLP leachate.

For samples containing ≥0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solid phase is reduced. The solids are then leached with an amount of extraction fluid equal to twenty (20) times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following the TCLP extraction, the leachate is separated from the solids by filtration through a 0.7µm filter.

If a liquid phase was present in the sample and set aside as described above, then this liquid is combined with the leachate from the solid phase, if the two are miscible, before metals or semivolatile organic preparation for analysis. If the liquid and the leachate are not miscible, the liquid and the leachate are analyzed separately, and the results are mathematically combined to yield a volume-weighted average concentration.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the bench sheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of measures taken to correct the errors that were found.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by processing and analyzing method blanks.

5. APPARATUS AND MATERIALS

Extraction vessels and filtration devices shall be made of inert materials that will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) are to be used only when evaluating the mobility of metals.

5.1 rotary tumbler with 30±2rpm capability, Associated Design and Manufacturing

Model 3740 or equivalent

5.2 pH meter, accurate to ±0.05 pH units @ 25°C
Meter must be calibrated prior to use (see Form 825).

5.3 pressure filtration device, Associated Design and Manufacturing Model 3750-LHWF or equivalent. A.K.A. "lunar lander"

5.4 fiber filters, borosilicate glass, Gelman™ #66256, 0.7µm nominal or equivalent

NOTE: The glass fiber shall contain no binder materials and shall have an effective particle size of 0.6 to 0.8µm. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1.0M HNO_3, followed by three consecutive rinses with deionized water (a minimum of 1000mL per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

5.5 bottle extraction vessel, 2L or slightly larger. Borosilicate glass, 2200mL Kontes™ #332100-021 or equivalent. If PVC coated for safety, do not place in kiln. HDPE plastic, 2000mL Eagle Picher #EP150-02WM or equivalent

Paragon typically uses disposable HPDE extraction bottles for metals and semivolatile organics. The use of HDPE extraction bottles has been demonstrated to generate leachates that are free of contaminants for the analyses being conducted.

5.6 balance, accurate to within ±0.01g

5.7 beakers or Erlenmeyer flasks, glass 500mL (or 4.5oz plastic cups)

5.8 watch glass, appropriate diameter to cover beaker or Erlenmeyer flask (or cap for plastic cup)

5.9 carboys for containerizing extraction fluids

5.10 stirring hot plate, with magnetic stir bar

5.11 graduated cylinders, sized as appropriate

5.12 centrifuge

5.13 drying oven, capable of maintaining 100±20°C

6. REAGENTS - Only reagent grade or better chemicals shall be used.

6.1 water, of sufficient purity that target analytes or interferences are not observed at levels of interest for the analytes of interest. For semivolatile organics and metals

analysis, laboratory deionized (DI) ASTM Type II water meets the definition of reagent water. Prior to being used for this procedure, this water is filtered through a Millipore Synergy 185® filtration system for further purification.

6.2 glacial acetic acid (CH_3COOH), suitable for use in metals analysis

6.3 sodium hydroxide solution (NaOH), 12N

6.4 **Extraction fluid 1:** Add 21L of reagent water to a HDPE carboy. Add 126mL glacial acetic acid and 140mL 12N NaOH. Bring final volume to 22L with reagent water. Mix thoroughly (pH must be 4.93 ±0.05). Volumes of acetic acid and NaOH may be adjusted to prepare larger or smaller volumes of Extraction fluid 1.

6.5 **Extraction fluid 2:** Add 21L of reagent water to a HDPE carboy. Add 108mL glacial acetic acid. Bring final volume to 22L with reagent water. Mix thoroughly (pH must be 2.88±0.05). Volume of acetic acid may be adjusted to prepare larger or smaller volumes of Extraction fluid 2.

6.6 1N hydrochloric acid solution (HCl): In a 100mL volumetric flask with approximately 50mL reagent water, add 8.3mL concentrated HCl, bring to volume with reagent water, and mix thoroughly.

6.7 1N nitric acid solution (HNO_3):): In a 100mL volumetric flask with approximately 50mL reagent water, add 6.3mL concentrated HNO_3, bring to volume with reagent water, and mix thoroughly.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 All samples should be collected using an appropriate sampling plan.

7.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state of the waste and the analytes of concern. An aliquot is needed for determination of which extraction fluid is to be used during this leaching procedure. Another aliquot is required to actually conduct the leaching procedure. If volatile organics are of concern, another aliquot is required. Quality control samples may require additional aliquots. Further, it is always wise to collect additional sample in case something goes wrong with the initial attempt to conduct the test.

7.3 Chemical preservatives are not added to solid samples. Some liquid samples may contain residual chlorine and the free chlorine should be deactivated with sodium thiosulfate or another dechlorinating reagent while in the field. Preservatives shall <u>not</u> be added to samples before extraction.

7.4 Samples should be collected in Teflon-lined septum capped bottles and stored at

4±2°C. Samples may be refrigerated unless refrigeration results in irreversible physical change of the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

7.5 TCLP leachate should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH<2, unless precipitation occurs. Refrigeration is generally the only preservation technique applied to the leachates intended for semivolatile organic analysis. Maximum hold times are:

SAMPLE HOLDING TIMES (DAYS)

Leachate Analysis	From Field Collection to TCLP Leaching	From TCLP Leaching to Preparation for Analysis	From Preparation to Analysis
Semivolatile organics (including Pesticides, Herbicides)	14	7	40
Mercury (Hg)	28	NA	28
Metals (except Hg)	180	NA	180

NA=Not Applicable

8. PROCEDURE

8.1 PRELIMINARY EVALUATION

Preliminary evaluation includes: (1) determination of the percent solids (8.1.1); (2) determination of whether the sample contains insignificant solids and is, therefore, its own leachate after filtration (8.1.2); (3) determination of whether the solid portion of the sample requires particle size reduction (8.1.3); and (4) determination of which extraction fluid is to be used for the nonvolatile TCLP extraction of the waste (8.1.4).

Select samples to be analyzed and record on benchsheet (Form 623). Perform preliminary TCLP evaluations on a minimum 100g aliquot of sample, assuming adequate volume of sample has been provided (notate on benchsheet if otherwise); this aliquot may not actually undergo TCLP extraction.

8.1.1 DETERMINATION OF PERCENT SOLIDS
PHASE SEPARATION

8.1.1.1 Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample), from which no liquid may be forced out by an applied pressure, as described below. Visual inspection may be sufficient for this determination.

If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids), then proceed to Section 8.1.3 - Particle Size Reduction Determination.

8.1.1.2 **Phase Separation**. If the sample is liquid or multiphasic, liquid/solid separation is required to make a preliminary determination of percent solids. This involves the filtration device described in Section 5.2, and performance of the procedures outlined below:

8.1.1.2.1 Pre-weigh the filter and foil that will receive the solids, the beaker and spatula. Acid wash the filter if evaluating the mobility of metals (5.4). Record the weights in the appropriate boxes on the TCLP % solids benchsheet (Form 623).

8.1.1.2.2 Assemble the filtration device and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

8.1.1.2.3 Weigh out a subsample of the waste (100g minimum) and record the weight. If sufficient sample is not available, record such on benchsheet.

8.1.1.2.4 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered, followed by filtration of the solid portion of the waste through the same filtration system.

8.1.1.2.5 Quantitatively transfer the waste sample to the filtration device (liquid and solid phases).

8.1.1.2.6 After transferring the waste sample to the filtration device, place the spatula in the beaker and record the combined weight of both. Then continue with the calculations prompted on the benchsheet.

8.1.1.2.7 Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature before filtering.

8.1.1.2.8 Gradually apply vacuum or gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If gas or air does not move through the filter at this range of pressures and if no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10psi increments to a maximum pressure of 50psi. **Note that instantaneous application of high pressure can rupture the glass fiber filter and may cause premature plugging.**

8.1.1.2.9 If after each incremental increase of 10psi, the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in a 2-minute interval, proceed to the next 10psi increment.

8.1.1.2.10 When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

8.1.1.2.11 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. However, even after applying vacuum or pressure filtration as outlined previously, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. **Do not replace the original filter with a fresh filter under any circumstances; use only one filter.**

8.1.1.2.12 Determine the weight of the liquid phase by subtracting the weight of the filtrate container, from the total weight of the filtrate-filled container; record on benchsheet.

8.1.1.2.13 Determine the weight of the solid phase by subtracting the weight of the liquid phase (8.1.1.2.12) from the weight of the total waste sample; record on benchsheet.

8.1.1.3 Calculate the percent solids as follows:

$$\%\ \text{solids} = 100 * \frac{\text{weight of solids (8.1.1.2.13)}}{\text{total weight of waste (from benchsheet)}}$$

8.1.2 DETERMINATION OF INSIGNIFICANT SOLIDS

If the percent solids as determined above (8.1.1.3) is equal to or greater than (≥) 0.5%, then proceed either to Section 8.1.3 (particle size reduction determination) or continue as outlined below (8.1.2.1), if it is noticed that a small amount of the filtrate is entrained in the wet filter.

If the percent solids determined (8.1.1.3) is less than (<) 0.5%, then proceed to Section 8.2 (Aliquots for Leaching).

8.1.2.1 Remove the solid phase and filter from the filtration apparatus.

8.1.2.2 Dry the filter and solid phase at 100±20°C until two successive weighings yield the same value (±1%). Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. If it is suspected that the material is flammable, drying in the hood overnight is recommended. When the filter paper is dry, re-weigh and calculate the % solids with the new value. This Step is performed when it is suspected that the weight from the moisture in the filter paper has caused the % solids value to rise above 0.5%. Perform this Step only in borderline cases.

8.1.2.3 Calculate the percent dry solids as follows:

$$\%\,\text{dry solids} = 100 * \frac{(\text{dry waste} + \text{filter}) - (\text{initial weight of filter})}{\text{initial weight of waste}} \quad (8.1.1.2.6)$$

8.1.2.4 If the percent dry solid is < 0.5%, then proceed to Section 8.2 if the nonvolatile TCLP is to be performed.

If the percent dry solid is ≥0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 8.1.3). **The portion of sample that has been dried is not to be used in the leaching procedure.**

8.1.3 PARTICLE SIZE REDUCTION DETERMINATION

8.1.3.1 Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1cm^2, or is smaller than 1cm in its narrowest dimension (i.e., is capable of passing through a 9.5mm [0.375 inch] standard sieve). If the particle size is larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above.

8.1.3.2 Note that the surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

8.1.3.3 Safety concerns such as dust control may preclude the grinding of samples for particle size reduction. These safety concerns must always be addressed before attempting to grind any sample. Generally due to health and safety concerns, grinding to reduce particle size is not practiced in the extractions area. Samples requiring particle size reduction have been sent to an appropriate facility before an extraction was performed.

8.1.3.4 If a particle size reduction of the solid portion of the waste is required, continue as follows:

8.1.3.4.1 Prepare the waste for extraction by crushing, cutting or grinding the solid portion of the waste to a suitable surface area or particle size.

8.1.3.4.2 *Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4±2°C prior to particle size reduction.*

8.1.3.4.3 *The means used to effect particle size reduction must not generate heat in and of itself.*

8.1.3.4.4 *Work carefully and quickly, as exposure of the waste to the atmosphere should be avoided to the extent possible.*

8.1.3.4.5 Note that sieving of the waste is not normally required. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth and similar) waste materials. Actual measurement of surface area is not recommended.

If the waste as received passes a 9.5mm sieve, quantitatively transfer the solid material into an extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to 8.4 - Tumbling.

8.1.3.4.6 When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into the extractor bottle. Include the filter used to separate the initial liquid from the solid phase. Then proceed to 8.3 - Filtration.

8.1.4 EXTRACTION FLUID DETERMINATION
If the solid content of the waste is ≥0.5%, then determine the appropriate fluid for the nonvolatiles extraction as follows:

8.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary), to a particle size of

approximately 1mm in diameter or less (i.e., it should pass through a 1mm sieve), and transfer 5.0g of the solid phase to a 250mL beaker or 4.5oz cup.

8.1.4.2 Add 96.5g of reagent water to the beaker, cover with a watch glass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use Extraction fluid 1; proceed to Section 8.2.

8.1.4.3 If the pH is ≥5.0, add 3.5mL 1N HCl, slurry briefly, cover with a watch glass, heat to 50°C, and hold at 50°C for a minimum of 10 minutes (up to 30 minutes).

8.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use Extraction fluid 1. If the pH is ≥5.0, use Extraction fluid #2. Record which fluid was used for each sample on the benchsheet (Form 623).

8.2 DETERMINATION OF ALIQUOTS FOR LEACHING

8.2.1 Label a 2000mL container with work order number, sample number, and fluid number (for metals, rinse the container with 0.1N HNO_3, followed by a rinse with deionized water). For each reagent blank, label a container with the date of tumbling, reagent blank number and fluid number.

8.2.2 Determine the number of analyses to be performed upon each sample: Herbicides, organochlorine pesticides, and semivolatiles analysis each require 100mL of tumbled fluid. Metals analysis requires 50mL of tumbled fluid. Each analysis also requires one (1) matrix spike sample/fluid/day tumbled, so these amounts may be doubled to ensure sufficient amount of fluid for all analysis and matrix spike.

Each analysis also requires a reagent blank/fluid/day tumbled, which consists of the appropriate fluid placed in an appropriate TCLP container (no solid added) and tumbled with the samples. The reagent blank should also be put on the benchsheet and carried through the tumbling/filtering/ extracting (analysis) process.

The amount of fluid added to the sample is equal to 20 times the weight of the solid (e.g., 20g of sample requires 400mL of fluid).

8.2.3 If the aliquot of the sample used for the preliminary evaluation was determined to be 100% solid (8.1.1.1), then that aliquot can be used for the nonvolatile extraction (assuming that aliquot is sufficient to generate enough leachate to support the requested analyses).

Do not use leach solid that was dried in the oven.

8.2.4 The amount of solid necessary is dependent upon whether a sufficient amount of leachate will be produced to support the required analyses. If an adequate amount of solid remains, proceed with the nonvolatile TCLP extraction (Section 8.4).

A minimum sample size of 100g (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content (8.1.1.3) of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous leachate of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough TCLP solids should be generated for extraction such that the volume of leachate will be sufficient to support all of the analyses required.

If the amount of leachate generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed, and the leachates from each combined and aliquoted for analysis.

8.2.5 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a subsample of the waste (100g minimum) and proceed to Section 8.3 - Filtration.

8.2.6 If the sample is liquid or multiphasic, liquid/solid separation is required as outlined in Section 8.1.1.2.

8.2.7 Weigh out an aliquot of the sample (100g minimum) and record the weight. If the waste contains <0.5% dry solids (Section 8.1.2.3), the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required.

8.2.8 For wastes containing $\geq$0.5% solids, use the percent solids information obtained in Section 8.1.1.3 to determine the optimum sample size (100g minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP leachate.

8.2.9 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered, followed by filtration of the solid portion of the waste through the same filtration system.

8.3 FILTRATION

8.3.1 Pre-weigh the container that will receive the filtrate; record weight.

8.3.2 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 5.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions if rinsed adequately prior to use (even when metals are not of concern).

8.3.3 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder. Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the total sample weight to determine the weight of the waste sample that will be filtered.

8.3.4 Gradually apply vacuum or gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10psi increments to a maximum of 50psi. **Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.**

8.3.5 When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

8.3.6 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, this material may not filter. If this is the case, the material

within the filtration device is defined as a solid and is carried through the extraction as a solid. **Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.**

8.3.7 Weigh the filtrate; record weight.

8.3.8 If the sample contains <0.5% dry solids, proceed to Section 8.5 - Preparation for Analysis.

If the sample contained no initial liquid phase, the filtrate is defined as the TCLP leachate; proceed to Section 8.5 - Preparation for Analysis.

8.3.9 EXTRACTION FLUID ALIQUOT DETERMINATION
Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (8.1.1.3)} \times \text{weight of waste filtered (8.3.3)}}{100}$$

8.4 EXTRACTION (TUMBLING)

8.4.1 Slowly add the calculated amount of appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal).

8.4.2 Secure the extractor bottle in the rotary tumbler, and rotate at 30±2 rpm for 18±2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23±2°C during the extraction period. SOP 663 describes the procedures for monitoring tumbler revolutions and room temperature.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically vented (e.g., after 15 minutes, 30 minutes, and 1 hour), into a hood.

8.4.3 Following the 18±2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter.

8.4.4 For final filtration of the TCLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration.

Filter(s) shall be acid-washed (see Section 5.4) if evaluating the mobility of metals.

8.4.5 Following collection of the TCLP leachate, the pH of the leachate should be recorded. Immediately aliquot and preserve the leachate for analysis.

8.4.6 The liquid phase may now be either analyzed (8.5) or stored at 4±2°C until time of analysis. If miscible, the initial liquid phase may be combined with the TCLP leachate. If the initial liquid phase of the waste is not or may not be compatible with the filtrate, do not combine these liquids. Although they are collectively defined as the TCLP leachate, they are to be analyzed separately, and their analysis results combined mathematically (8.5.2).

8.5 PREPARATION FOR ANALYSIS

8.5.1 Metals leachates must be acidified with nitric acid to pH<2. If precipitation is observed upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate for metals analyses shall not be acidified, and the leachate shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4±2°C) until analyzed.

8.5.2 The TCLP leachate shall be prepared and analyzed according to appropriate analytical methods. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ±0.5%), conduct the appropriate preparations and analyses, and combine the results mathematically, by using a volume-weighted average as shown below:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = volume of the first phase (L)

C_1 = concentration of the analyte of concern in the first phase (mg/L)

V_2 = volume of the second phase (L)

C_2 = concentration of the analyte of concern on the second phase (mg/L)

9. QUALITY CONTROL

9.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel. No more than 20 field samples may be included in a batch.

9.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.). A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

9.2.1 Matrix spikes are to be added after filtration of the TCLP leachate and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

9.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP leachate as that which was analyzed for the unspiked sample.

9.2.3 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%\ \text{Recovery}) = 100\ (Xs - Xu)/K$$

where:

Xs = measured value for the spike sample
Xu = measured value for the unspiked samples
K = known value of the spike in the sample

10. DEVIATIONS FROM THE METHOD

There are no known deviations from the SW-846 Method 1311 with the following exception: Paragon allows for the use of HDPE bottles for metals and semivolatile organics leaching, if approved by the client (see LIMS program specifications), and if this type of container can be shown to meet the criteria discussed in Section 5.5 (i.e., inert and does not adsorb or release target analytes).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses and a lab coat when working with chemical

materials (e.g., standards, solvents, reagents, or samples).

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.2 WASTE DISPOSAL

11.2.1 Unused sample leachate may be disposed of in the Aqueous Laboratory Waste profile.

11.2.2 Unused sample leachate solids may be disposed of in the Contaminated Soils and Solids and Solids Waste.

11.2.3 Radioactive sample disposal - the extracted solid sample residues and solid sample/Na_2SO_4 residue shall be disposed of in the Radioactive Soils and Solids container. Mixed waste solids shall be disposed of in the appropriate mixed waste container.

11.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

Test Methods for Evaluating Solid Waste, US EPA, Volume 1c. Method 1311. Rev 0. July 1992.

DOCUMENT REVISION HISTORY

3/4/08: Minor clarifications throughout. Augmented LIMS program specification language Section 3.3. Added instructions for making 1N HNO_3 Section 6. Reformatted Section 8, included temperature monitoring and SOP 663 reference. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

LEACHING FLUIDS LOG

Lot Nos.: Sodium Hydroxide _____ Glacial Acetic Acid _____

Solution Name	Date Prepared	Initials	Volume NaOH Used (mL)	Volume Glacial Acetic Acid Used (mL)	Total Volume Made (mL)	Final pH	Comments

Reviewed by _____ Date _____

FORM 646r1.doc (4/17/02)

Paragon Analytics

PERCENT SOLIDS (% SOLIDS) DETERMINATION

Logbook No./Page _____ A **(For Samples on Following Logbook Page)**

Units = grams	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
Sample No.	Weight of Beaker, Spatula & Sample	Weight of Beaker, Spatula & Residue	Total Sample Weight (a - b)	**Weight of Filter**	Weight of Collection Flask	Weight of Flask & Filtrate	Filtrate Weight (f - e)	Total Solids Weight (c - g)	% Solids (Wet) (h / c) * 100	Weight of Filter & Dried Solids	Weight of Dried Solids (j - d)	% Solids (Dry) (k / h) * 100

CONFIDENTIAL

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Logbook No./Page ________________ B

LEACHING PROCEDURE WORKSHEET

Work Order # ___________________________
Batch ID # ______________________________
Method **SOP** **Rev**

(Start) Date ________ **Time** ______
(Start) RPM _______ **Temp.** _____ **°C** *(from min/max* SN 21251556*)*
(Start) Analyst _____ RESET MIN/MAX AFTER READING OBTAINED

(Stop) Date _______ **Time** ______ **RPM** ______
(Stop) Temp. ____ **°C** **Tumble Min/Max** ___/___ **°C**
RESET AFTER EACH READING **(Stop) Analyst** _____

Extraction Fluid ID ______________________ **Filtration Date/Time/** ____________________ **Initials** ________

Reviewed By / Date __________________________

Preliminary Solids[a]	Particle Reduction[b]	Sample Number	Initial pH	Fluid Determination				Sample Weight (g)	Fluid (mL)	Final pH	Leachate No.	Comments
				HCl (mL)	Final pH	Fluid #	Fluid pH					
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
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I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											

[a] I = insignificant (< 0.5%); S = 100%; M = Multiphasic (see attached % Solids Determination form).

[b] Y = Yes - reduction required / performed; N = no partical size reduction required.

INTERNAL COC TRANSFER: Relinquished by _______ (initials) to _______________________ (RU# & location) _____________________ (Date & Time)

Form 623r10.doc (1/17/2006)

Paragon Analytics

Corning Model 320 pH Meter Calibration & Maintenance Log

Result Units = pH units

Date	Time	Analyst	4.01 Solution Lot No./ Result	10.01 Solution Lot No./ Result	% Slope	7.00 Solution Lot No./ Result	Check Solution Result
			/	/		/	
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Comments/Maintenance Notes:

Form 825r0.xls (4/18/2003)

Paragon Analytics

TEMPERATURE LOGBOOK

ORGANIC EXTRACTIONS - TCLP ROOM

Acceptable Range 23 ± 2 °C

A current temperature reading must be recorded at the onset of TCLP tumbling, and the min/max memory must be reset. DO NOT initiate tumbling if temperature is not within acceptable limits. The current temperature and min/max information must be recorded at the completion of tumbling. Both the Department and QA Managers must be notified in a timely manner if an excursion occurs.

		Thermometer: 41406316 (min/max)				
DATE	TIME	Current Temp. (°C)	Temp. Min (°C) Date/Time Occurred	Temp. Max (°C) Date/Time Occurred	INITIALS	COMMENTS

Reviewed by / date _____ **Form 345r1.doc (7/10/06)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 617 REVISION 13

TITLE: **CONTINUOUS LIQUID-LIQUID EXTRACTION (CLE) -- METHOD SW3520C**

FORMS: **605, 606, 609, 616** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3-7-08

QUALITY ASSURANCE MANAGER _____ DATE 3/6/08

LABORATORY MANAGER _____ DATE 3-7-08

HISTORY: Rev0, 2/22/92; Rev1, 7/20/92; Rev2, PCN #118; 1/26/94; Rev3, PCN #378, 2/17/95; Rev4, 4/12/96; Rev5, 4/10/97, Rev6, 2/9/99; Rev7, 2/13/02; Rev8, 3/1/02; Rev9, 12/5/02; Rev10, 2/20/04; Rev11, 1/28/05; Rev12, 9/1/06; Rev13, 3/4/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- Method SW3520C -- describe a procedure for isolating organic compounds from aqueous samples. This procedure is applicable to the isolation of water-insoluble and slightly soluble organics in preparation for a variety of determinative chromatographic procedures. This procedure is intended for use of extraction solvents with a density greater than that of the sample. Methylene chloride is typically used, as its density is greater than that of water.

2. SUMMARY

A measured volume of sample (usually one liter) is placed into a continuous liquid-liquid extractor, adjusted to a specific pH if necessary, and extracted with methylene chloride for 18-24 hours. The extract is dried, concentrated, and, if necessary, solvent exchanged according to the analysis required. Paragon SOPs 607 and 637 describe the solvent concentration and solvent exchange procedures utilized after this extraction procedure.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the

technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Interference from phthalate esters can be minimized by using plastic-free solvent containers and scrupulously cleaned glassware (SOP 334) that has been kiln-baked or solvent-rinsed prior to use. Use of low phthalate gloves, such as nitrile, may also be important. These practices are important both in the field and in the laboratory.

4.2 Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides may degrade in the presence of soap residue. Glassware shall be kiln-baked or solvent-rinsed prior to use.

4.3 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

4.4 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is hindered due to interferences, further cleanup of the sample extract may be necessary. Refer to SW-846 Method 3600C for guidance on cleanup procedures.

5. APPARATUS AND MATERIALS

5.1 continuous liquid-liquid extractors (CLEs)

5.2 condenser columns with circulating cooling water

5.3 heating mantles, rheostat controlled

5.4 round flat-bottom flasks, 500mL

5.5 PTFE boiling chips, Chemware™ D1069103 or equivalent, pre-rinsed with methylene chloride

5.6 pH indicator paper, wide (0-14) and narrow range (0-2.5 and 11-13)

5.7 syringes, 1mL or as needed

5.8 graduated cylinders, 1L and 2L

5.9 powder funnels

6. REAGENTS

NOTE: Only reagent grade or better chemicals may be used; solvents must be pesticide residue grade or equivalent. With the exception of the sodium hydroxide solution, all reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

6.1 Organic-free reagent water; laboratory deionized (DI) water is suitable for use.

6.2 Sodium hydroxide solution (NaOH). Used for pH adjustments. Made in-house from NaOH pellets (EMD or JT Baker #3722-07 or equivalent), as follows: In a large Pyrex™ beaker with magnetic stirrer, prepare a 12M solution by *slowly* adding 480g NaOH pellets per liter of reagent water. A cold-water bath is typically used to keep the solution cool while mixing, as the addition of NaOH pellets generates heat when added to the water. Store in a HDPE container, a glass container will slowly dissolve at high pH. Or, if an amber glass bottle is used, mark the bottle to be replaced in less than or equal to one year of service.

6.3 Sulfuric acid (H_2SO_4), concentrated. Used for pH adjustments. EMD #SX1247-2 or equivalent.

6.4 Methylene chloride (CH_2Cl_2, $MeCl_2$), Burdick & Jackson #299-4 or equivalent.

7. SAMPLE COLLECTION, PRESERVATION AND HOLD TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Aqueous samples intended to be analyzed for semivolatile organics, organochlorine pesticides, polychlorinated biphenyls, or herbicides are collected in 1L amber glass bottles, possessing a Teflon™-lined lid. Aqueous samples are not typically preserved. However, this SOP may also be used to process aqueous samples that have been preserved with acid (some State fuels programs) or dechlorinated with sodium thiosulfate ($Na_2S_2O_3$).

7.3 All samples are stored at 4±2°C.

7.4 The samples must be extracted within 7 days of collection.

8. PROCEDURE

8.1 Fill an appropriate number of round flat-bottom flasks and CLE extractors each with approximately 200mL of methylene chloride. Add several boiling chips to each round bottom flask.

8.2 Typically the entire contents of a sample bottle are extracted by this procedure, so any lack of homogeneity is likely due to the field sampling process. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. When only a portion of sample from a bottle is extracted, care must be taken to thoroughly mix the sample before taking the aliquot for analysis.

NOTE: The guidance of SW-846 suggests rinsing the sample bottle with 60mL of methylene chloride, however it is Paragon's practice to decant the sample volume for aqueous analysis. Paragon does not rinse the sample bottle to better avoid the introduction of solids as a component of the aqueous phase analysis, and also when high concentrations are anticipated or known and only a portion of the sample volume will be extracted.

8.3 If the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. Transfer the sample directly from the sample bottle to the CLE. A powder funnel may be used to pour the sample into the CLE. Refill the bottle with tap water up to the sample level previously marked. Measure and record the volume of sample that was in the bottle using an appropriate size graduated cylinder. Alternatively, use an appropriate size graduated cylinder to measure 1 liter (nominal) of sample and transfer it quantitatively to the CLE.

8.4 If sufficient sample volume has been provided, prepare one matrix spike/matrix spike duplicate (MS/MSD) set per batch of 20 or fewer environmental samples.

8.5 Use two separate aliquots of DI water to serve as the batch method blank (MB) and laboratory control sample (LCS).

8.6 Check the initial pH of the samples with wide range pH paper and record on the laboratory benchsheet. If necessary, adjust the pH using sulfuric acid solution or 12N sodium hydroxide to the pH indicated for the specific determinative method that will be used. Record the adjusted pH on the laboratory benchsheet. See Table 1 for required pH values.

NOTE: For most preparations, the pH is checked/adjusted *before* adding any spikes. However, when preparing for semivolatiles analysis, the pH is checked/adjusted *after* the required spikes are added.

8.7 Add the appropriate volume of spike (usually 1.0mL) to the MS/MSD samples. Add the appropriate volume of spike (usually 1.0mL) to the LCS sample. Spike

all client and laboratory QC samples with an appropriate amount of surrogate (usually 1.0mL).

8.8 Add sufficient reagent water to the CLE to ensure proper operation, and extract for 18-24 hours. *Be sure the water for the condensers is circulating before switching on the heating mantles.* Record start and stop times of methylene chloride cycling on the benchsheet.

8.9 After the extraction period, allow the extractor to cool for at least one half hour, then detach the boiling flask. If extraction at a secondary pH is not required, the extract is dried and concentrated using procedures from SOP 607 (Kuderna Danish procedure) and SOP 637 (nitrogen blowdown procedure). See Table 1 for pH information.

8.10 If extraction at a secondary pH is required, attach a clean round bottom flask containing 200mL of methylene chloride to the CLE. Carefully, while stirring, adjust the pH of the aqueous phase to the second pH indicated in Table 1. Extract for 18-24 hours, allow to cool, and detach the boiling flask. *Note that if performing Method SW8270, the acid/neutral and base extracts may be combined prior to concentration.*

9. QUALITY CONTROL

Re-extraction of the sample may be warranted if any of the following should occur:

- If the cooling water in the condenser column is left off and solvent volume is lost through the condenser or the flat bottom flask boils to dryness.
- If an emulsion forms that blocks the flow of solvent through the dump tube, the entire contents of the CLE should be transferred to a separatory funnel, the emulsion broken, and the contents quantitatively transferred to a clean CLE.
- Contamination of extracts or samples.
- Cross-contamination resulting from transferring the sample/extract to or from the wrong funnel or flask indicated for that sample or extract.

If re-extraction is not possible due to extenuating circumstances (e.g., no sample remaining, past holding time) the extract should be kept and the benchsheet noted accordingly. The Project Manager and Department Manager should be notified. In all cases, whether or not re-extraction is possible, a "NonConformance" (NCR) form must be initiated and processed (see SOP 928).

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW3520C. There are no known deviations from the method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples).

11.1.3 Any chemicals with a Threshold Limit Value of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Methylene chloride has a TLV ≤50ppm.

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Expired standards are returned to the analytical group that prepared them to be disposed of in a proper waste stream.

11.2.2 Methylene chloride is disposed in the halogenated organic waste satellite collection vessel.

11.2.3 Extracted non-radioactive water is disposed of in the CLE aqueous waste stream.

11.2.4 Extracted radioactive water is disposed of in the radioactive CLE aqueous waste stream.

11.2.5 All empty solvent bottles are disposed of according to the appropriate SOPs. All labels and markings must be defaced prior to disposal.

12. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Volume 1B, "Method 3520C", Revision 3, December 1996.

DOCUMENT REVISION HISTORY

9/1/2006: Sample representativeness procedure and preparation of 1:1 sulfuric acid reagent clarified. Updated format. Forms and DOCUMENT REVISION HISTORY section added.

3/4/08: Added Timer posting as 'Operator's Aid' to SOP; checked Form iterations (updated as needed).

TABLE 1

SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative Method (SW-846)	Initial Extraction pH	Secondary Extraction pH
8081	5-9	None
8082	5-9	None
8141	As received	None
8270**	< 2	> 11

** Extraction pH sequence in the order shown may better separate acid and base/neutral waste components. **Extraction of the acid fraction first may prevent oxidation of acid surrogates and target compounds.**

Paragon Analytics

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) -- EXTRACTION & CLEANUP WORKSHEET

WO #s _____ **Matrix** AQ SO Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____ **Balance ID** ___

Ext Code 8310 E610 **Meth** (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)W Dilute **SOP** (617)CLE (647)SONC (625)SOX (626)SEP **Rev** ___ **Initials** ____

Ext Start Date _____ **Time** _____ **End Date** _____ **Time** _____ **Cleanup** (3630C) Silica Gel **SOP 604 Rev** ___ **Date** _____ **Time** _____ **Initials** ____

SAMPLE						EXTRACT / CLEANUP							
Sample No.	Amount (g /mL)	**pH**	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hexane Exchange	Date KD (Final)	Date Methanol Exchange	**A-Disk Size**	Final Volume (mL)	Vialed Date	**Comments**

Reagent Lots: MeCl, _____ Hexane _____ Methanol _____ Silica Gel _____ Na_2SO_4 _____ Reviewed by / Date _____

Form 605r5.frm (8/10/2001)

Paragon Analytics

ORGANOPHOSPHOROUS PESTICIDES -- EXTRACTION WORKSHEET

WO #s _____ **Matrix** AQ Solid Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____
Balance ID _____ **Extraction Code** 8141A E614 **Method** (3520C) CLE (3540C) SOX (3580A) Waste Dilute **SOP** (617)CLE (625)SOX **Rev** ____ **Initials** _____
Extr. Start Date/Time _____ **Extr. End Date/Time** _____ **Reviewed by/Date** _____ **Form 606r6.doc (7/7/05)**

SAMPLE						EXTRACT						
Sample No.	Amount (g/mL)	**pH**	Surrogate(mL)	Matrix Spike (mL)	Initials Spike Witness	Initial Rvap Date / Analyst	Cleanup Date / Analyst	Final Rvap Date / Analyst	Date Hexane Exchange / Analyst	Final Volume (mL)	**Date Vialed / Analyst**	**Comments**

Reagent Lots: $MeCl_2$ _____ Hexane _____ Na_2SO_4 _____

Paragon Analytics

SEMIVOLATILES EXTRACTION / CLEANUP WORKSHEET

WO #s _____ **Matrix** ___ **Batch ID** _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** __ **Extr SOP/Rev** __ **Extr Code:** 8270C CLP SOW E625

Extr Method: (3520C)CLE (3550C)SONC (3540C)SOX (3510C)SEP (3580A)Waste Dilution **Initials** _____ **Extr Start Date/Time** _____ **Extr Stop Date/Time** _____

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Silica Gel _____ (See other GPC forms) H_2SO_4 _____ NaOH _____ Na_2SO_4 _____

Steam bath ___°C **Proper N-Evap station flow settings used?** Y **Cleanup Code:** (3620B)Florisil (3640A)GPC (See other forms) Silica Gel **Cleanup SOP/Rev** ___ **Date/Time** _____

Initials ____ **Reviewed by / date** _____ Form 609r13.doc (12/24//07)

SAMPLE								EXTRACT / CLEANUP					
Sample No.	Amount (g / mL)	Initial pH	pH (≤ 2)	pH (11-13)	Surrogate (mL)	Matrix Spike (mL)	Sur / Matrix Spike Witnessed	Date KD (Initial)	Cleanup Date	Date KD (Final)	Final Volume (mL)	Date Vialed	Comments

_____________ A

PESTICIDES / PCBs -- EXTRACTION WORKSHEET

Paragon Analytics

WO #s __________________________ **Batch ID** ______________________ **Surr Code** ________________ **Matrix Spike Code** ____________

Ex Date/Time _____________ (start) ______________ (stop) **Matrix** Aq Solid Other _________ **Balance ID** ______ **Ex SOP** ____ **Rev**___ **Initials** ____

Ex Method: (3520C)**CLE** (3550B)**SONC** (3540C)**SOX** (3510)**SEP** (3580)**Wdilute** (SOP 673)**Wipes** **EX Code:** 8081B **(pest)** 8082 **(PCB)** 608 **(pest)** 8081B **(TCLP pest)**

Lots: MeCl$_2$ ____________ **Hexane** ____________ **Na$_2$SO$_4$** ___________ **Proper N-Evap station flow settings used? Y** **Form 616r14.xls (12/24/07)**

Sample No.	Amount (g / mL)	pH	Surr. Spike Amt. (mL)	Matrix Spike Amt. (mL)	Spike Analyst / Witness	Date KD / Analyst	Final Solvent	Final Vol. (mL)	Cleanup Req. (y / n)	Comments
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_____ B

PESTICIDES / PCBs -- CLEANUP WORKSHEET

Paragon Analytics

WO #s _____ **Batch ID** _____ **Cleanup SOP** _____ **Rev**____ **Initials** _____

Method: (3620B)**Florisil** (3665A)**Sulfuric** (3640A)**GPC** (see GPC forms) Other _____

Lots: $MeCl_2$ _____ **Hexane** _____ **Acetone** _____ **Florisil** _____ **Sulfuric acid** _____ **Na_2SO_4**_____ **Reviewed by / date** _____

	FLORISIL: Has lot check been done? y/n _____				**GPC** (Note: half the extract is lost during cleanup)				**SULFURIC ACID**		
Sample No.	Amount Extract (mL)/ Solvent	Date Cleanup / Analyst	Final volume (mL) / Solvent	Date Vialed / Analyst	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Date KD / Analyst	Final volume (mL) / Solvent	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Comments

Timer Operation

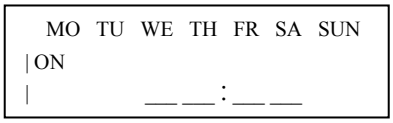
1) **CLLE only** - check that the plugs connected to the power strip correspond to the heating mantles you wish to use.

   Soxhlet only - unplug the Variac(s) power cord(s) from the 3-outlet heavy-duty extension cord. Variac cords are marked with either the Variac # or "aqua" colored tape, or both. **MAKE SURE** the Variac(s) you are using correspond to the six-position set-up you want to run. Then, plug the Variac cord(s) into either (or both) of the 2 outlets on the digital timer. Each Variac is labeled as to which digital timer it should be plugged into. Check that the timer # on the Variac matches the timer # you are plugging it into. After plugging the Variac(s) into the timer, turn the Variac(s) on, using either the toggle or circular switch, depending on the model. Flip the appropriate toggle switches on the soxhlet heating mantle bank, to activate the position(s) you want to run.

2) Check that the **day-of-week**, **time**, and **AM/PM** on the timer are correct (press "CLOCK" on the timer). If any of the date/time display is incorrect, reset the clock as described in **Appendix A**.

3) Program the timer as follows:

   a: Press "PROG" button on the timer once. The left-hand side of the timer display should look like this:

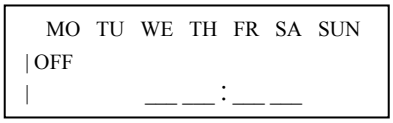
   

   b: Press "DAY" button until the day of the week you want the timer to start (i.e., begin extraction) is indicated at the top of the display screen.

   c: Press "HOUR" button until the hour you want the timer to start is displayed. **MAKE SURE** that the hour selected is correct, with respect to AM/ PM, as timer does not display or run on "military" time.

   d: Press "MIN" button until the minute you want the timer to start is displayed. Holding down the "MIN" button will cause it to scroll.

   e: Once date/time to turn **ON** is established, press "PROG" again. The left-hand side of the timer display should now look like this:

   f: **Repeat steps b-d** to program what time you want the timer stop (i.e., stop extraction). When complete, press "CLOCK" to return to the current date/time display.

   g: Check/confirm program **ON** date and time, by pressing "PROG" once. Check/ confirm program **OFF** date and time, by pressing "PROG" again. Press "CLOCK" to go back to the current date and time display.

   h: Lastly, press the "MODE" button until "**AUTO**" is displayed to the left on the date/ time display. **MAKE ABSOLUTELY SURE** that timer is set to "AUTO" mode, and not "OFF," "ON," or "RDM;" as these other modes will either cause timer to not turn on, turn on immediately, or turn on at a semi-random time.

4) The timer is now ready to run your program!

Important Notes:

- While the timer(s) will accept up to 7 different event programs, it is **not advised** that you use this feature. Rather, reprogram the timer under Event 1 (indicated by the little number "1" in the Program display) each time you want to program start / stop dates and times.
- When you are done using timer (i.e., your extraction is complete and you are finished using the timer to run samples) **it is important that you unplug the Variac cord** from the timer and plug it back into the 3-outlet heavy-duty extension cord; **as well as turning off the Variac power switch**. If you leave the Variac(s) plugged into the timer, the set program will run again in 1 week (if timer is on AUTO mode), regardless of whether CLLEs/Soxhlets are actually set up. This is a potential fire hazard, as the heating mantles get hot enough to scorch paper. Also, **press "MODE" on timer until "OFF" is displayed to the left of the date/ time display**. This turns the set program off, preventing the timer from re-running the program in seven days.
- The timer's clock runs on one "AA" battery. The battery in each timer should be replaced approximately every June and December to ensure performance of the timers. To replace, use a small Phillips-head screwdriver to remove the battery cover on the back of the timer, and install a fresh battery in the correct orientation.

APPENDIX A
SETTING CLOCK

1) Press "CLOCK" to view the currently programmed date and time. If it is not correct… while holding down "CLOCK":
   a: Press "DAY" until correct day-of-week is displayed.
   b: Press "HOUR" until correct hour is displayed, **remember to set correct hour by AM/ PM.**
   c: Press "MIN" until correct minute is displayed.
2) Release "CLOCK" button. The display should now give the correct date and time. As an example, if it is three-o-clock in the afternoon on Wednesday, the display should read:

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 622 REVISION 6

TITLE: WASTE DILUTION EXTRACTION -- METHOD SW3580A

FORMS: NONE

APPROVED BY:
TECHNICAL MANAGER _____ DATE 27 Feb 06
QUALITY ASSURANCE MANAGER _____ DATE 2/27/06
LABORATORY MANAGER _____ DATE 2-27-06

HISTORY: Rev0, 7/17/92; Rev1, PCN #383, 2/17/95; Rev2, 7/15/99; Rev3, 3/01/02; Rev4, 3/14/03; Rev5, 4/27/04; Rev6, 2/27/06. re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the extraction of waste samples by SW-846 Method SW3580A and pertains to oil samples or other methylene chloride or hexane miscible organic liquids that are to be analyzed for a variety of organic compounds, generally utilizing SW-846 methods.

2. OVERVIEW

Approximately 1g of sample is diluted with hexane, methylene chloride or other appropriate solvent to 10mL in a Class A volumetric flask. Cleanup procedures are generally recommended and vary depending on the analytical method to be employed. Appropriate cleanups include methods SW3620 (SOP 648), SW3665 (SOP 651), SW3630 (SOP 604), and SW3640 (SOP 641).

3. RESPONSIBILITIES

3.1 Analysts must demonstrate the capability to generate acceptable It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the bench sheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of measures taken to correct those errors.

3.4 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the processing of the samples on the bench sheet. Any discrepancies must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

4.1 volumetric flasks, Class A, 10mL or as appropriate

4.2 vials, screw-top with Teflon liner, 40mL or as appropriate

4.3 analytical balance (±0.0001g sensitivity)

4.4 Pasteur pipettes, disposable

4.5 pipette bulb

5. REAGENTS – Only pesticide residue grade or equivalent may be used.

5.1 hexane (C_6H_{14}), pesticide residue grade or equivalent

5.2 methylene chloride (CH_2Cl_2), pesticide residue grade or equivalent

5.3 surrogate and matrix spike standard solutions

6. PROCEDURES

6.1 To ensure homogenous sub-sampling, even single-phase liquids generally require homogenization by stirring or mixing prior to taking an aliquot. If liquids are multiphasic, the phases may need to be separated prior to taking an aliquot. Multiphasic liquids often have an aqueous phase and an organic phase. This procedure is not suitable for preparing aqueous phases. If two or more organic phases are present then all of the organic phases may be prepared by this procedure.

Measure and record the proportion of each phase prior to taking an aliquot. Weigh out approximately 1g of sample into a 10mL volumetric flask. Record the weight (to ±0.0001g) in the appropriate logbook. Lesser volumes of sample can be weighed out if prior knowledge indicates this is appropriate. Repeat for the matrix spike/matrix spike duplicate (MS/MSD) pair, as applicable.

6.2 Prepare a method blank (MB) in a volumetric flask using an aliquot of solvent (typically 9mL). Likewise, prepare aliquots for the laboratory control sample (LCS, typically 8mL) and the laboratory control sample duplicate (LCSD), if

applicable. Typical solvents for this procedure are hexane for SW8081 or SW8082, and methylene chloride for SW8270.

6.3 Add the appropriate volume of surrogate to all field and quality control (QC) samples (typically 1mL).

6.4 For the LCS and LCSD, and the MS/MSD, spike with the proper volume of matrix spike standard solution (typically 1mL).

6.5 Dilute samples and QC to full volume (10mL) with the appropriate solvent for the analytical method.

NOTE: It is important to bring the samples to final volume ***exactly***. The bottom of the solution's meniscus should rest exactly on the top of the line etched on the volumetric flask.

6.6 Stopper all volumetric flasks and shake until well mixed (approximately two minutes).

6.7 The extracts are now ready for appropriate cleanups. If no cleanups are required, the extracts may be delivered to the appropriate analytical group (observe SOP 318 internal chain of custody procedures). Extracts should be transferred to appropriate vials before delivery to the analytical group.

7. SAFETY, HAZARDS AND WASTE

7.1 SAFETY AND HAZARDS

7.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

7.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

7.1.3 Any chemicals with a Threshold Limit Value (TLV) ≤50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). **Methylene chloride and hexane have a TLV = 50ppm and use of these solvents must be performed in an adequately ventilated fume hood.**

7.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name; NFPA Health, Flammability, and Reactivity ratings; and date.

7.2 WASTE DISPOSAL

7.2.1 Any hexane, acetone, or other nonhalogenated organic solvents may be disposed of in the Acetonitrile/Nonhalogenated Waste.

7.2.2 Methylene chloride should be disposed of in the Halogenated Waste stream.

7.2.3 The extract vials and the associated extracts are disposed of by the analytical group receiving them in the appropriate waste stream.

7.2.4 All empty solvent bottles are disposed of according to the appropriate procedures. Please note that all labels and markings must be defaced prior to disposal.

8. REFERENCE

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III. Method 3580A, Revision 1, July 1992.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 625 REVISION 11

TITLE: **SOXHLET EXTRACTION - METHOD SW3540C**

FORMS: **605, 606, 609, 616** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3-7-08

QUALITY ASSURANCE MANAGER _____ DATE 3/6/08

LABORATORY MANAGER _____ DATE 3-7-08

HISTORY: Rev0, 2\19\92; Rev1, PCN #133, 2/11/94; Rev2, PCN #438, 4/18/95; Rev3, 5/20/96; Rev4, 2/16/99; Rev5, 3/1/02; Rev6, 5/1/02; Rev7, 12/2/02; Rev8, 3/6/04; Rev9 11/22/04; Rev10, 7/5/06; Rev11, 3/4/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references - SW846 Method 3540C, describe a procedure for extracting non-volatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. This method is applicable to the isolation and concentration of water-insoluble and slightly water soluble organics in preparation for various determinative chromatographic procedures.

2. SUMMARY OF METHOD

A weighed sample is chemically dried by mixing with anhydrous sodium sulfate, then placed in an extraction thimble. The thimble is then loaded into the Soxhlet apparatus and spiked appropriately. The sample is extracted for 16-24 hours. The extract is then dried, concentrated, and as necessary, exchanged into a solvent compatible with the clean up or determinative method that follows. Paragon SOPs 607 and 637 describe the solvent concentration and solvent exchange procedures utilized after this extraction procedure.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the

technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

3.5 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

4. INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

4.2 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is hindered due to interferences, further clean up of the sample extract may be necessary. Refer to SW-846 Method 3600C for guidance on clean up procedures.

4.3 Interference from phthalate esters can be minimized by using plastic-free solvent containers and scrupulously cleaned glassware (SOP 334) that has been kiln-baked or solvent-rinsed prior to use. Use of low phthalate gloves, such as nitrile, may also be important. These practices are important both in the field and in the laboratory.

4.4 Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides may degrade in the presence of soap residue. All glassware should be hand-rinsed thoroughly with hot water after washing with soap. Soxhlet glassware is also kilned after washing (SOP 334).

5. APPARATUS AND MATERIALS

5.1 Soxhlet extractors

5.2 condenser columns with circulating cooling water

5.3 round flat-bottom flasks, 500mL

5.4 heating mantles, rheostat controlled

5.5 Teflon™ boiling stones, or glass boiling chips, or equivalent

5.6 syringes, 1.0mL or as needed

5.7 glass or paper thimble or glass wool (used when sample aliquot will not fit into thimble)

5.8 laboratory balance, capable of weighing to 0.01g, and verified per SOP 305

5.9 beakers, 400mL

5.10 spatula, metal or wooden

6. REAGENTS

6.1 Ottawa sand, EMD, Cat. SX0075-3 or equivalent.

6.2 Sodium sulfate (Na_2SO_4), anhydrous, granular, ACS grade. EMD, Cat. SX0760E-5, or equivalent. *Purify by heating at approximately 450°C for two to six hours or by pre-cleaning with methylene chloride.*

6.3 Methylene chloride (CH_2Cl_2), Burdick & Jackson, Cat. 299-4, or other extraction solvents as appropriate, pesticide residue grade or equivalent

NOTE: Paragon has historically used methylene chloride only for Method SW3540C preparations. This follows the guidance of SW-846, which allows for the use of alternative extraction solvents. Documentation of performance is contained in REPORT: DCM_Acetone (J:\Audits and Corrective Actions\Findings and Corrective Actions\Topical Corrective Actions\DCM_Acetone).

Note that information regarding spike solutions (i.e., surrogate, laboratory control sample, matrix spike) is contained in the associated determinative SOP.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 Soil samples intended to be analyzed for semivolatile organics, organochlorine pesticides, polychlorinated biphenyls or herbicides are collected in a wide-mouth glass jar with Teflon™-lined lid. Soil samples are not chemically preserved.

7.3 Soil samples must be extracted within 14 days of collection.

7.4 All samples and extracts are stored at 4±2°C.

8. PROCEDURE

8.1 SAMPLE HANDLING

8.1.1 Decant and discard any water layer. Take care to discard any foreign objects (e.g., sticks, leaves, rocks) or any portion of the sample that appears to ***not*** be representative of the sample. Mix sample thoroughly

to ensure that a representative sample is obtained, especially composited samples. *Note that samples that consist of multiple phases must be prepared by the phase separation method in Chapter Two of SW-846. This SOP addresses solids only.*

8.1.2 Safety concerns such as dust control may preclude the grinding of samples for particle size reduction. These safety concerns must always be addressed before attempting to grind any sample. Generally, grinding to reduce particle size is not practiced in the extractions area. Samples requiring size reduction have been sent to an appropriate facility before an extraction was performed.

8.1.3 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing and maximum exposure of the sample surfaces for extraction. *Consult the Department Manager regarding difficult, unusual matrices.* The addition of anhydrous sodium sulfate to the sample (in a 1:1 ratio) may make the mixture amenable to grinding.

8.2 Place approximately 300mL of extraction solvent into a 500mL round bottom flask containing several clean boiling stones. Attach the flask to the Soxhlet extractor, and label the round bottom flask appropriately.

8.3 Weigh 30g (nominal) of sample and record the weight to the nearest ±0.01g on the benchsheet.

8.4 Blend the sample aliquot with approximately 30-60g of anhydrous sodium sulfate and place the mixture in an extraction thimble. Load the thimble in a way that allows it to drain freely for the duration of the extraction period. Carefully place the thimble into a Soxhlet setup. If sufficient sample is available, prepare one field sample per batch in triplicate (extra sample aliquots to serve as the matrix spike and matrix spike duplicate, MS/MSD). Some clients may require the preparation of an unspiked sample duplicate (DUP).

8.5 For each batch of 20 or fewer samples, prepare two aliquots of Ottawa sand as described above, one to serve as the method blank (MB) and one to be spiked as the laboratory control sample (LCS). Note that three aliquots of Ottawa sand may need to be prepared if an LCSD is to be analyzed.

8.6 Add the appropriate volume (usually 1.0mL) of surrogate standards to all prepared field and quality control (QC) samples. If aliquots for matrix spiking have been prepared, spike these with the appropriate volume (usually 1.0mL) of matrix spike standard. Also spike (typically 1.0mL) the aliquot(s) of Ottawa sand designated as the LCS.

8.7 Extract the samples for 16-24 hours at a rate of 4-6 cycles per hour. Record the start and stop times of methylene chloride cycling on the laboratory benchsheet.

8.8 After the extraction is complete, allow the extracts to cool. Then dry and concentrate the extracts per SOP 607 (Kuderna Danish procedure) and SOP 637 (nitrogen blowdown procedure).

9. QUALITY CONTROL

Re-extraction of the sample may be warranted if any of the following should occur:

- If the condenser column cooling water is left off and solvent volume is lost through the condenser or the round bottom flask boils to dryness.
- Phthalate contamination due to contact of extracts or sample with latex or vinyl gloves worn by technicians.
- Cross-contamination resulting from transferring the sample/extract to or from the wrong Soxhlet indicated for that sample or extract.

If re-extraction is not possible due to extenuating circumstances (e.g., no sample remaining, past holding time) the extract should be kept and the benchsheet noted accordingly. The Project Manager and Department Manager must be notified. In all cases, whether or not re-extraction is possible, an NCR (SOP 928) must be initiated and processed.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW3540C. Extraction is performed with dichloromethane. Method SW3540C calls for dichloromethane:acetone or hexane:acetone extraction. The suitability and performance of dichloromethane only is documented in REPORT: DCM_Acetone (J:\Audits and Corrective Actions\Findings and Corrective Actions\Topical Corrective Actions\DCM_Acetone).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Methylene chloride has a TLV ≤50ppm.

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Methylene chloride solutions are disposed of in the Halogenated Organic Waste satellite collection vessel.

11.2.2 The solid sample residues and solid sample/Na_2SO_4 residue shall be disposed of in the Contaminated Soils and Solids Waste. Radioactive solid sample residues and solid sample/Na_2SO_4 residue shall be disposed of in the Radioactive Soils and Solids Waste satellite collection vessel. Note that mixed waste solids/prepared sample residues must be disposed of in the appropriate Mixed Waste container.

11.2.3 Expired standards shall be returned to the analytical group that prepared them; the expired standards will then be disposed of in the proper waste stream.

11.2.4 All empty solvent bottles shall be disposed of according to the appropriate SOPs; all labels and markings must be removed or defaced prior to disposal.

12. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Volume 1B, "Method 3540C", Revision 3, December 1996.

DOCUMENT REVISION HISTORY

7/5/06: Clarified LIMS program specification, checked extraction time and cycle compliance. Defined deviation (use of methylene chloride-only as extraction solvent) and referenced technical justification report. Added DOCUMENT REVISION HISTORY.

3/4/08: Added Timer posting as 'Operator's Aid' to SOP.

Paragon Analytics

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) -- EXTRACTION & CLEANUP WORKSHEET

WO #s _____ **Matrix** AQ SO Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____ **Balance ID** ___

Ext Code 8310 E610 **Meth** (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)W Dilute **SOP** (617)CLE (647)SONC (625)SOX (626)SEP **Rev** ___ **Initials** ___

Ext Start Date _____ **Time** _____ **End Date** _____ **Time** _____ **Cleanup** (3630C) Silica Gel **SOP 604 Rev** ___ **Date** _____ **Time** _____ **Initials** ___

SAMPLE						EXTRACT / CLEANUP							
Sample No.	Amount (g / mL)	pH	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hexane Exchange	Date KD (Final)	Date Methanol Exchange	A-Disk Size	Final Volume (mL)	Vialed Date	Comments

Use most current iteration of Form.

Reagent Lots: MeCl, _____ Hexane _____ Methanol _____ Silica Gel _____ Na_2SO_4 _____ Reviewed by / Date _____

Form 605r5.frm (8/10/2001)

ORGANOPHOSPHOROUS PESTICIDES -- EXTRACTION WORKSHEET

Paragon Analytics

WO #s _____ **Matrix** AQ Solid Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____

Balance ID _____ **Extraction Code** 8141A E614 **Method** (3520C) CLE (3540C) SOX (3580A) Waste Dilute **SOP** (617)CLE (625)SOX **Rev** ____ **Initials** _____

Extr. Start Date/Time _____ **Extr. End Date/Time** _____ **Reviewed by/Date** _____ **Form 606r6.doc** (7/7/05)

SAMPLE						EXTRACT						
Sample No.	Amount (g / mL)	**pH**	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Initial Rvap Date / Analyst	Cleanup Date / Analyst	Final Rvap Date / Analyst	Date Hexane Exchange / Analyst	Final Volume (mL)	**Date Vialed / Analyst**	**Comments**
						Use most current iteration of Form.						

Reagent Lots: $MeCl_4$ _____ Hexane _____ Na_2SO_4 _____

Form 609r12.doc (7/7/05) *Paragon Analytics*

SEMIVOLATILES EXTRACTION / CLEANUP WORKSHEET

WO #s _____ **Matrix** ___ **Batch ID** _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** __ **Extr SOP/Rev** __ **Extr Code:** 8270C CLP SOW E625

Extr Method: (3520C)CLE (3550C)SONC (3540C)SOX (3510C)SEP (3580A)Waste Dilution **Initials** _____ **Extr Start Date/Time** _____ **Extr Stop Date/Time** _____

Cleanup Code: (3620B) Florisil (3640A) GPC (See other forms) Silica Gel **Cleanup SOP/Rev** ____ **Date/Time** _____ **Initials** _____ **Reviewed by / date** _____

SAMPLE								EXTRACT / CLEANUP					
Sample No.	Amount (g / mL)	Initial pH	pH (≤ 2)	pH (11-13)	Surrogate (mL)	Matrix Spike (mL)	Sur / Matrix Spike Witnessed	Date KD (Initial)	Cleanup Date	Date KD (Final)	Final Volume (mL)	Date Vialed	Comments

Use most current iteration of Form.

Steam bath _____ °C.

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Silica Gel _____ (See other GPC forms) H_2SO_4 _____ NaOH _____ Na_2SO_4 _____

_____ A

PESTICIDES / PCBs -- EXTRACTION WORKSHEET

Paragon Analytics

WO #s _____ **Batch ID** _____ **Surr Code** _____ **Matrix Spike Code** _____

Ex Date/Time _____ (start) _____ (stop) **Matrix** Aq Solid Other _____ **Balance ID** _____ **Ex SOP** ____ **Rev**___ **Initials** ____

Ex Method: (3520C) CLE (3550B) SONC (3540C) SOX (3510) SEP (3580) Wdilute (SOP 673) Wipes **EX Code:** 8081B (pest) 8082 (PCB) 608 (pest) 8081B (TCLP pest)

Sample No.	Amount (g / mL)	pH	Surr. Spike Amt. (mL)	Matrix Spike Amt. (mL)	Spike Analyst / Witness	Date KD / Analyst	Final Solvent	Final Vol. (mL)	Cleanup Req. (y / n)	Comments
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Use most current iteration of Form.

Lots: $MeCl_2$ _____ Hexane _____ Na_2SO_4 _____

Form 616r13.xls (3/29/05)

__________ B **PESTICIDES / PCBs -- CLEANUP WORKSHEET** ***Paragon Analytics***

WO #s ______________________________ **Batch ID** _________________________ **Cleanup SOP** _____ **Rev**____ **Initials** ______
Cleanup Method: (3620B) Florisil (3665A) Sulfuric (3640A) GPC (See additional forms) Other ____________

FLORISIL: Has lot check been done? y/n _____ **GPC** (Note: half the extract is lost during cleanup) **SULFURIC ACID**

Sample No.	Amount Extract (mL)/ Solvent	Date Cleanup / Analyst	Final volume (mL) / Solvent	**Date Vialed / Analyst**	Amount Extract (mL) / Solvent	**Date Cleanup / Analyst**	Date KD / Analyst	Final volume (mL) / Solvent	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Comments

Use most current iteration of Form.

Lots: $MeCl_2$ ________ Hexane _________ Acetone _________ Florisil _________ Sulfuric acid _________ Na_2SO_4_________ **Reviewed by / date** ________________

Timer Operation

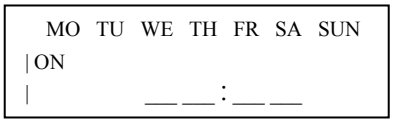
1) **CLLE only** - check that the plugs connected to the power strip correspond to the heating mantles you wish to use.

Soxhlet only - unplug the Variac(s) power cord(s) from the 3-outlet heavy-duty extension cord. Variac cords are marked with either the Variac # or "aqua" colored tape, or both. **MAKE SURE** the Variac(s) you are using correspond to the six-position set-up you want to run. Then, plug the Variac cord(s) into either (or both) of the 2 outlets on the digital timer. Each Variac is labeled as to which digital timer it should be plugged into. Check that the timer # on the Variac matches the timer # you are plugging it into. After plugging the Variac(s) into the timer, turn the Variac(s) on, using either the toggle or circular switch, depending on the model. Flip the appropriate toggle switches on the soxhlet heating mantle bank, to activate the position(s) you want to run.

2) Check that the **day-of-week**, **time**, and **AM/PM** on the timer are correct (press "CLOCK" on the timer). If any of the date/time display is incorrect, reset the clock as described in **Appendix A**.

3) Program the timer as follows:

a: Press "PROG" button on the timer once. The left-hand side of the timer display should look like this:

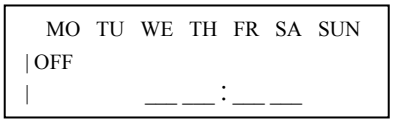


b: Press "DAY" button until the day of the week you want the timer to start (i.e., begin extraction) is indicated at the top of the display screen.

c: Press "HOUR" button until the hour you want the timer to start is displayed. **MAKE SURE** that the hour selected is correct, with respect to AM/ PM, as timer does not display or run on "military" time.

d: Press "MIN" button until the minute you want the timer to start is displayed. Holding down the "MIN" button will cause it to scroll.

e: Once date/time to turn **ON** is established, press "PROG" again. The left-hand side of the timer display should now look like this:



f: **Repeat steps b-d** to program what time you want the timer stop (i.e., stop extraction). When complete, press "CLOCK" to return to the current date/time display.

g: Check/confirm program **ON** date and time, by pressing "PROG" once. Check/ confirm program **OFF** date and time, by pressing "PROG" again. Press "CLOCK" to go back to the current date and time display.

h: Lastly, press the "MODE" button until "**AUTO**" is displayed to the left on the date/ time display. **MAKE ABSOLUTELY SURE** that timer is set to "AUTO" mode, and not "OFF," "ON," or "RDM;" as these other modes will either cause timer to not turn on, turn on immediately, or turn on at a semi-random time.

4) The timer is now ready to run your program!

Important Notes:

- While the timer(s) will accept up to 7 different event programs, it is **not advised** that you use this feature. Rather, reprogram the timer under Event 1 (indicated by the little number "1" in the Program display) each time you want to program start / stop dates and times.
- When you are done using timer (i.e., your extraction is complete and you are finished using the timer to run samples) **it is important that you unplug the Variac cord** from the timer and plug it back into the 3-outlet heavy-duty extension cord; **as well as turning off the Variac power switch**. If you leave the Variac(s) plugged into the timer, the set program will run again in 1 week (if timer is on AUTO mode), regardless of whether CLLEs/Soxhlets are actually set up. This is a potential fire hazard, as the heating mantles get hot enough to scorch paper. Also, **press "MODE" on timer until "OFF" is displayed to the left of the date/ time display**. This turns the set program off, preventing the timer from re-running the program in seven days.
- The timer's clock runs on one "AA" battery. The battery in each timer should be replaced approximately every June and December to ensure performance of the timers. To replace, use a small Phillips-head screwdriver to remove the battery cover on the back of the timer, and install a fresh battery in the correct orientation.

APPENDIX A

SETTING CLOCK

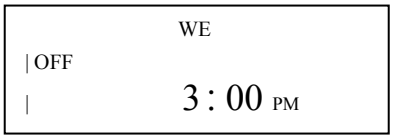
1) Press "CLOCK" to view the currently programmed date and time. If it is not correct… while holding down "CLOCK":

   a: Press "DAY" until correct day-of-week is displayed.

   b: Press "HOUR" until correct hour is displayed, **remember to set correct hour by AM/ PM.**

   c: Press "MIN" until correct minute is displayed.

2) Release "CLOCK" button. The display should now give the correct date and time. As an example, if it is three-o-clock in the afternoon on Wednesday, the display should read:



Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 626 REVISION 9

TITLE: **SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION -- METHOD SW3510C**

FORMS: **602, 605, 606, 609, 616**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9.5.06

QUALITY ASSURANCE MANAGER _____ DATE 9/5/06

LABORATORY MANAGER _____ DATE 9-5-06

HISTORY: Rev0, 2/10/92; Rev1, PCN #282, 11/10/94; Rev2, 4/12/96; Rev3, 2/12/99; Rev4, 2/13/02; Rev5, 3/01/02; Rev6, 12/03/02; Rev7, 2/23/04; Rev8, 11/22/04; Rev9, 9/1/06.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW-846 Method 3510C -- describe a procedure for isolating organic compounds from aqueous samples. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for various chromatographic procedures.

2. SUMMARY

A measured volume of sample, usually 1 liter, is serially extracted at a specified pH with methylene chloride, using a separatory funnel. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup and analysis to follow. See Table 1 for specified pH values. Paragon SOPs 607 and 637 describe the solvent concentration and solvent exchange procedures utilized after this extraction procedure.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the extraction according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data and/or the associated extracts as appropriate.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented..

4. INTERFERENCES

4.1 Interference from phthalate esters can be minimized by using plastic-free solvent containers and scrupulously cleaned glassware (SOP 334) that has been kiln-baked or solvent-rinsed prior to use. Use of low phthalate gloves, such as nitrile, may also be important. These practices are important both in the field and in the laboratory.

4.2 Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides may degrade in the presence of soap residue. Glassware shall be kiln-baked or solvent-rinsed prior to use.

4.3 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

4.4 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is hindered due to interferences, further cleanup of the sample extract may be necessary. Refer to SW-846 Method 3600C for guidance on cleanup procedures.

5. APPARATUS AND MATERIALS

5.1 separatory funnels, adequate size to allow adequate mixing of sample and solvent, with Teflon™ stopcock, and Teflon™ or glass stopper

5.2 graduated cylinder, 1 or 2L

5.3 powder funnels

5.4 pH paper, wide and narrow range

5.5 solvent collection vessels -- Erlenmeyer or round flat-bottom flask of appropriate size (250-500mL)

5.6 syringes, 1mL or as needed

6. SOLVENTS AND REAGENTS

NOTE: Only reagent grade chemicals may be used. Reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

6.1 Organic-free reagent water; the laboratory deionized (DI) water is suitable.

6.2 Sodium hydroxide (NaOH). JT Baker #3722–07 or equivalent. Used for pH adjustments. In a large Pyrex™ beaker with magnetic stirrer, prepare 12M solution by slowly adding 480g NaOH pellets per liter of reagent water. A cold-water bath is typically used to keep the solution cool while mixing, as the addition of NaOH pellets generates heat when added to the water. Should be stored in an HDPE container, as a glass container might slowly dissolve at high pH.

6.3 Sulfuric acid (H_2SO_4), concentrated. Used for pH adjustments. EMD #SX1247-2 or equivalent.

6.4 Sodium sulfate (Na_2SO_4), anhydrous, granular. EMD #SX0760E-5 or equivalent. Purify by heating at 450°C for two hours or by pre-cleaning with methylene chloride.

6.5 Methylene chloride (CH_2Cl_2), Burdick & Jackson #299-4 or equivalent.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 Aqueous samples intended to be analyzed for semivolatile organics, organochlorine pesticides, polychlorinated biphenyls, organophosphorous pesticides, Cal LUFT or herbicides are collected in 1L amber glass bottles equipped with a Teflon™-lined lid. Aqueous samples are not typically preserved. This SOP may, however, be used to process aqueous samples that have been preserved with acid (per some State fuels programs) or dechlorinated with sodium thiosulfate ($Na_2S_2O_3$).

7.3 All samples are stored at 4±2°C.

7.4 Samples must be extracted within 7 days of collection.

8. PROCEDURE

8.1 Carefully solvent rinse all glassware, stoppers, and stopcocks to be used in the extraction procedure with appropriate solvent. Glassware that has been kilned

and sealed need not be solvent rinsed.

8.2 Assemble the separatory funnel, being careful not to touch the center portion of the Teflon™ stopcock.

8.3 Typically the entire contents of a sample bottle are extracted, so any lack of homogeneity is likely due to the field sampling process. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1L. When only a portion of sample from a bottle is extracted, care must be taken to thoroughly mix the sample before obtaining the aliquot.

NOTE: The guidance of SW-846 suggests rinsing the sample bottle with 60mL of methylene chloride, however, it is Paragon's practice to decant the sample volume for aqueous analysis. Paragon does not rinse the sample bottle to better avoid the introduction of solids as a component of the aqueous phase analysis, and also when high concentrations are anticipated or known and when only a portion of the sample volume is extracted.

8.4 If the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. Transfer the sample directly from the sample bottle to the separatory funnel. A dedicated powder funnel may be used to pour the sample into the separatory funnel.

Refill the bottle with tap water up to the sample level previously marked. Pour the bottle's tap water contents out into a graduated cylinder of appropriate size to determine the volume of sample that was used. Record on benchsheet.

Alternatively, use an appropriate size graduated cylinder to directly measure 1L (nominal) of sample and transfer it quantitatively to the separatory funnel.

8.5 If sufficient sample volume has been provided, one matrix spike/matrix spike duplicate (MS/MSD) set per batch of 20 or fewer environmental samples will be prepared (typically 1.0mL of spike standard is added to the designated aliquot). Use two separate aliquots of DI water to serve as the batch method blank (MB) and laboratory control sample (LCS); typically 1.0mL of spike standard is added to the designated aliquots.

Add the appropriate volume (usually 1.0mL) of surrogate to all client and QC samples. The spikes are added before pH adjustment.

8.6 Check the initial pH of the sample with wide range pH paper and record on the laboratory benchsheet. If necessary, adjust the pH using sulfuric acid solution or 12N sodium hydroxide to the pH indicated for the specific determinative method that will be used. Record the adjusted pH on the laboratory benchsheet. See Table 1 for required pH values.

8.7 Add 60-80mL of methylene chloride to the separatory funnel.

NOTE: **Methylene chloride creates excessive pressure very rapidly.** Therefore, initial venting should be performed immediately after the separatory funnel has been sealed and shaken once, and then again after shaking it twice.

Always vent funnel into the hood and away from any person to avoid methylene chloride exposure.

Vent funnel slowly or sample will be lost due to rapid reversal of vapor pressure.

8.8 Seal and shake the separatory funnel vigorously for two minutes with frequent venting to release excess pressure.

8.9 Allow the organic phase to separate from the aqueous phase completely (for at least 10 minutes).

If an emulsion layer forms, it must be broken up. The optimum technique to break the emulsion depends on the sample, and may require stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. More details follow.

After the ***last*** shake out has been performed, the emulsion may be broken up by pouring it into a beaker and slowly adding Na_2SO_4 and stirring until the water is absorbed into the Na_2SO_4. If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for the water solubility of methylene chloride), then transfer the sample, solvent, and emulsion into the extraction chamber of a continuous liquid-liquid extractor (CLE) and proceed as described in SOP 617. If transferred to a CLE, a set of new QC samples will also have to be prepared.

8.10 Collect the methylene chloride (solvent phase) in a 250mL Erlenmeyer flask or other appropriate collection vessel.

8.11 Repeat the extraction two more times using 60mL of fresh solvent each time. Combine the three solvent extracts in an appropriate glass flask (i.e., 500mL flat bottom flask).

8.12 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH (see Table 1). Serially extract three times with 60mL portions of methylene chloride as described above. Collect and combine these three extracts and label the combined extract appropriately.

8.13 If the extracts are to be analyzed by method SW8270, the acid/base-neutral extracts may be combined prior to concentration.

8.14 The extract is dried and concentrated using procedures from SOP 607 (Kuderna Danish procedure) and SOP 637 (nitrogen blowdown procedure).

9. QUALITY CONTROL

9.1 Re-extraction of the sample may be warranted if any of the following should occur:

- An emulsion layer forms that cannot be broken up using physical methods and is greater than 20 percent of the total volume.
- The Teflon™ stopcock or stopper leak solvent when shaken.
- Either solvent or sample is lost due to inadequate venting of the separatory funnel.
- Phthalate contamination due to contact of extracts or sample with latex or vinyl gloves worn by technicians.
- Cross-contamination resulting from transferring the sample or extract to or from the wrong separatory funnel or flask indicated for that sample or extract.

If re-extraction is not possible due to extenuating circumstances (e.g., no sample remaining, past holding time) the extract should be kept and a notation made on the benchsheet. Notify the Project Manager and Department Manager.

In all cases, whether or not re-extraction is possible, an NCR (see SOP 928) must be initiated.

9.2 All QC samples must be subjected to exactly the same procedures as those used on actual samples.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW3510C. Section 8.3 details Paragon's procedure for achieving representative and reproducible sample aliquots. There are no known deviations from the method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples).

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Methylene chloride has a TLV ≤ 50ppm.

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Return expired standards to the analytical group that originally prepared them for proper disposal.

11.2.2 Methylene chloride is disposed in the Halogenated Organic Waste satellite collection vessel.

11.2.3 Extracted water is disposed of in the CLE aqueous waste stream.

11.2.4 Extracted radioactive water is disposed of in the radioactive CLE aqueous waste stream.

11.2.5 All empty solvent bottles are disposed of according to the appropriate SOPs. All labels and markings must be defaced prior to disposal.

12. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Volume 1B, "Method 3510C", Revision 3, December 1996.

DOCUMENT REVISION HISTORY

9/1/2006: Sample representativeness procedure and preparation of 1:1 sulfuric acid reagent clarified. Updated format. Forms and DOCUMENT REVISION HISTORY section added.

TABLE 1

SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative Method (SW-846)	Initial Extraction pH	Secondary Extraction pH
8081	5-9	None
8082	5-9	None
8141	As received	None
8270**	<2	>11
DRO-Cal-Luft	<2	None

** Extraction pH sequence in the order shown may better separate acid and base/ neutral waste components. Extraction of the acid fraction first may prevent oxidation of acid surrogates and target compounds.

Paragon Analytics

DIESEL RANGE ORGANICS (DRO) -- EXTRACTION BENCHSHEET

WO #s _____ **Matrix:** AQ SO _____ **Batch #** _____ **Surrogate Code** _____ **M Spike Code** _____ **Initials** ___ **Balance ID** ___

Extr. Start Date/Time _____ **Stop Date/Time** _____ **Ext Code** 8015M Cal Luft **Method** 8015M Cal Luft **SOP 603 Rev** __ **Reviewed by / Date** _____

SAMPLE							EXTRACT		
Sample Number	Amount (g / mL)	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Extract Solvent	Solvent Volume (mL)	Final Volume (mL)	**Date Vialed**	**Comments**

Reagents: MeOH DCM 80% MeOH / 20% H_2O Prep ID/ Date Hexane Na_2SO_4 Form 602r9.frm (4/12/2002)

Paragon Analytics

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) -- EXTRACTION & CLEANUP WORKSHEET

WO #s _____ **Matrix** AQ SO Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____ **Balance ID** ___

Ext Code 8310 E610 **Meth** (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)W Dilute **SOP** (617)CLE (647)SONC (625)SOX (626)SEP **Rev** ___ **Initials** ____

Ext Start Date _____ **Time** _____ **End Date** _____ **Time** _____ **Cleanup** (3630C) Silica Gel **SOP 604 Rev** ___ **Date** _____ **Time** _____ **Initials** ____

SAMPLE						EXTRACT / CLEANUP							
Sample No.	Amount (g /mL)	**pH**	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hexane Exchange	Date KD (Final)	Date Methanol Exchange	**A-Disk Size**	Final Volume (mL)	Vialed Date	**Comments**

Reagent Lots: $MeCl_2$ _____ Hexane _____ Methanol _____ Silica Gel _____ Na_2SO_4 _____ Reviewed by / Date _____

Form 605r5.frm (8/10/2001)

Paragon Analytics

ORGANOPHOSPHOROUS PESTICIDES -- EXTRACTION WORKSHEET

WO #s _____ **Matrix** AQ Solid Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____
Balance ID _____ **Extraction Code** 8141A E614 **Method** (3520C) CLE (3540C) SOX (3580A) Waste Dilute **SOP** (617)CLE (625)SOX **Rev** ____ **Initials** _____
Extr. Start Date/Time _____ **Extr. End Date/Time** _____ **Reviewed by/Date** _____ **Form 606r6.doc (7/7/05)**

SAMPLE						EXTRACT						
Sample No.	Amount (g/mL)	**pH**	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Initial Rvap Date / Analyst	Cleanup Date / Analyst	Final Rvap Date / Analyst	Date Hexane Exchange / Analyst	Final Volume (mL)	**Date Vialed / Analyst**	**Comments**

Reagent Lots: $MeCl_2$ _____ Hexane _____ Na_2SO_4 _____

Form 609r9.frm (3/7/2002)

Paragon Analytics

SEMIVOLATILES EXTRACTION / CLEANUP WORKSHEET

WO #s _____ **Matrix** ____ **Batch ID** _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** ____ **Extr SOP/Rev** ___ **Extr Code:** 8270C CLP SOW E625

Extr Method: (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)Waste Dilution **Initials** _____ **Extr Start Date/Time** _____ **Extr Stop Date/Time** _____

Cleanup Code: (3620B) Florisil (3640A) GPC (See other forms) Silica Gel **Cleanup SOP/Rev** ___ **Date/Time** _____ **Initials** _____ **Reviewed by / date** _____

SAMPLE								EXTRACT / CLEANUP					
Sample No.	Amount (g / mL)	Initial pH	**pH** (≤ 2)	**pH** (11-13)	Surrogate (mL)	Matrix Spike (mL)	Sur / Matrix Spike Witnessed	Date KD (Initial)	Cleanup Date	Date KD (Final)	Final Volume (mL)	Date Vialed	Comments

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Silica Gel _____ (See other GPC forms) H_2SO_4 _____ NaOH _____ Na_2SO_4 _____

Form 616r9.frm (11/9/2001)

Paragon Analytics, Inc.

PESTICIDES / PCBs -- EXTRACTION / CLEANUP WORKSHEET

WO #s _____ **Matrix:** AQ Solid Other _____ **Batch ID** _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** __ **Ex Date/Time** _____ **Initials** ___

Ex Code: 8081A (Pest&PCB) 8081B (Pest Only) 8082 (PCB) 608 (Pest) 8081B (TCLP Pest) **Ex Method:** (3520C)CLE (3550B)SONC (**3540C**)**SOX** (3510C)SEP (3580A)WDilute

Ex SOP/Rev _____ **Cleanup Code:** (3620B)Florisil (3665A)Sulfuric (3640A)GPC (See other forms) **Cleanup SOP/Rev** _____ **Date/Time** _____ **Initials** ____

SAMPLE							EXTRACT						
Sample No.	Amount (g / mL)	**pH**	Surrogate (mL)	Matrix Spike (mL)	Sur / Matrix Spike Witnessed	Extraction Date /Time Off	Date KD (Initial)	Date KD (Final)	Date Hexane Exchange	Final Volume (mL)	Type of Cleanup	Date Vialed	Comments

Reagent Lots: MeCl, _____ Hexane _____ Acetone _____ Florisil _____ Sulfuic Acid _____ Na_2SO_4 _____ **Reviewed by/Date** _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 629 REVISION 10

TITLE: **DETERMINATION OF IGNITABILITY BY THE PENSKY-MARTENS CLOSED-CUP TESTER -- METHODS SW1010A AND ASTM93-80**

FORM: **632** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-14-07

QUALITY ASSURANCE MANAGER _____ DATE 11/12/07

LABORATORY MANAGER _____ DATE 11-14-07

HISTORY: Rev0, 2/12/92; Rev1, PCN #135, 2/11/94; Rev2, PCN #441, 4/18/95; Rev3, 3/15/96; Rev4, 1/29/98; Rev5, 10/25/99; Rev6, 3/01/02; Rev7, 3/14/03; Rev8, 5/12/04; Rev10, 2/27/06; 11/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedure used to determine ignitability (flash point). This SOP is based on EPA SW-846 Method 1010A and ASTM Method 93-80. A Pensky-Martens closed-cup tester is used to determine the flash point of various liquids (e.g., fuel oils, lube oils), including those that tend to form a surface film under test conditions. Liquids containing non-filterable, suspended solids may also be tested using this method. A modified test for analyzing soils is also included.

2. SUMMARY OF METHOD

The sample is heated at a slow, constant rate (with liquid samples undergoing continuous stirring). A small flame is directed into the sample cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature, corrected to a barometric pressure of 101.3kPa (760mm Hg), at which application of the test flame ignites the vapor above the sample.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible.

The criteria defined in the Program Specification supercede PAR's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the bench sheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of measures taken to correct the errors that were found during review.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Interferences that may affect flash point values are: sudden changes in ambient pressure, sample homogeneity, drafts, and operator bias.

4.2 Samples having a pH≤2 or pH≥12 should not be placed in the sample cup as corrosion of the brass may occur.

4.3 Tars and or asphalt-like material may ruin the cup. The analyst should use caution in placing these organic solids in the cup.

5. APPARATUS AND MATERIALS

5.1 Pensky-Martens closed-cup flash tester, as described in Annex A1 of ASTM Method D93-80.

5.2 verified thermometer with a range of -20 to 150°C.

5.3 ignition source such as cigarette lighter or matches

6. REAGENTS

6.1 p-xylene – 1,4-dimethylbenzene ($C_6H_4(CH_3)_2$), (at least 97% pure)

6.2 acetone (CH_3COCH_3) and/or dichloromethane (CH_2Cl_2), for cleaning cup between samples

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 All samples should be collected according to an approved sampling plan.

7.2 Samples must be collected in glass containers and stored at 4±2°C. Samples should NOT be collected in plastic bottles, since volatile compounds may diffuse though the walls of the bottle.

7.3 Preservatives shall not be added to samples.

7.4 Method SW1010A does not specify a holding time for this analysis. Paragon's policy-defined maximum holding time allowance for conducting this test is 28 days from sample collection.

8. PROCEDURES

8.1 INSTRUMENT VERIFICATION PROCEDURE

A verification of instrument performance must be done at the beginning of each analytical batch (i.e., immediately before samples are analyzed), after every 10 samples, and immediately after the last field sample is analyzed. See Section 9.3 for acceptance criteria and corrective action if instrument verification fails.

8.1.1 Thoroughly clean and dry all parts of the sample cup and its accessories before starting the verification. Wash the cup with soap and water, rinse thoroughly with water, rinse with acetone three times, and then rinse with dichloromethane three times. Place the cup in the hood to air dry. Be sure that the stirrer is in place before beginning verification.

8.1.2 When the sample cup is clean and dry, the tester must be checked to demonstrate that it is in proper working order.

8.1.3 Add p-xylene to the cup until it reaches the fill line (approximately 75mL). Place the lid on the cup, making sure the locating device is properly engaged. Temporarily turn off the fume hood so that drafts will not affect the verification or analysis. It may be necessary to cool the sample cup before proceeding if the cup begins to retain heat from previous analyses. To cool the cup, gently place the sample cup in the cooling cup on the right side of the apparatus after adding a small amount of ice. Generally, rinsing the cup with methylene chloride will cool the cup enough to start the process.

NOTE: After p-xylene has been added to the cup, do not agitate the cup excessively.

8.1.4 Insert the thermometer into the appropriate slot on top of the sample cup. When the temperature of the p-xylene has dropped below 15°C, remove the sample cup from the cooling cup, wipe off any excess water from the sample cup, and place the sample cup into the heating mantle so that the cup fits securely. Attach the stirring probe to the stirrer on top of the sample cup.

8.1.5 Connect the gas line to the tester. Turn on the gas valve and apply the ignition source to the gas port outlet located on the top front of the

sample cup. Adjust the flame to a 3.2-4.8mm diameter (the flame should be under ~13mm in length).

NOTE: Be sure that all flammable materials are removed from the immediate vicinity of the tester before igniting the lighter and that the hood is off.

8.1.6 Turn on the toggle switch labeled "ON." This switch starts the stirring motor.

8.1.7 The white dial located to the right of the toggle switch turns on the heating element. The heating element will not work if the toggle switch is off. Turn the white dial to initiate heating at a rate of approximately 2°C per minute. Usually the first mark on the white dial is sufficient.

8.1.8 Apply the test flame at intervals of less than 5°C by operating the mechanism on the cover that controls the shutter and test flame burner. Lower the flame into the vapor space of the cup, for approximately 1 second, and quickly raise it to its high position.

8.1.9 The p-xylene (or any sample) is deemed to have a flash when a large flame appears and instantaneously propagates over the surface of the sample. The temperature at which this occurs is the flash point.

NOTE: Occasionally, when a temperature just below the flashpoint is reached, the application of the test flame will cause a blue halo or an enlarged flame**; this is not a flash point and the appearance of this halo should not be mistaken for a true flash.**

8.1.10 Under normal operating conditions, the corrected flash point for p-xylene should be 27±1°C. If the flash is outside this range then check the instrument and thermometer and determine the flash point of p-xylene again. If corrected flash point is not within ±1°C of 27°C, then analysis of samples can not proceed until the instrument can be verified to be working properly.

8.1.11 Verification of instrument performance must be done after every 10 samples, and after the last field sample is analyzed. See Section 9.3 for acceptance criteria and corrective action if this QC check fails.

8.2 SAMPLE PREPARATION

Reference methods allow for samples that are known to not contain high concentrations of volatiles, or that are very viscous, to be 'warmed' until they are reasonably fluid before being tested.

Note that if the sample *is* suspected to contain a high concentration of volatile components, or is a soil/solid, this treatment is not to be performed.

Per method directives, no sample is to be heated more than is absolutely necessary, and no sample should ever be heated to a temperature that is within 17°C of the expected flash point.

Because Paragon generally does not have *a priori* knowledge of samples, this warming as described is not performed, because it cannot be conducted without compromising the sample's integrity.

8.3 PROCEDURE FOR LIQUID SAMPLES

8.3.1 Follow the cleaning procedure as outlined in Section 8.1.1.

8.3.2 Fill the sample cup, as outlined in Section 8.1.3, with an aliquot of client sample.

8.3.3 Follow the procedure outlined in Section 8.1.4, with the exception of lowering the temperature of the sample down to a maximum of 4±2°C before placing the sample cup on the apparatus' stove. Therefore, samples should be left in the refrigerator until just prior to analysis.

8.3.4 Follow the procedure outlined in Sections 8.1.5 through 8.1.11 and apply the test flame approximately every 5°C, until a flash point has been observed, or until a temperature of 96.5°C is reached.

NOTE: Occasionally the test flame will ignite the vapor in the cup to such an extent that a flame will shoot out of the cup, or the test flame will grow very large when the shutter is opened, yet the vapors inside the cup do not ignite and propagate across the surface of the liquid. *Both of these phenomena are called a vapor flash, and the temperature at which this was observed must be noted on the benchsheet*. This occurrence is not a flash point.

8.3.5 Occasionally the test flame will be extinguished as the shutter is opened, but before the test flame can be fully lowered into the cup. The temperature at which this is first observed should be noted on the benchsheet as follows: "Non-flammable vapors began extinguishing the test flame at X°C."

When this occurs, gas will continue to flow into the sample cup, and may ignite the next time the flash point is checked, thus giving a false flash point. Be aware that as soon as the test flame begins to be

extinguished, the observation of a true flash point is practically impossible from that point to the completion of the test.

8.3.6 After a flash point has been observed or the temperature has reached 96.5°C, remove the sample cup from the stove and place in the cooling cup so the cup may cool down. Adding ice to the cooling cup will facilitate this step.

8.3.7 If no flash point is observed, report **"The flash point is >96.5 °C."**

8.3.8 If a flash point is observed, it must by confirmed by repeating the determination of the flash point.

The original aliquot shall be discarded, the cup cleaned, and the test repeated with a fresh test aliquot. The 2nd determination should be within ±5°C of the first determined flash point.

When performing the confirmation analysis, apply the test flame approximately every 5°C until a temperature of 15°C below the first observed flash point is reached, and then apply the test flame at intervals of 1-2°C.

Record second observed flash point. If the flash point cannot be confirmed, write in the comments section that the observed flash point could not be confirmed.

8.4 PROCEDURE FOR SUSPENSIONS OF SOLIDS AND HIGHLY VISCOUS LIQUIDS

Bring the material to be tested and the tester to a temperature of 20±5°C. Stirring in a downward direction, raise the temperature throughout the duration of the test at a rate of not less than 1-5°C/min.. With the exception of these requirements for rates of stirring and heating, proceed as prescribed in Section 8.3.

8.5 PROCEDURE FOR SOLIDS AND SOILS

Follow the same procedure as for liquids as outlined in Section 8.3, with the following exceptions:

8.5.1 Remove the stirrer from the sample cup; **Do Not Stir Soil/Solid Samples.** If the stirrer is not removed, either the stirrer will break or the thermometer will break when the toggle switch is turned on.

8.5.2 If non-flammable vapor begins to extinguish the test flame, note in the comments section the temperature at which this was first observed. Water vapor will continue to extinguish the test flame as the temperature is increased, so increase the rate of heating to a rate of 5°C

per minute, and apply the test flame at intervals of approximately every 5°C.

8.5.3 Continue testing the sample following the procedure as outlined in section 8.3.5-8.3.7

8.5.4 If a flash point is observed, confirm the flash point by running the confirmation analysis as outlined in Section 8.3.8.

8.6 CALCULATIONS

8.6.1 Call the CSU Atmospheric Sciences weather station or locate their web site (currently http://atmos.colostatee.edu/~autowx/) and record or print the ambient barometric pressure at the Fort Collins Weather Station on the University campus at the time of the test. When the pressure differs from 101.3 kPa (760 mm Hg), correct the flash point as follows:

corrected flash point = C+0.25 (101.3-K) (1)

corrected flash point = C+0.033 (760-P) (2)

where:

C= observed flash point, degrees Celsius

P= ambient barometric pressure, mm Hg

K= ambient barometric pressure, kPa

8.6.2 The barometric pressure used in the correction calculation is the pressure for the laboratory at the time of the test. Many aneroid barometers, like the ones used at weather stations and airports, are pre-corrected to give sea level readings, which would be incorrect for this test. However, the CSU Atmospheric Sciences Fort Collins Weather Station provides an uncorrected barometric pressure, and its readings may be used for this correction.

9. QUALITY CONTROL

9.1 Method blanks, matrix spike samples, matrix spike duplicate samples, and blank spike samples are *not* required for this test.

9.2 One duplicate analysis (on a new aliquot of sample) must be performed after every 10 samples. If one of the samples analyzed in a batch has a flash point that was confirmed, then this sample may be used as the duplicate sample for that batch. If there are no samples in a batch that exhibited a flash point, then any sample in the batch may be selected for duplicate analysis. For this test, a duplicate analysis of the same test sample should have results that agree to within ±5°C of the original. In the event that this criteria is exceeded for a sample that

does exhibit a flash point, the operator should examine the results of the p-xylene calibration verifications that preceded and follow the test samples. If these calibration verifications are acceptable, then a non-homogeneous sample matrix is suspected, and this conclusion will be noted in the case narrative.

9.3 Verify the instrument performance at the start of an analytical sequence, after every 10 samples, and again after the last sample, as described in Section 8.1. The acceptance criteria for this verification check standard is that the measured corrected flash point for p-xylene must agree to within ±1°C of the known flashpoint for p-xylene. If the instrument performance cannot be verified, then the test apparatus should be thoroughly cleaned, dried, and the verification performed again. If the second attempt at verification is successful, then the samples preceding the verification can be reported. If on a second attempt the flashpoint of p-xylene is not within acceptance criteria, then the preceding samples cannot be reported. Maintenance or repairs will be necessary, and successful verification of instrument performance must be completed before samples can be analyzed and reported.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW1010A. Method 1010A directs the reader to ASTM Method D93-80 for additional information, and those requirements have been incorporated into this SOP. There are no known deviations from these referenced Methods.

11. HEALTH, SAFETY AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Acetone and dichloromethane each has a TLV≤50ppm.

11.1.4 The analyst must minimize his/her exposure to p-xylene - prolonged overexposure can adversely affect the central nervous system.

11.1.5 The analyst must remove all flammable materials from the immediate vicinity of the testing apparatus, and make other analysts aware of the use of the flame so they do not bring any flammable materials into the vicinity of the apparatus while testing is being performed.

11.1.6 The analyst must exercise and take appropriate safety precautions during the initial application of the test flame, since samples containing low flash material may give an abnormally strong flash when the test flame is applied to the sample.

11.1.7 Perform this test in a fume hood. To prevent disturbance of the flame when samples are tested, the hood should be turned off so as not to be drawing air. Turn the hood back on between analyses.

11.1.8 Any non-original containers being used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Any p-xylene, hexane, acetone, or other nonhalogenated organic solvents may be disposed of in the Acetonitrile/Nonhalogenated Waste Profile.

11.2.2 Dichloromethane (methylene chloride) solutions are disposed of in the Halogenated Organic Waste satellite collection vessel.

11.2.3 Allow sample aliquots to cool before disposing into appropriate Solid or Liquid waste profile.

11.2.4 All empty solvent, reagent, and sample containers are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, Method 1010A Revision 1, December 2004.

12.2 American Society for Testing and Materials, Designation D93-94 vol, 05:01, 093, 1995 edition. Refer to D93-79 or D93-80 for more information.

DOCUMENT REVISION HISTORY

11/12/07: Added language forbidding the use of plastic bottles for sample collection Section 7. Changed reference (from D93-94) to D93-80 Section 10, and Title and Section 1 accordingly. General word-smithing. Added DOCUMENT REVISION HISTORY Section and Form.

Paragon Analytics

IGNITABILITY WORKSHEET (IGNIT) - METHOD SW1010

Workorder # _____ **Batch ID** _____ **Date** _____ **Initials** _____

Start Time _____ **End Time** _____ **p-Xylene Lot ID** _____ **SOP 629 Rev** __ **Reviewed by/date** _____

SAMPLE #	FLASH #1 (°C)	FLASH #2 (°C) (Confirmation) Reported Value	CORR. FLASH (°C) (see formula below)	CALC. BAROMETRIC PRESSURE (mm Hg) (see formula below)	COMMENTS
P-XYLENE **					
DUP (as applicable)					
P-XYLENE **					

Note that 2nd flash confirmation is run (sample volume permitting) when flash is seen on first test. 2nd flash must be within ±5 °C of first flash for confirmation; if not, see Supervisor. **Calculation for Corrected Flash Point:** n °C + 0.033 (760 mm - P), where P equals current barometric pressure (mm). **Calculated Barometric Pressure:** Access website to obtain current barometric pressure (inches). Convert to mm Hg as follows: barometric pressure (inches) X 25.4 = barometric pressure mm Hg. ** **Control Limits for p-xylene ignition temperature:** 27±1°C **

Form 632r8.frm (11/5/2002)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 634 REVISION 6

TITLE: **SULFUR CLEANUP -- METHOD SW3660B**

FORM: **645** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3/1/07

QUALITY ASSURANCE MANAGER _____ DATE 3/28/07

LABORATORY MANAGER _____ DATE 3-1-07

HISTORY: Rev0, 2/11/92; Rev1, PCN #139, 2/15/94; Rev2, 11/18/99; Rev3, 4/9/02; Rev4, 9/30/03; Rev5, 7/26/05; Rev6, 3/1/07.

re-released without revision 3/9/09 DAS

1. SCOPE AND APPLICATION

Elemental sulfur is encountered in many sediment samples, marine algae, and some industrial wastes. The solubility of elemental sulfur in various extraction solvents is very similar to the solubility of polychlorinated biphenyls and organochlorine pesticides in the extraction solvents. Therefore, the sulfur interference follows along with the pesticides through normal extraction and cleanup techniques.

This standard operating procedure (SOP) and the referenced method, SW3660B, describe procedures to remove elemental sulfur from extracts using metallic copper. Method SW3660B also provides a procedure to minimize sulfur using tetrabutyl-ammonium sulfite reagent. Paragon currently only performs the cleanup utilizing copper.

This cleanup procedure is performed on organochlorine pesticide and PCB extracts in which sulfur is present, or when sulfur may be expected in the sample extract. Cleanup is performed prior to analysis on electron capture detectors (ECDs). Figure 1 shows a PCB extract analyzed before sulfur cleanup was performed. An Aroclor pattern can be seen, but the quantification is hindered by the presence of sulfur in the extract. Figure 2 shows the same extract analyzed after sulfur cleanup was performed. The Aroclor pattern is much easier to identify and quantify after the sulfur has been removed.

2. SUMMARY OF PROCEDURE

Sample extracts that require cleanup are mixed with copper. The mixture is shaken and the extract is then removed from the copper reagent.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review (e.g., benchsheet).

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration of capability may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file indicates that this review for completeness, precision and accuracy has been done and found to be satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

This procedure requires that the copper powder be very reactive, as evidenced by a bright shiny appearance (see Step 7.2 for the preparation of this reagent). However, care must be taken to remove all traces of the acid used to prepare the copper, in order to avoid possible degradation of some analytes.

5. APPARATUS AND MATERIALS

5.1 micro spatulas

5.2 Pasteur pipettes, disposable

5.3 glass vials with PTFE-lined caps, assorted sizes

6. REAGENTS - only reagent grade chemicals and pesticide residue grade or equivalent solvents may be used

6.1 copper (Cu) turnings or powder, Aldrich 26609-4 or equivalent

6.2 organic-free reagent water, laboratory deionized (DI) water is suitable

6.3 nitric acid (HNO_3), dilute: add a few drops conc. nitric acid (J.T. Baker #9598-34 or equivalent) to 50mL reagent water

6.4 acetone (CH_3COCH_3), Burdick & Jackson, Cat. #010-4 or equivalent

6.5 hexane (C_6H_{14}), Burdick & Jackson, Cat. #216-4 or equivalent

6.6 nitrogen gas, high purity

7. REMOVAL OF SULFUR USING COPPER

7.1 The sample extract is exchanged to hexane and concentrated to the desired final volume by Organic Extractions personnel per SOPs 607 and 637. If yellow sulfur crystals are present, centrifuge or let the crystals settle, draw-off the extract with a Pasteur pipet and transfer to a glass vial. If no sulfur crystals are visible, transfer approximately 1mL of the extract to a vial or other suitable container.

7.2 Remove oxides from the surface of the copper particles by treating with dilute nitric acid. Rinse several times with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.

7.3 Add 0.1-2g of cleaned copper to each vial and cap.

7.4 Vigorously shake each vial containing copper and extract for at least 1 minute.

7.5 Allow the copper to sink to the bottom of the vial.

7.6 Separate the extract from the copper using a Pasteur pipet. Place the extract in a clean vial.

7.7 If the surfaces of copper remaining in the vial are discolored from copper sulfide (CuS) precipitation, then repeat Steps 7.2 to 7.6.

8. QUALITY CONTROL

The method blank (MB) and laboratory control sample (LCS) associated in the sample extraction batch to be cleaned, are to be carried through this cleanup procedure exactly as the samples are processed. All reagents should be checked prior to use to verify that interferences do not exist.

9. DEVIATIONS FROM METHOD

There are no known deviations from the referenced method.

10. SAFETY, HAZARDS AND WASTE DISPOSAL

10.1 SAFETY AND HAZARDS

10.1.1 Read the MSDSs before prior to using any solvents or reagents for the first time.

10.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

10.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Concentrated nitric acid and hexane have TLVs ≤50ppm.

10.2 WASTE DISPOSAL

10.2.1 Any hexane, acetone, or other nonhalogenated organic solvents may be disposed of in the Acetonitrile/Nonhalogenated Waste.

10.2.2 The extract vials and associated extracts may be disposed of intact in the Discarded Extract Vial waste.

10.2.3 All empty solvent bottles are to be disposed of appropriately. Note that all labels and markings must be defaced prior to disposal.

10.2.4 Copper solids are disposed of in the Contaminated Soils and Solids Waste.

11. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, "Method 3660B", December 1996.

DOCUMENT REVISION HISTORY

7/26/05: Added LIMS program specification reference.

3/1/07: In REAGENTS Section, provided for equivalents, indicated laboratory DI water suitable, added nitrogen gas. Minor format corrections throughout. DOCUMENT REVISION HISTORY Section and Form added.

Figure 1: **Before Sulfur Cleanup**

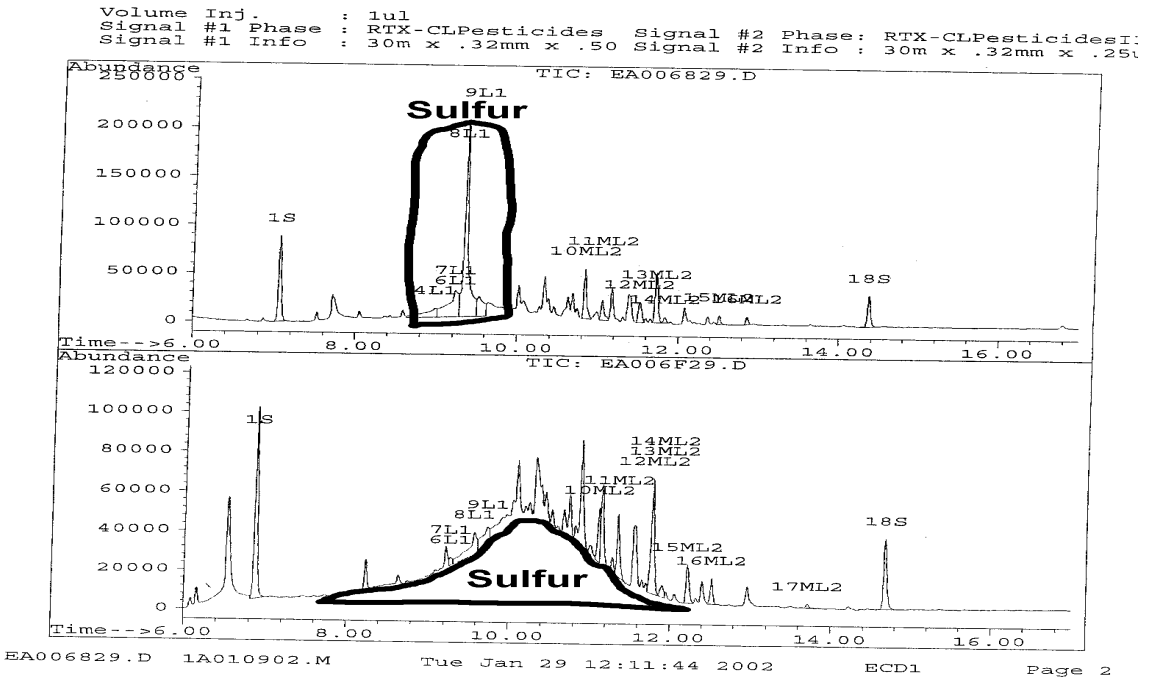
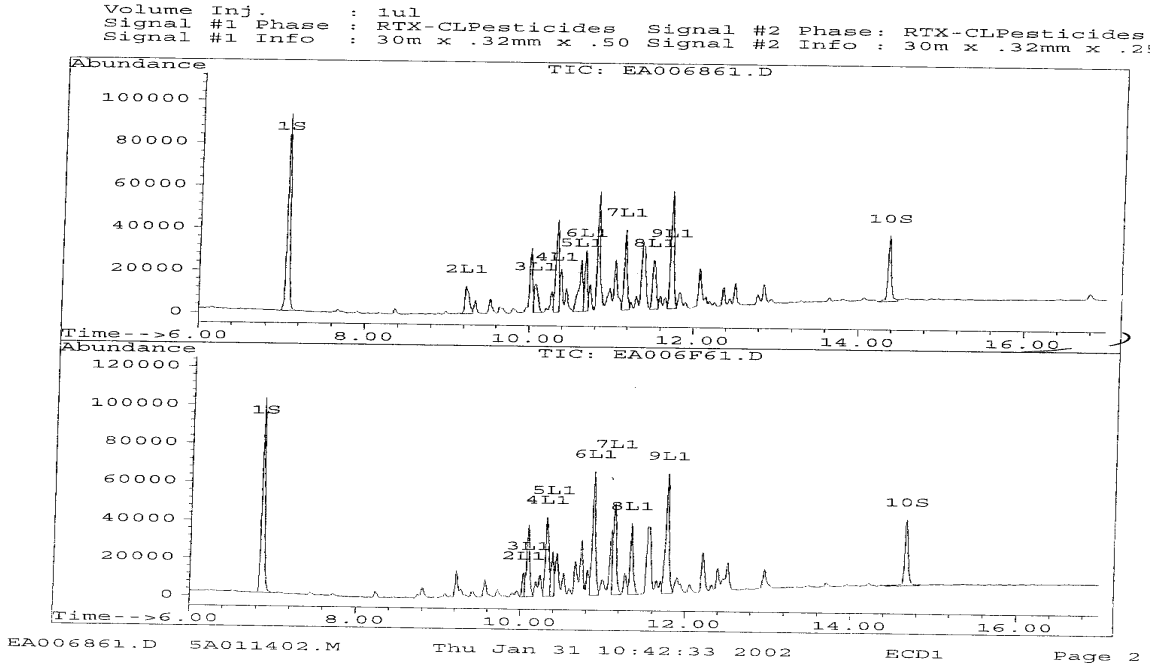


Figure 2: **After Sulfur Cleanup**



Paragon Analytics

SULFUR CLEANUP (COPPER OR TBA SULFITE) OF PEST/PCB EXTRACTS

WO #s _____ **Cleanup Code:** 3660 **Cleanup SOP/Rev** _____ **Cleanup Date/Time** _____ **Initials** _____

Sample Extract Number	Extract Aliquot (mL)	Technique Used (Cu or TBA)	Comments

Reagent Lots: Copper _____ **TBA Solution ID / Exp** _____ **Isopropyl Alcohol** _____

Reviewed by / Date _____

Form 645r1.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

Amended 12/26/07. Note re: flow documentation following Section 7.3 added. Benchsheets updated to accomodate flow setting verification (replacement pages issued, training conducted -- see training records. 12/26/07 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 637 REVISION 9

TITLE: CONCENTRATION AND SOLVENT EXCHANGE BY THE NITROGEN BLOWDOWN TECHNIQUE

FORMS: ~~604, 609, 611, 616, 635~~ **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/12/07

QUALITY ASSURANCE MANAGER _____ DATE 11/12/07

LABORATORY MANAGER _____ DATE 11-12-07

HISTORY: Rev0, 1/15/92; Rev1, PCN #144, 2/25/94; Rev2, PCN #445, 4/18/95; Rev3, 3/1/99; Rev4, 4/9/02; Rev5, 12/5/02; Rev6, 3/6/04; Rev7, 11/22/04; Rev8, 11/20/06; Rev9, 11/12/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedure for concentrating extracts to a final volume by the nitrogen blowdown (N-Evap) technique. This SOP is based on procedures described in SW-846 Methods 3510C, 3520C, 3540C and 3550B.

2. SUMMARY

An aliquot of sample is extracted with solvent per SOPs 617, 625, 626, 664 or 665. The extracts from these procedures (except SOP 665) are dried, and then concentrated in a Kuderna-Danish (K-D) apparatus (SOP 607). During the K-D procedure, the extracts are concentrated to approximately 6-10mL. If necessary, the extracts are further concentrated to a smaller final volume by the N-Evap technique described in this SOP. This final concentration is accomplished by applying a steady stream of nitrogen gas over the extract to gently evaporate solvent. Changeover to another solvent can also be performed as part of the N-Evap process.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the LIMS program specification supercede Paragon's

standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

4.2 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is hindered due to interferences, further cleanup of the sample extract may be necessary. Refer to SW-846 Method 3600C for guidance on cleanup procedures.

4.3 Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides may degrade in the presence of soap residue. All glassware should be hand rinsed thoroughly with hot water after washing with soap (SOP 334).

4.4 Interference from phthalate esters can be minimized by using plastic-free solvent containers and scrupulously cleaned glassware that has been kiln-baked or solvent-rinsed prior to use (SOP 334). KD concentrator tubes are also kilned after washing.

Use of low phthalate gloves, such as nitrile, may also be important. These practices are important both in the field and in the laboratory.

5. APPARATUS AND MATERIALS

5.1 Organomation N-Evap Model 115, 40 positions or equivalent

5.2 concentrator tubes, glass, 10mL or other size as needed

5.3 Pasteur pipettes, glass, disposable

5.4 graduated pipettes, glass, disposable

5.5 glass syringes, 0.5-2mL or as appropriate

5.6 glass vials with PTFE-lined screw caps, various sizes

6. REAGENTS

6.1 SOLVENTS – **must be pesticide residue or HPLC grade**

methylene chloride (CH_2Cl_2)

hexane (C_6H_{14})

acetonitrile (CH_3CN)

6.2 Nitrogen (N_2), 99.999% purity

7. PROCEDURE

NOTE: This procedure must be performed in a fume hood. **Plastic tubing must not be used, as it may introduce contaminants.**

7.1 Place the 10mL concentrator tubes in the N-Evap rack. **Be careful to hold the retaining spring back when you place the tube in the slot, as it may spring forward and break the tube.** Place a Pasteur pipette into the Teflon™ holder that corresponds to each concentrator tube.

7.2 Close the main flow valve on the N-Evap using the small black knob to the right. Open the valve on the nitrogen tank (approximately 1/4 turn).

7.3 Open the appropriate nitrogen flow valve at the top of each pipette by slowly turning 1/2 turn counterclockwise and then slowly open the main flow valve on the N-Evap a small amount. Adjust the flow so that each concentrator tube receives a steady, gentle stream of nitrogen that creates an indentation on the top of the extract without causing splashing. To ensure effective blowdown, lower the tip of the pipette to approximately 0.5-1cm above the solvent surface. Use the individual flow valves to adjust and maintain the flow rate. **The nitrogen flow rate must be kept low enough so that only a small indentation in the solvent is observed. Flow rates that cause splashing also cause target analytes to be lost during the blowdown.**

NOTE: Because flow is controlled at the N_2 tank, by the main flow valve of the N-Evap, and by each pipette controller, flow rate varies per N-Evap station. Hence, documentation of actual gas flow received by the sample at the pipette level is not possible. To verify proper flow was used, however, the 'Y' (yes) for the 'Gas flow properly set per station?' prompt, must be circled on the benchsheet."

Amended

7.4 As the solvent volume decreases, the internal walls of the concentrator tube must be rinsed several times with solvent. **Do not evaporate the sample to dryness.** Also, lower the pipettes as necessary to maintain the 0.5-1cm distance from the tip of the pipette to the solvent surface.

7.5 If solvent exchange is required, blow the extract down to approximately 0.5mL, then add 5-6mL of exchange solvent to each concentrator tube (exchange solvents are listed in Table 1). Continue the blowdown procedure until the solvent level reaches 0.5mL again. Repeat this step at least two times. Stop the procedure if volume is 0.5mL or less (when the volume of extract is reduced below 0.5mL, target analytes may be lost).

7.6 When the apparent volume of the extract is reduced to approximately the desired final volume (0.5-10mL depending on the analysis to be performed), remove the concentrator tube, **being careful to hold the retaining spring back as it may snap on the concentrator tube and cause sample loss through breakage or spillage.**

7.7 Bring the extract to the required final volume during quantitative transfer of each sample to a labeled glass vial with a PTFE-lined screw cap. Extracts with a final volume of 2mL or less (e.g., SW8270, SW8330), are generally measured using glass gas tight syringes. Those extracts with final volumes of greater than 2mL are quantitatively transferred to vials of appropriate size. Transfer all extract and rinsate from the concentrator tube to the vial.

For extracts with final volumes of greater then 2mL, a standard vial with appropriate final solvent is created using a volumetric pipette. Fill a vial to the desired final volume with solvent and label with date on cap to avoid confusing it with sample extracts. When vialing sample extracts, place the standard vial on a level surface and top off sample extracts to the desired final volume dropwise using a fine tipped solvent bottle or pipette. Final volume is achieved when the meniscus in the extract vial is level with that in the standard vial.

Observe proper chain-of-custody procedures (SOP 318) to deliver the extracts to the appropriate analytical group for refrigerated storage.

7.8 Turn off the main N_2 valve when the N-Evap is not in use.

8. QUALITY CONTROL

Note that all field and laboratory quality control (QC) samples must be processed in the same manner. Re-extraction of the sample may be warranted if any of the following should occur:

The extract is concentrated to dryness.

The extract is spilled.

The extract is solvent exchanged into the wrong solvent.

If re-extraction is not possible due to extenuating circumstances (e.g., no volume remaining, hold time exceeded), then the extract should be kept and the occurrence noted on the benchsheet. A Non-Conformance Report (NCR, SOP 928) must be initiated, and the Department and Project Managers notified.

9. DEVIATIONS FROM THE METHOD

This SOP meets the requirements of SW-846 Chapter 4 methods. There are no known deviations from these methods (i.e., SW3510C, 3520C, 3540C and 3550B).

10. SAFETY, HAZARDS AND WASTE DISPOSAL

10.1 SAFETY AND HAZARDS

10.1.1 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

10.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

10.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Methylene chloride, hexane and acetonitrile have TLVs ≤ 50ppm.

10.1.4 Any non-original containers being used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

10.2 WASTE DISPOSAL

10.2.1 Disposal of remaining extracts and vials is the responsibility of the analytical group receiving the extracts.

10.2.2 All empty solvent, reagent, or sample containers shall be disposed of appropriately. All labels and markings must be defaced prior to disposal.

11. REFERENCES

11.1 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3510C. December 1996.

11.2 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3520C. December 1996.

11.3 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3540C. December 1996.

11.4 US EPA SW-846, Test Method for Evaluating Solid Waste – Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3550B. December 1996.

DOCUMENT REVISION HISTORY

11/12/07: Updated LIMS program specification reference Section 3.3, and INTERFERENCES Section 4. Added DOCUMENT REVISION HISTORY Section.

12/24/07: Added flow documentation Note to Section 7.3, updated benchsheets.

Table 1

TYPICAL EXTRACTION AND EXCHANGE SOLVENTS

Analytical Method	Extraction Solvent	Exchange Solvent for Cleanup	Exchange Solvent for Analysis
*SW 8015 (CaL-Luft)	methylene chloride	methylene chloride for PAR Si-gel	methylene chloride
SW 8081	methylene chloride	methylene chloride for SW3640 GPC hexane for SW3620 florisil	hexane
SW 8082	methylene chloride	hexane for SW3665 sulfuric acid	hexane
*SW 8141	methylene chloride	methylene chloride for SW3640 GPC	hexane
SW 8151	diethyl ether	N/A	hexane
SW 8270	methylene chloride	methylene chloride for SW3640 GPC methylene chloride for PAR Si-gel	methylene chloride
SW 8330 (waters)	acetonitrile	N/A	acetonitrile

* These are most commonly concentrated using the Rapid-Vap (i.e., NOT N-evap).

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HERBICIDE EXTRACTION / CLEANUP BENCHSHEET

WO #s _____ **Matrix** AQ Solid Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____

Extraction: Code 8151A E615 E515 **Method** (3540C)SOX (3510C)SEP (3580A)WDilute **SOP** ___ **Rev** ___ **Initials** _____ **Acidified glass wool & Na_2SO_4 used?** Y

Balance ID ____ **Cleanup** GPC (3640A, SOP 641; see other forms) Florisil (3620B, SOP 648) **Rev** ___ **Florisil Lot No.** _____ **Initials** ____ Reviewed by / date _____

Extraction Start Date _____ **Time** _____ **Extraction End Date** _____ **Time** _____ **Proper N-Evap station flow settings used?** Y

$MeCl_2$ _____ **Hexane** _____ **NaCl** _____ **Acidified Na_2SO_4** _____ **H_2SO_4** _____ **NaOH** _____

KOH _____ **Diazald** _____ **Carbitol** _____ **Diethyl Ether** _____ **HCl** _____ Form 604r10.doc (12/24/07)

SAMPLE							EXTRACT							
Sample No.	Amount (g / mL)	pH (≥ 12)	pH (≤ 2)	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hydrolysis (SO only)	Date KD (Final)	Date Partitioning (SO only)	Date Hexane Exchange	Final Volume (mL)	Date Vialed	Type of Cleanup

Comments:

Amended

Paragon Analytics

SEMIVOLATILES EXTRACTION / CLEANUP WORKSHEET

WO #s _____ **Matrix** ___ **Batch ID** _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** __ **Extr SOP/Rev** __ **Extr Code:** 8270C CLP SOW E625

Extr Method: (3520C)CLE (3550C)SONC (3540C)SOX (3510C)SEP (3580A)Waste Dilution **Initials** _____ **Extr Start Date/Time** _____ **Extr Stop Date/Time** _____

Lots: MeCl, _____ Hexane _____ Acetone _____ Florisil _____ Silica Gel _____ (See other GPC forms) H_2SO_4 _____ NaOH _____ Na_2SO_4 _____

Steam bath ___°C **Proper N-Evap station flow settings used?** Y **Cleanup Code:** (3620B)Florisil (3640A)GPC (See other forms) Silica Gel **Cleanup SOP/Rev** ___ **Date/Time** _____

Initials ____ **Reviewed by / date** _____ Form 609r13.doc (12/24//07)

SAMPLE								EXTRACT / CLEANUP					
Sample No.	Amount (g / mL)	Initial pH	**pH** (≤ 2)	**pH** (11-13)	Surrogate (mL)	Matrix Spike (mL)	Sur / Matrix Spike Witnessed	Date KD (Initial)	Cleanup Date	Date KD (Final)	Final Volume (mL)	Date Vialed	Comments

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Form 611r5.doc (12/24/07)

Paragon Analytics

MISCELLANEOUS EXTRACTIONS / CLEANUP WORKSHEET

WO #s ____________________ **Matrix** AQ Solid Other ______ **Batch ID** ______________ **Sur Code** _______________ **M Spike Code** ______________ **Balance ID** ____

Extraction: Method (3520C)CLE (3550B)SONC (3540C)SOX (3510C)SEP (3580A)W Dilute **SOP** ____ **Rev** __ **Date** ________ **Time** ______ **Initials** ____

Solvent Lots: MeCl₂ ______________ **Hexane** ______________ **Acetone** ______________ **Florisil** ______________ (see other forms for GPC info.) Proper N-Evap station flow settings used? Y

Cleanup: Code (3620B)Florisil (3640A)GPC (see other forms) **SOP**____ **Rev** __ **Date** __________ **Time** _______ **Initials** ______ **Reviewed by / date** ________________________

SAMPLE								EXTRACT / CLEANUP						
Sample No.	Amount (g / mL)	Initial pH	pH (≤ 2)	pH (11-13)	Surro-gate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	GPC Date	Florisil Date	Date KD (Final)	Final Volume (mL) / Solvent	Date Vialed	**Comments**
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PESTICIDES / PCBs -- EXTRACTION WORKSHEET

Paragon Analytics

WO #s ________________________ **Batch ID** ____________________ **Surr Code** _______________ **Matrix Spike Code** ____________

Ex Date/Time _____________ (start) _____________ (stop) **Matrix** Aq Solid Other _________ **Balance ID** _______ **Ex SOP** ____ **Rev**___ **Initials** ____

Ex Method: (3520C)**CLE** (3550B)**SONC** (3540C)**SOX** (3510)**SEP** (3580)**Wdilute** (SOP 673)**Wipes** **EX Code:** 8081B **(pest)** 8082 **(PCB)** 608 **(pest)** 8081B **(TCLP pest)**

Lots: MeCl$_2$ ____________ **Hexane** ____________ **Na$_2$SO$_4$** ___________ **Proper N-Evap station flow settings used? Y**

Form 616r14.xls (12/24/07)

Sample No.	Amount (g / mL)	pH	Surr. Spike Amt. (mL)	Matrix Spike Amt. (mL)	Spike Analyst / Witness	Date KD / Analyst	Final Solvent	Final Vol. (mL)	Cleanup Req. (y / n)	Comments
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_____________ B

PESTICIDES / PCBs -- CLEANUP WORKSHEET

Paragon Analytics

WO #s ___________________________ **Batch ID** _______________________ **Cleanup SOP** _____ **Rev**____ **Initials** _____

Method: (3620B)**Florisil** (3665A)**Sulfuric** (3640A)**GPC** (see GPC forms) Other ___________

Lots: MeCl$_2$ ________ **Hexane** ________ **Acetone** ________ **Florisil** ________ **Sulfuric acid** ________ **Na$_2$SO$_4$**_________ **Reviewed by / date** _______________

	FLORISIL: Has lot check been done? y/n _____				GPC (Note: half the extract is lost during cleanup)				SULFURIC ACID		
Sample No.	Amount Extract (mL)/ Solvent	Date Cleanup / Analyst	Final volume (mL) / Solvent	Date Vialed / Analyst	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Date KD / Analyst	Final volume (mL) / Solvent	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Comments

Amended

Paragon Analytics

EXPLOSIVES (8330) / NITROGLYCERIN (NG) and/or PETN (8332) -- EXTRACTION WORKSHEET

Form 635r8.doc (12/24/07)

Batch # _____ **WO #s** _____ **Initials** _____ **Matrix:** AQ SO Other _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** ___

SOP 665 Rev__ **Extr Code:** 8330 (AQ) 8330 (SO-SONC) 8332 (AQ) 8332 (SO-SONC) **Extr: Date/Time (Start)** _____ **(End)** _____ **Reviewed/date** _____

Lots: MeCl, _____ Acetonitrile _____ NaCl _____ $CaCl_2$ _____ HPLC Water _____ Proper N-Evap station flow settings used? Y

SAMPLE					EXTRACT			
Sample Number	Amount (g / mL)	Amount Surrogate (mL)	Matrix Spike (mL)	Initials Surrogate and Matrix Spike Witness	Volume $CaCl_2$ (mL)	Final Volume (mL)	Date Vialed	Comments

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Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 640 REVISION 7

TITLE EXTRACTION AND GRAVIMETRIC DETERMINATION OF HEXANE EXTRACTABLE MATERIAL IN SOLIDS – METHOD SW9071B

FORMS: 603 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3/1/07

QUALITY ASSURANCE MANAGER _____ DATE 2/28/07

LABORATORY MANAGER _____ DATE 3-1-07

HISTORY: Rev0, 12/15/91; Rev1, PCN # 155, 3/7/94; Rev2, PCN #358, 2/16/95; Rev3, 1/10/00; Rev4, 8/29/02; Rev5, 2/23/04; Rev6, 2/27/06; Rev7, 3/1/07. re-released without revision 3/9/09 DAS

1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW-846 Method 9071B -- describe procedures for measuring the hexane extractable matter (HEM) in soils, sludges, sediments or other solid samples. These procedures are applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

Note that these procedures are **not** recommended for measurement of light hydrocarbons that volatilize at temperatures below 85°C. Under the conditions of this SOP, petroleum fuels, from gasoline through Fuel Oil Number 2, are completely or partially lost in the solvent extraction process.

Some crude oils and heavy fuel oils contain a significant percentage of residue materials that are not soluble in the solvents used in this procedure. Accordingly, recoveries of these materials will be low.

2.0 SUMMARY

A representative portion of solid is acidified with concentrated HCl and mixed with a drying agent (sodium sulfate). The sample is then extracted with hexane, using a Soxhlet apparatus. The hexane is evaporated from the sample and the dry residue (hexane extractable material, HEM) is measured gravimetrically.

3.0 RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of

Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4.0 INTERFERENCES

4.1 Organic residues on glassware, dust or other particulate matter can interfere with this procedure.

4.2 The method is strictly empirical. Meaningful results can be obtained only by strict adherence to all details of the process.

5.0 APPARATUS AND MATERIALS

5.1 analytical balance, 0.0001g sensitivity, calibration verified per SOP 305

NOTE: A 2mg weight is used in addition to the standard (SOP 305) calibration verification. This 2mg calibration verification is recorded on the benchsheet.

5.2 beaker, 500mL

5.3 autopipetor (for acidification)

5.4 spatula, wooden, disposable

5.5 boiling flask, flat bottom, 500mL

5.6 PTFE-boiling chips: pre-clean by rinsing with methylene chloride, then dry

5.7 lint-free wipes, such as KimWipes®

5.8 desiccator, containing indicating Drierite™

5.9 hot plates

5.10 soxhlet apparatus, including glass (re-useable) thimbles

5.11 steam generator and S-Evap unit or equivalents

5.12 vacuum pump, with inlet hose

6.0 SOLVENTS

6.1 n-hexane, 85% purity, 99% minimum saturated C_6 isomers, residue less than 1mg/L

6.2 acetone, ACS grade, residue less than 1mg/L

6.3 dichloromethane, pesticide grade

7.0 REAGENTS - Only reagent grade or better chemicals shall be used.

7.1 hydrochloric acid (HCl), concentrated

7.2 sodium sulfate (Na_2SO_4), anhydrous, granular: Kiln for a minimum of 4 hours; cool to room temperature before use.

7.3 Ottawa sand.

8.0 STANDARDS

8.1 All standards are maintained per PAR SOP 300. Unopened stock standards are valid until the manufacturer's expiration date, and may be stored at room temperature in flame-sealed ampules or as otherwise recommended by the manufacturer. After opening ampule, the stock solution may be stored at room temperature in a tightly capped vial, and retained for up to six months (typically, the remainder of stock is discarded, instead). Intermediate standards (e.g., OPR Spiking Solution) may also be stored in a tightly sealed container at room temperature, and retained for up to six months. Standards may be replaced sooner if laboratory quality control (QC) analyses or other factors indicate deterioration.

All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials, and also documents the concentration of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer.

8.2 corn oil reference standard, Mazola™ or equivalent: Dilute in acetone to appropriate concentration (typically 0.1g/mL).

9.0 SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

9.1 Samples should be collected according to an approved sampling plan.

9.2 Soil samples should be collected in a wide-mouth glass jar and must be kept cool (4±2°C). Chemical preservation consists of addition of 1mL concentrated HCl to 100g of sample in the field. If this cannot be accomplished, then the sample is acidified prior to extraction.

9.3 No holding time has been established for this determination; Paragon observes a 28-day holding time to extraction for this procedure.

10.0 PROCEDURE

10.1 PREPARED GLASSWARE

A sufficient number of boiling flasks must be prepared to accommodate all field and QC samples (e.g., MB, LCS/LCSD, MS/MSD) in the batch. Label, add 3-5 boiling chips, wipe and weigh each flask on the analytical balance to the nearest 0.1mg. Record the weight on the benchsheet.

NOTE: Because the flasks are cleaned (SOP 334) and dried in a kiln, they do not need to be rinsed with hexane and dried prior to use. Because of potential residues, the flasks should not be touched by bare hands (use clean gloves, tongs, etc.) Store the flasks in a desiccator until needed.

One method blank (MB) and one laboratory control sample (LCS), consisting of a 50g aliquot of acidified, prepared Ottawa sand (see below), must be prepared with each batch of twenty or fewer field samples. If the client provided sufficient sample volume, prepare one sample in the batch in triplicate; the two additional acidified, prepared sample aliquots serve as the matrix spike and matrix spike duplicate (MS/MSD). If not enough sample volume was provided, prepare the LCS in duplicate (LCSD). The spiking of the MS and LCS aliquots are discussed below.

10.2 SAMPLE PREPARATION

10.2.1 Decant and discard any standing water from samples. Mix each sample thoroughly, and discard any foreign material such as sticks, leaves and rocks, that is not representative of the sample matrix. **Some clients may want the sample analyzed as submitted; refer to lab notes/LIMS Program Specification.**

10.2.2 Weigh an appropriate volume (10-50g) of sample into a 250mL beaker. Add concentrated HCl (0.3-1.0mL, typically 0.5mL is added) if sample is not already acidified. Bubbling may occur upon the first addition of HCl, strongly alkaline samples will require additional acid; up to 2mL HCl may be added.

10.2.3 Next, add an equal weight of granular sodium sulfate. Mix the sodium sulfate with the sample matrix until the sample aliquot is completely

dry. Note that if the sample was wet or particularly alkaline, more sodium sulfate may be needed.

10.3 Transfer an aliquot of prepared sample (typically 50g) to a glass thimble. **Rinse the beaker with hexane, allowing the wash to drain into the soxhlet thimble, thus effecting a quantitative transfer.**

10.4 Spike the MS and LCS and duplicate (MSD or LCSD) with corn oil solution (typically, 1mL of 0.1g/mL solution is spiked).

10.5 Assemble the soxhlet apparatus, add approximately 300mL hexane to each soxhlet unit. Apply heat to the flat bottom flask, and allow to reflux for 18±2hrs.

10.6 Transfer the flask to the S-Evap unit and evaporate the extracts to dryness. The temperature of the S-Evap should be maintained at <85°C to ensure that the more volatile components extracted into the hexane are not lost. Use the vacuum pump with inlet hose to remove residual hexane vapors from the flasks.

10.7 Place each flask in the desiccator for several hours.

10.8 Remove each flask from the desiccator and weigh on the analytical balance; record weight on benchsheet. Return each flask to the desiccator and allow to sit for several more hours. Re-weigh. **If the flask hasn't achieved constant weight, it may still contain residual solvent or water vapors. Continue to store then weigh until constant weight is achieved.**

10.9 Calculate HEM per Section 11 below.

11.0 CALCULATIONS

11.1 Calculate the sample HEM as follows:

$$\text{HEM (mg/kg)} = \frac{\text{gain in weight of flask (mg)}}{\text{Weight of wet solids(kg) x dry weight fraction}}$$

11.2 Calculate the recovery of the LCS using the following equation:

$$\text{Recovery (\%R)} = \frac{\text{measuredconc.of HEM}}{\text{spikedconc.of HEM}} \text{ X } 100$$

11.3 Calculate the recovery of the MS/MSD samples as follows:

$$\text{Recovery (\%R)} = \frac{\text{HEM}_{\text{Found}} - \text{HEM}_{\text{Sample}}}{\text{HEM}_{\text{Target}}} \text{ X } 100$$

where:

HEM_{Found} = calculated HEM concentration in the MS or MSD

HEM_{Sample} = calculated HEM concentration in the field sample

HEM_{Target} = the target concentration of the added HEM spike

11.4 Calculate the Relative Percent Deviation (RPD) of the MS/MSD samples using the following equation:

$$RPD\ (\%) = \frac{\left|HEM_{MS} - HEM_{MSD}\right|}{\left(\frac{HEM_{MS} + HEM_{MSD}}{2}\right)} X\ 100$$

where:

HEM_{MS} = calculated HEM concentration in the MS

HEM_{MSD} = calculated HEM concentration in the MSD

12.0 QUALITY CONTROL

12.1 DEFINITION OF BATCH

A batch is defined as a group of $\leq$20 field samples of like matrix that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the MB, LCS (LCSD) and matrix spike and duplicate (MS/MSD). All QC samples must be carried through all stages of the sample preparation and measurement steps.

12.2 METHOD BLANK

Method blanks are aliquots of clean matrix (i.e., Ottawa sand) that have been prepared and analyzed in the same manner as the associated field samples. To be acceptable, concentrations of analytes of interest detected (if any) in the MB must be below the analyte reporting limit, or as otherwise specified in the LIMS program specification. If this criterion is not met, analyses should be halted and the source of the contamination found and corrected. See also attached QC Table.

12.3 LCS SAMPLE

This sample is comprised of a known concentration of target analyte contained in a clean matrix (Ottawa sand). The laboratory control sample (LCS) is analyzed to demonstrate the accuracy of the analytical test. LCS recovery is calculated as shown in Section 11. See QC Table for evaluation criteria.

12.4 MS AND DUPLICATE

Matrix spikes consist of field samples into which known concentrations of target analytes are added and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. MS recovery is calculated as shown in Section 11, see QC Table for evaluation criteria.

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this analysis, either the matrix spike analysis (MSD) or the laboratory control sample (LCSD) can be performed in duplicate. Recovery is calculated as shown in Section 11, and precision (see Section 11 for calculation), is evaluated in terms of RPD. See QC Table for acceptance limits.

Possible causes for matrix spiked failure include:

- sample heterogeneity
- a sample matrix which inhibits extraction of spiked compounds
- high levels of HEM that "swamp out" the small amount of extractable materials added with the spike.

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived, and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation will be made in the data package narrative.

12.5 A METHOD DETECTION LIMIT (MDL) STUDY shall consist of the ANALYSIS of a minimum of seven replicate analyses for a target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at a minimum, annually, following the guidance of SOP 329.

13.0 DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW9071B, with the following exceptions:

- Up to 50g of sample is extracted for 18±2 hrs, rather than the 10g sample aliquot extracted for 4hrs as suggested in the Method.
- Corn oil is used as the reference standard, in place of a hexadecane/stearic acid standard.

14.0 SAFETY, HAZARDS AND WASTE DISPOSAL

14.1 SAFETY AND HAZARDS

14.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

14.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

14.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

14.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

14.2 WASTE DISPOSAL

14.2.1 Any hexane or other nonhalogenated organic solvents that have not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste or Radioactive Lab Waste, as appropriate.

14.2.2 All empty solvent bottles shall be disposed of appropriately; note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

15.0 REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, "Method 9071B", Revision 2, April 1998.

DOCUMENT REVISION HISTORY

3/1/07: Format updated, minor clarifications added. Added DOCUMENT REVISION HISTORY Section and Form.

Paragon Analytics.

OIL & GREASE -- PREPARATION / ANALYSIS / CLEANUP – BENCHSHEET

Form 603r9.frm (9/23/2003)

WO _____ AQ Solid _____ **Batch ID** _____ **M Spike Code** _____ **Analysis Code:** 9070A 9071 1664 **Balance ID** ____ **SOP** _____ **Rev** ___
Ex. Date/Time _____ (start) **Date/Time** _____ (stop) **Initials** _____ **Cleanup Code:** (3630C)Silica Gel **Cleanup Date/Time** _____ **SOP 644/Rev** __ **Initials** ____

SAMPLE					EXTRACT					
Sample No.	Amount (g / mL)	Matrix Spike (mL)	Matrix Spike Witnessed	Acidified? If so, amount used? (mL)	Date Evaporated to Final	Silica Gel (g)	Beaker Initial (g)	Beaker Final (g)	Difference (g)	Balance #5 2 mg weight check yielded result between 0.0019 – 0.0021 g ? Y / N Comments

Reagent Lots: HCl _____ H_2SO_4 _____ Silica Gel _____ Hexane _____ $NaSO_4$ _____ Reviewed by / Date _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 641 REVISION 8

TITLE: **GEL-PERMEATION CHROMATOGRAPHY (GPC) CLEANUP -- METHOD SW3640A**

FORMS: 630

APPROVED BY:

TECHNICAL MANAGER _____ DATE 28 Feb 2006
QUALITY ASSURANCE MANAGER _____ DATE 2/28/06
LABORATORY MANAGER _____ DATE 2-28-06

HISTORY: New, Rev0, 2/18/92; Rev1, 2/10/94; PCN #131; Rev2, 4/18/95; PCN #641; Rev3, 7/15/99; Rev4, 10/28/99; Rev5, 3/6/02; Rev6, 4/7/03; Rev7, 4/16/04; Rev8, 2/27/06.

re-released without revision 3/9/09 DAS

1. SCOPE AND APPLICATION

Gel-Permeation Chromatography (GPC) is primarily used as a cleanup procedure in the extraction of soils/sediments/tissues that contain high molecular weight organic compounds such as lipids, polymers, proteins or resins. Typical indicators of the need for GPC cleanup are thick, viscous, or opaque extracts that likely cannot be concentrated to the required final volume. Extracts for Method SW 8081, SW 8082 and SW 8270 analysis can be cleaned using this method. This standard operating procedure (SOP) pertains to all extracts suitable for GPC cleanup. Consult with supervisor for other applications including SW 8141.

2. SUMMARY

Molecules are separated in the GPC column on the basis of their size. Smaller molecules enter the pores of the column's packing material, thereby eluting later than larger molecules that flow more directly through the column as they are excluded from the gel pores. The column effluent containing the larger molecules is ("dumped") discarded into the waste container. The later-eluting solvent fractions that contain the compounds of interest are "collected" in a flask. The GPC cleaned sample is then concentrated using a Kuderna Danish apparatus (SOP 607) followed by nitrogen blowdown (SOP 637) to appropriate final volume.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency evaluation test.

3.3 The Department Supervisor or designee performs final review and sign-off of the

data. Initialing and dating the bench sheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the processing of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

A reagent blank should be analyzed for all compounds of interest prior to the use of this method. The levels of interferences should be below the reporting limits of the analytes of interest before this method is performed on actual samples.

5. APPARATUS AND MATERIALS

5.1 GPC Autoprep 1000 (O.I. Analytical.)

5.2 glass column, 25mm I.D. x 600-700mm length

5.3 syringe, 10mL with Luerlock fittings (syringe with a Teflon plunger is preferred)

5.4 PTFE filters, 0.45µm

5.5 UV detector, Milton Roy, or equivalent

5.6 recorder: Kipp and Zonen BD 40, or equivalent

5.7 aluminum foil

5.8 volumetric flask, 500mL or as needed

5.9 SX-3 Bio-Beads (O.I. Analytical)

5.10 graduated cylinders

5.11 250-500mL flasks

6. REAGENTS

6.1 methylene chloride (CH_2Cl_2) - pesticide residue grade

6.2 calibration standards - generally purchased as a concentrate and contains the following compounds at the listed concentrations and is diluted prior to use:

corn oil	250mg/mL
bis(2-ethylhexyl)phthalate	5mg/mL
methoxychlor	1mg/mL
perylene	0.2mg/mL
sulfur	0.8mg/mL

NOTE: In order to monitor the instrument elution profile, a check standard is analyzed at a minimum of once each 7 days when samples are being cleaned up. One mL of the solution above is diluted to 10mL with methylene chloride and the entire volume is used for calibration of the instrument.

NOTE: If the standard is prepared from neat compounds caution must be taken to ensure that the sulfur is dissolved in the standard. Molecular sulfur is not very soluble in methylene chloride. However, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. If prepared from neat standards, then store the calibration solution in an amber glass bottle with a Teflon-lined screw-cap at 4±2°C, and protect from light (refrigeration may cause the corn oil to precipitate). Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves).

Ampules of calibration standard obtained from a vendor should be stored as recommended by the manufacturer. Unopened ampules of calibration standard expire per the maufacturer's date. If a stock is prepared in house the calibration standard solution expire in 6 months from date of preparation, or more frequently if necessary following the guidance from the latest revision of SOP 300.

6.3 Gases -ultra high purity
nitrogen
helium

7. PROCEDURES

7.1 OVERVIEW OF DAILY PROCEDURES

7.1.1 Re-swell the gel as described in Section 7.3, if necessary. Solvent is typically pumped continuously through the gel in the column to avoid drying and shrinking of the resin.

7.1.2 Fill solvent bottle with methylene chloride. Make sure the waste container has enough volume to catch the waste from the cleanup run to

be performed.

7.1.3 Set the flow-rate. (See Section 7.4)

7.1.4 Turn on the UV detector to warm up for a minimum of ten minutes. Turn on the recorder, and turn off the chart speed. Set variance to a span of 50mV and the chart speed to 5mm per minute.

7.1.5 Calibrate the GPC (see Section 7.5). Typical GPC settings obtained from the calibration are listed below:

	8270	8081/8082
dump time	23 min.	29 min.
collect time	26 min.	19 min.
wash time	11 min.	12 min.

These times are determined from the calibration and vary depending upon the results of the calibration standards. Set the times into the controller before loading the samples. The UV detector and chart recorder are usually turned off after the calibration. Some clients may require UV traces of each sample injected for clean up, so the detector and chart recorder would then be left on.

7.1.6 Load samples. (See Section 7.6)

7.1.7 Label 250mL flat bottom flasks (or 500mL flat bottom flasks if the sample is split) with the appropriate test, work order number, and sample number. This will be the collection vessel. Make sure that GPC is written somewhere on the collection vessel. Insert the appropriate numbered tubule into the collection vessel.

7.1.8 When all samples have been run through, the GPC will shut itself off. If traces of each sample were required, turn off the power to the UV detector and recorder, cap the pen. Close the nitrogen valve if desired, but the nitrogen is typically left on for solvent recycling. Remove collection vessels. Cap them with 24/40 stoppers or aluminum foil , and empty the waste container.

7.2 COLUMN PACKING

7.2.1 Place approximately 70g of SX-3 Bio-beads in a flask. The beads are typically purchased in 70g jars. Cover the beads with at least two inches methylene chloride. Swirl to insure the wetting of all the beads. Cover with aluminum foil, and allow the beads to swell for a minimum of 2 hours (preferably overnight in a hood).

7.2.2 The plunger assemblies of the column should be equidistant from the

column ends. Secure the upper plunger in the column by inserting and turning clockwise until snug.

7.2.3 Invert the column and clamp to a ring stand. Place the tubing into a waste beaker. Allow excess methylene chloride to drain from the column. Leave a small amount of methylene chloride in the column to minimize the formation of bubbles.

7.2.4 Swirl the bead/solvent slurry to get a homogeneous mixture. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column. Maintain contact between the flask and column wall while draining. A small glass funnel can aid this process. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached), and allow the excess solvent to drain. Raise the tube to stop the flow, and close the stopcock when the methylene chloride level is just above the top of the gel. Add additional methylene chloride to rewet the gel. Rinse any remaining beads from the inner walls of the top of the columns with methylene chloride. Attempt to slurry all beads into the column before proceeding to Step 7.2.5 below.

7.2.5 Insert lower plunger (the longer one) into the column until it touches the gel, and tighten the plunger by turning it clockwise until snug. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage. If this happens, immediately pull the plunger out and rinse it with methylene chloride to remove beads. Wipe the inside portion of the column with a Kimwipe to remove beads.

7.2.6 Compress the column as much as possible without applying excessive force. The following steps may not be necessary if all beads were slurried into the column in Step 7.2.4 above. If necessary, loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat this step until the plunger can be inserted and pushed in without allowing the beads to escape the seal. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure

until the plunger is inserted successfully. Push the plunger until it meets the gel.

7.2.7 Connect the column input and output lines to the column and install the column on the GPC.

7.2.8 Connect the column input and output lines to the appropriate lines coming from the GPC.

7.2.9 Nitrogen must be connected to the GPC so solvent flow can take place. Start pumping solvent through the column at approximately 5mL per minute for about one hour.

7.2.10 Turn the pump off and connect column output line to the solvent line leading to the UV Detector.

7.2.11 Follow the procedure to "Re-swell" the gel for an additional 1-2 hours minimum and preferably overnight (see Section 7.3).

7.2.12 If the column still has air pockets after re-swelling the gel, turn off the pump. Loosen the lower column plunger and compress the column. Then re-tighten and start the pump to continue pumping solvent through the column. Continue with this procedure until approximately 6-10psi backpressure is achieved. Inverting the column and running solvent "backwards" can also be helpful when trying to remove air bubbles.

7.2.13 When the GPC column is not to be used for several days, turn off the pumps, and connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention times have not changed.

7.3 RE-SWELLING THE PACKING MATERIAL.

7.3.1 If the column has been disconnected from the GPC, re-connect the column input and output lines to the appropriate lines from the GPC.

7.3.2 Press INDEX on the controller box until "CHECK SOLVENT FLOW RATE" is displayed. Start pump by pressing "run/stop" button on GPC. This is an excellent time to ensure that standards are ready and equilibrated to room temperature.

7.3.3 If the GPC was not used for a while, the methylene chloride may have

evaporated from the pump and caused the pump to lose its prime. If this occurs, the pump will not operate effectively and thus will not be able to pump methylene chloride out of the reservoir. The pump will need to be primed.

7.3.4 Continue pumping methylene chloride through the column until the column is saturated. No bubbles should be coming out of the column, and the system pressure should remain steady.

7.4 FLOW-RATE CHECK

7.4.1 After the column has been saturated, the flow rate of the solvent should be checked in order to determine if the system is functioning properly. The flow rate of the solvent should be 5.0±0.1mL/minute.

7.4.2 Obtain a stopwatch, and a 100mL graduated cylinder. The pump should still be working. Make sure that gloves are worn.

7.4.3 Disconnect the column output line from the GPC. At the instant the column output line is placed in the graduated cylinder, start the stopwatch timing for ten minutes. At the end of ten minutes take the column output line out of the graduated cylinder and reconnect to the GPC. Read the volume collected in the graduated cylinder. This volume should be between 49-51mL. If the volume is not within this range, adjust the flow rate as indicated in Section 7.4.4.

7.4.4 The flow rate can be adjusted by the controls located on the front panel of the GPC between the pump start/stop button and the pump prime button. Push the up arrow to increase the flow and push the down arrow to lower the flow.

7.4.5 After adjustment, allow the GPC to run for 30 minutes. Repeat the flow check above to confirm that the flow rate is correct.

7.5 CALIBRATION

7.5.1 The GPC must be calibrated every time the column is changed, when channeling is suspected (indicated by dramatic changes in flow rate, see Section 7.4), or every seven days, to show that the instrument is functioning properly and that the condition of the column has not changed.

7.5.2 After checking the flow rate, allow the GPC to run for 30 minutes. Turn on the UV detector and chart recorder. Warming up the UV detector for a minimum of 30 minutes helps to ensure stable absorbance readings.

7.5.3 Put 10mL calibration solution (Section 6.2) into a syringe. Filter the

solution through a 0.45µm PTFE filter into a GPC tube. Make sure the top of the GPC tube is not chipped or defective. Place the tube on a position on the GPC after rinsing the sample pickup line with methylene chloride. When screwing the GPC tube onto the loading station, make sure the tube fits snugly.

7.5.4 Press INDEX on the controller box until "DUMP TIME = 22:00?" is displayed. The number displayed will be the dump time of the previous run, so it may not be 22 minutes. Press 60:00, and then press ENTER. The display should read "DUMP TIME = 60:00".

7.5.5 Press INDEX once. The display should now read "COLLECT TIME = 28:00?". Press zero (0) four times and then press ENTER. The display should now read "COLLECT TIME = 00:00". If the question mark remains on the display, you forgot to press ENTER.

7.5.6 Press INDEX once. The display will now read "WASH TIME = 10:00?". Press zero (0) four times and then press ENTER. The display should now read "WASH TIME = 00:00".

7.5.7 Press INDEX once. The display will now read "START WITH SAMPLE NUMBER = 06?", or with whatever station number the GPC was last programmed to begin processing. Press 01 if calibration standard is at position 1, and then press ENTER.

7.5.8 Press INDEX once. The display will now read "TERMINAL SAMPLE NUMBER = 21", or with whatever station number the GPC was last programmed to end processing. Press the same number as you had for beginning processing, and then press ENTER.

7.5.9 Press INDEX twice. The display should now read "SMPLS 01-01 MODE GPC ONLY TIME=60:00 PUSH RUN?". The last number after SMPLS 01-01 above indicates which position the run will stop at. "TIME" indicates the dump time. To insure that all data is correctly entered, press INDEX and read the display. If the display is correct, continue pressing INDEX until the display reads "PUSH RUN".

7.5.10 Start the paper running on the recorder. The variance should be set at 50mV, and the chart speed should be set at 5mm per minute. For clients with special requirements, see the supervisor. Uncap the pen and zero the pen on the first thick horizontal line. When the pen reaches a vertical line, push RUN and make a mark on the chart where the pen was when started.

7.5.11 When 60 minutes has gone by, processing will be complete, and the GPC will shut itself off. This is indicated by a repetitious and loud

clicking sound that will continue for five to ten seconds. Go to the GPC and press INDEX twice until the pump can be restarted again by pushing "run/stop" on the GPC. Otherwise methylene chloride will drain out of the column, and the column conditions may change. If this occurs, the GPC must be re-calibrated.

7.5.12 Take the chart from the recorder and lay it out on a flat surface. The plot on the chart should consist of five peaks in the following elution order:

corn oil (generally two peaks)
bis(2-ethylhexyl)phthalate
methoxychlor
perylene
sulfur

For SW 8270 analysis the corn oil represents the high molecular weight compounds that will be dumped, and the phthalate/methoxychlor/perylene represent the compounds of interest. For SW 8081 analysis the corn oil and the phthalate represent the high molecular weight compounds, and the methoxychlor/perylene represent the compounds of interest.

7.5.13 Calculate the dump time: Measure the number of centimeters it took for the corn oil to go through, and multiply this value by two. This is the amount of time that it took for all the corn oil to elute through the column.

For SW 8270 analysis, calculate the dump time so that corn oil is dumped and >85% of bis(2-ethylhexyl)phthalate is recovered. Collection should stop after perylene elutes but before sulfur elutes.

For SW 8081 analysis, the dump time should be a value that allows removal of the corn oil and ≥ 85% removal of phthalate. Greater than 95% recovery of the methoxychlor is needed. Stop collection after perylene elutes but before sulfur elutes.

7.5.14 Calculate the collect time: Measure the number of centimeters it took for the phthalate/methoxychlor/perylene to elute through the column from the end of the dump time. Multiply this value by two. Continue to collect until just prior to the elution of sulfur.

7.5.15 Calculate the wash time: Add the dump time and collect time, and subtract the sum from 60 minutes. The wash time should be at least 10 minutes.

7.5.16 Enter the calculated dump time, collect time, and wash time into the GPC. and record these times on the GPC bench sheet and chromatogram. Once entered the program must be saved to the GPC memory by pushing "Program Save" and "enter". Record the system pressure on the GPC bench sheet and chromatogram.

- The UV trace must exhibit the following requirements:

  Peaks must be observed and should be symmetrical for all compounds in the calibration solution. Corn oil typically partially separates into two peaks.

  Corn oil and phthalate peaks must exhibit >85% resolution.

  Phthalate and methoxychlor peaks must exhibit >85% resolution.

  Methoxychlor and perylene peaks must exhibit >85% resolution.

  Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution. In addition, the retention times of the calibration compounds must be within ±5% of their retention time in the previous calibration. A copy of the UV trace of the calibration solution must be submitted with the data for the associated samples.

  If these requirements cannot be met, a new column may need to be packed. Old packing material may be cleaned by processing several 5mL volumes of butyl chloride through the system. Butyl chloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts. This may correct the problem. If column maintenance does not restore the performance of the column, the column must be repacked with new packing and recalibrated.

- Record on GPC bench sheet which column/GPC this was run on, the "dump" time, "collect" time, "wash" time, date, analysis, analyst, methylene chloride lot #, flow rate, calibration solution and expiration date, system pressure, room temperature and what samples were placed on which stations. Record on the chromatogram the date, "dump" time, "collect" time, "wash" time, what compound each peak represents and the percent resolution of each peak. A baseline needs to be drawn on the chromatogram so resolution can be calculated.

  For both SW 8270 and SW 8081, analyze a GPC reagent blank (see section 4). Pipette 10mL of clean methylene chloride into clean GPC tube, rinse the sample pickup line of Station 2 for

example and place the 10mL GPC reagent blank on Station 2. Treat this GPC reagent blank as a regular sample through the rest of the extraction process. **The position used for the GPC blank must be random.**

- Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no permanent darkening is visible, GPC calibration must be checked not less than once every seven days the GPC is in use. In many cases, the SX-3 Bio Beads may be used for several months as long as the column calibration and flow rate remains constant.

7.6 SAMPLE LOADING

It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard no longer will be appropriate. The ideal laboratory temperature to prevent out gassing of the methylene chloride is 72°F.

7.6.1 All samples going through the GPC must be filtered using a 0.45µm PTFE filter, and must be in methylene chloride. It may be easiest to blow down the sample to approximately 2mL on the N-evap before filtering the sample into a GPC tube. Make sure the tube is labeled correctly. Very viscous samples may be separated into several aliquots to enable filtering.

7.6.2 Rinse each GPC tube three times with methylene chloride before filtering samples into the tube. Filtering is accomplished by drawing or pipetting sample into a 5 to 10mL syringe with a luerlock tip, connecting the PTFE filter via the Luer fitting and forcing the extract through the filter into a GPC tube. After filtering, additional methylene chloride is passed through the filter and into the GPC tube, then at least 3 "air purges" (pulling air into the syringe) of the filter are performed to ensure complete transfer of compounds of interest.

7.6.3 Take a clean GPC tube, pipette in 10mL of methylene chloride, and tightly seal the top of the tube with aluminum foil. Bring the volume in the GPC tubes containing the filtered samples to 10mL using the sealed tube as a guide. After bringing sample to 10mL, tightly seal the tube with aluminum foil.

NOTE: Highly viscous extracts will not be injected onto the GPC column effectively so they must be split and diluted. If after

bringing a sample to 10mL the sample is viscous and/or opaque, the sample should be split to avoid overloading the column. Split the sample by pipetting 5.0mL into another GPC tube, and bring the volume of both up to 10mL. Place both GPC tubes on stations in sequential order. Any sample extract with a viscosity greater than that of a 1:1 glycerol: water solution also should be split. Several splits may be necessary for highly viscous samples.

7.6.4 When the samples have been brought to a volume of 10mL, place the samples on the GPC with the lightest colored samples on first, and the darkest samples on last. If none of the samples are dark or viscous, the order placed on the GPC is up to the discretion of the analyst.

7.6.5 Rinse the line of the station with methylene chloride. Place the line into the GPC tube, and screw the tube on until it fits snugly. Pumping methylene chloride through the sample lines may be needed to ensure no sample carryover occurs.

7.6.6 As each GPC station is loaded, make notations in the GPC bench sheet indicating station numbers, corresponding samples loaded onto the stations numbers, whether the sample was split, how many times, and analysis if more than one analysis is being run.

7.6.7 Label a 250mL flask with the appropriate test, work order and sample number. This will be used as a collection vessel. Make sure that GPC is written somewhere on the collection vessel. Insert the appropriate numbered tube (that corresponds to the station on which the sample was placed) into the collection vessel after rinsing the tube with methylene chloride. If the sample was split between two stations, place both tubes into a 500mL flask.

7.6.8 Enter the station on which processing is to begin, and enter the station on which processing will terminate. All stations between these two stations must have samples loaded on them, because the GPC will load samples in sequential order.

7.6.9 If the client requires all chromatographs to be delivered with the results of the analysis, then a chromatograph of the samples going through GPC clean up must also be included in the final package. Follow the procedure outlined above in Section 7.5.10 if this is required. Make sure there is enough paper and the pen has enough ink. Record the date and analysis on the chart paper.

7.6.10 Check to make sure that both methylene chloride reservoirs are full. Also, check to make sure there is at least 500-1000psi of nitrogen in the

tank. When everything has been checked, press RUN.

7.6.11 Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure.
- Increase in column operating pressure due to the absorption of particles or gel fines onto the analytical column gel.
- Leaks in the system or significant variances in room temperature.

7.6.12 When processing is completed, shut off the nitrogen valve, cap the pen, turn off the recorder and UV detector and if the GPC will not be used that day, connect the column outlet line to the column inlet as described in Step 7.2.12. Alternatively, put the column outlet into the larger methylene chloride reservoir to recycle solvent through column.

7.6.13 Seal the collection vessel with a ground glass or Teflon stopper, and continue processing the sample as required by the appropriate method, and according to the appropriate SOPs.

8. DEVIATIONS FROM METHOD

This SOP meets the requirements of Method SW 3640A, with the following exception: Gravimetric screening is not performed. Instead, samples are split on the basis of darkness and viscosity. There are no other known deviations to the method.

9. SAFETY HAZARDS AND WASTE DISPOSAL

9.1 SAFETY AND HAZARDS

9.1.1 Read the MSDSs before prior to preparing standards or using any solvents or reagents.

9.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

9.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked within a laboratory fume hood (e.g., solvents and acids). Dichloromethane has a TLV ≤50ppm.

9.1.4 The exhaust system for the GPC room must be on at all times the GPC is being used.

9.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with

compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

9.2 WASTE DISPOSAL

9.2.1 The GPC methylene chloride waste collection vessel is drained into the Halogenated Waste when full.

9.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

10. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 3640A, Revision 1, September 1996.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 642 REVISION 8

TITLE: **GRAVIMETRIC DETERMINATION OF PERCENT MOISTURE FOR SOLID MATRICES**

FORM: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/17/07
QUALITY ASSURANCE MANAGER _____ DATE 8/16/07
LABORATORY MANAGER _____ DATE 8-20-07

HISTORY: Rev0, 2/11/92; Rev1, PCN #447, 4/18/95; Rev2, 3/11/97; Rev3, 1/10/00; Rev4, 3/1/02; Rev5, 3/17/03; Rev6, 4/16/04; Rev7, 2/27/06; Rev8, 8/16/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the process for determining percent moisture in solid materials (soil, sludge, etc.). The value obtained is then used for correcting analysis results that are reported on a dry weight basis.

2. SUMMARY

A measured aliquot of solid sample is taken from a field sample and placed in a tared drying dish. The sample is placed in a drying oven at 105±5°C. After drying to a constant weight, the dried sample is weighed and compared to the initial wet weight of the sample. From these measurements, the percent moisture of the initial sample is obtained.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to the SOP and to complete all documentation required for review. Any anomalies or out-of-control events must be noted and corrective action taken and documented.

3.2 It is the responsibility of all personnel who work with the samples or data involving this method to consult applicable LIMS program specification for client specific requirements prior to initiating handling of samples or data.

4. INTERFERENCES

Soil or other solid materials containing large pieces of rock or other debris make reproducibility of the sub-sampling process difficult. Therefore, percent moisture reproducibility and interpretation may also be affected.

5. APPARATUS AND MATERIALS

5.1 tongue depressors, wood

5.2 aluminum weighing dishes, 57mm

5.3 laboratory balance, 0.01g sensitivity, typically interfaced to computer so that Paragon LIMS can automatically capture the data

5.4 vented drying oven, capable of maintaining 105±5°C

5.5 desiccator cabinet with viable Drierite® dessicant

6. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Soil samples received from the field are stored in sealed containers that prevent the loss of moisture during storage.

7. PROCEDURE

7.1 Record the balance ID in the open LIMS prep batch. Place a labeled, empty weighing dish onto a verified (SOP 305) zeroed balance. Record the mass of each dish in the 'dish weight' column in the open LIMS prep batch. Tare the balance with the empty weighing dish on the balance.

7.2 Pour off any standing water from the sample. Mix the sample thoroughly after removing rocks and sticks. Add approximately 10g of "wet" sample to the tared weighing dish. Record the mass of sample in the 'wet sample' column in the open LIMS prep batch. Care shall be taken to ensure homogeneity in the sample and its duplicate and in all other samples. Non-homogenous samples may not be representative and may yield high Relative Percent Difference (RPD) values.

7.3 Place the prepared samples in the vented drying oven, and record the oven identification number and the time the drying starts in the LIMS prep batch. Note that ovens are operated per SOP 320, temperatures are checked and recorded each business day.

7.4 Dry the samples for at least 10 but not more than 24 hours. If dried less than ten hours, it must be documented that constant weight (±0.01g) was attained. At least one hour of drying time is required between repetitive weighing of the sample to document constant weight. Drying time is defined as the elapsed time heated in the oven.

7.5 Remove the dried sample from the oven and immediately place it in the desiccator cabinet to cool for 15 to 30 minutes. Record the time the samples were removed from the oven in the LIMS prep batch.

7.6 Weigh and record the mass of the dish plus the dried sample in the appropriate column of the LIMS prep batch. Do not use the dried sample for any other analysis (with possible exception of some radiochemistry analyses).

8. CALCULATIONS

Calculations are performed in LIMS based on the following:

a. Mass of dried sample (M) = $m_3 - m_1$

b. %moisture = $(1 - M/m_2) \times 100$

where:

m_1 = mass of weighing dish
m_2 = mass of "wet" sample
m_3 = mass of weighing dish with dried sample

9. QUALITY CONTROL

9.1 METHOD BLANK

A labeled, empty weighing dish is the "blank" for each batch of ≤20 moisture samples analyzed.

9.2 DUPLICATE

One sample per 10 or less field samples from each batch of twenty or less samples is prepared in duplicate. Precision is measured as Relative Percent Difference (RPD), which is calculated in LIMS as follows:

$$RPD = \frac{(\%moisture\ sample - \%moisture\ duplicate)}{1/2(\%moisture\ sample + \%moisture\ duplicate)} * 100$$

If the samples used for duplicate analysis contain less than 10% moisture, then the RPD quality control limit is <67%. If the samples used for duplicate analysis contain > 10% moisture, then the RPD quality control limit is <30%.

9.3 Moistures below 1% are not accurately measured using this procedure. Thus, Paragon views 1% as a practical quantitation limit for this procedure.

10. DEVIATIONS FROM THE METHOD

This SOP is based on information presented in SW-846, Method 3540C, Section 7.2. There are no known deviations from the method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.2 Samples known to contain explosive or highly flammable material or samples that require explosive analyses should not be placed in the drying oven. Fibrous samples that are known to or suspected to contain asbestos should not be dried in this manner. They may be dried in a desiccator to a constant weight.

11.2 WASTE DISPOSAL

11.2.1 The dried solid sample residues and solid sample removed from the sample container but not used shall be disposed of in the Contaminated Soils and Solids Waste.

11.2.2 Radioactive solids must be placed in the Radioactive Solids waste stream.

11. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3540C, Revision 3, December 1996.

DOCUMENT REVISION HISTORY

8/16/07: Updated and corrected format. Added DOCUMENT REVISION HISTORY Section.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 648 REVISION 7

TITLE: FLORISIL CLEANUP – METHOD SW3620C

FORMS: 616 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-14-07

QUALITY ASSURANCE MANAGER _____ DATE 11/14/07

LABORATORY MANAGER _____ DATE 11-14-07

HISTORY: NEW, Rev0, 5/92; Rev1, PCN #162, 3/14/94; Rev2, 11/18/99; Rev3, 4/9/02; Rev4, 3/14/03; Rev5, 4/16/04; Rev6, 3/9/06; Rev7, 11/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references -- SW3620C, describes the use of Florisil to clean up interferences from extracts prior to analysis for organochlorine pesticides. Florisil, a registered trade name of U.S. Silica Co., is a magnesium silicate with basic properties. At Paragon, it is used to separate analytes from interfering compounds prior to analysis by gas chromatographic methods (SW8081 or EPA 608). Method SW3620 describes cleanup of extracts for other analytical processes, which are not addressed in this SOP.

2. SUMMARY

This procedure describes Florisil cleanup of solvent extracts of environmental samples using solid phase extraction cartridges. Each cartridge is washed with solvent immediately prior to use. The extract is loaded onto the cartridge, which is then eluted with suitable solvents. A vacuum manifold is used to obtain reproducible results. The eluate is then further concentrated prior to gas chromatographic analysis. This cleanup is only effective if there are differences in polarity of target and interfering compounds. The procedure described separates polar non-target analytes from the non-polar organochlorine pesticide target compounds.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review. The Technician must demonstrate the capability to generate acceptable results utilizing these methods, this demonstration may come in the form of Supervisory/training review or the results of precision and accuracy tests performed.

3.2 It is the responsibility of all personnel who work with the samples or data involving this method to consult applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Any anomalies or out-of-control events must be noted and corrective action taken and documented.

4. INTERFERENCES

Method SW3620C states that phthalate esters have been detected in extracts processed with solid phase extraction cartridges. Phthalate esters are not analyzed as part of the process described here. However, phthalate esters may interfere with subsequent analysis by electron capture detectors. The batch method blank(s) prepared with the sample set must also be subjected to this cleanup procedure and serve to monitor this potential interference.

5. APPARATUS AND MATERIALS

5.1 Vacuum manifold, VacElute Manifold SPS-24 (Analytichem International) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials (test tubes, ~15mL capacity), replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500mL sidearm flask fitted with a one-hole stopper and glass tubing.

5.2 Glass vials, appropriate sizes, with PTFE-lined caps

5.3 Volumetric pipettes, glass, disposable

6. SOLVENTS AND REAGENTS- ALL SOLVENTS SHOULD BE ACS GRADE

6.1 Florisil cartridges, 40µm particles, 60 Angstrom pores, 1g, B&J #7108G or equivalent. The cartridges consist of an appropriately-sized glass or polypropylene tube, with the 1g of Florisil held between two polyethylene or stainless steel frits with 20µm pores.

6.2 Hexane (C_6H_{14})

6.3 Acetone (CH_3COCH_3)

6.4 Hexane/Acetone (90/10, v/v), used as the eluent solution

6.5 2,4,5-trichlorophenol Florisil cartridge check solution: Prepare a solution of 2,4,5-trichlorophenol in acetone or hexane (concentration - 100ng/mL or as suitable).

6.6 Single component pesticide Florisil cartridge check solution: Use a solution containing all single component target compounds in hexane (concentration - 100ng/mL or as suitable).

6.7 Check mixture for the Florisil cartridges: Combine 0.5mL of the 2,4,5-trichlorophenol solution (Section 6.4) and 0.5mL of the pesticide check solution (Section 6.5) with 1mL of hexane. This solution is to be used whenever the cartridge check is to be performed (Section 7.3).

7. PROCEDURES

The extract has previously been concentrated to a predetermined volume following SOPs 607 and 637.

7.1 CARTRIDGE SET-UP AND CONDITIONING

7.1.1 Arrange the cartridges on the manifold in the closed-valve position and place wash collection test tubes in holders below the cartridges.

7.1.2 Turn on the vacuum and adjust to 5-10”Hg (5”Hg provides better control of the flow rates).

7.1.3 Condition the cartridges by washing with a minimum of 5mL hexane/acetone (90:10, v/v). This is accomplished by passing at least 5-10mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied so that the flow rate through each cartridge is approximately equal. When there is still approximately 1mm of solvent above the sorbent bed, stop the conditioning process. **Do not allow cartridges to become dry after they have been washed.**

7.1.4 After the cartridges have been conditioned, the vacuum is released, the test tubes with the washing solution are removed, and labeled 15mL test tubes are placed in the holders below the cartridges. Other collection vials may be used as appropriate. Care must be taken to ensure that the solvent line from each cartridge is placed inside the corresponding collection vial as the manifold top is replaced.

7.2 CARTRIDGE PROCEDURE FOR ORGANOCHLORINE PESTICIDES

7.2.1 Load 2.0mL of the extract (or cartridge check solution) on to the cartridge. Lesser volumes may be used as appropriate, particularly for extracts thought to contain high concentrations of interferences. Allow the extract to pass through the cartridge bed at approximately 2mL/minute. If entire extract is to be transferred, proceed to Section 7.2.2. If only a measured aliquot of extract is to be loaded on to the cartridge, proceed to Section 7.2.3.

7.2.2 After the entire extract has passed into the top frit of the cartridge, but before the cartridge becomes dry, rinse the sample vial with an additional 0.5-1mL hexane. Add the rinse to the cartridge to complete the quantitative transfer.

7.2.3 Add 3-4mL hexane/acetone (90:10, v/v) to the cartridge. Turn on the vacuum pump and adjust the pressure to 5-10”Hg. Allow the solvent to soak the sorbent bed for about 1min before drawing through the cartridge. Slowly let the eluting solvent through the cartridge (1-

2mL/min) and collect the eluate into the test tube. Repeat additions of elution solvent until approximately 9mL has been taken through the cartridge. It is not necessary to soak the sorbent bed for each addition, but **do not** allow the cartridge to dry between each addition of eluent.

7.2.4 Concentrate the extract to a final volume of 2.0mL (or the original volume of the extract aliquot taken) per SOP 637 (nitrogen blowdown), and vial the finished extracts.

7.2.5 Complete benchsheet (Form 616) and observe proper internal chain-of-custody procedures (SOP 318) to deliver the extracts to the appropriate analytical area.

7.3 CARTRIDGE CHECK PROCEDURE

7.3.1 Whenever a new lot of Florisil cartridges are received or for every 300 cartridges used of a lot, one cartridge must be tested to ensure acceptability (see Section 8.2 for acceptance criteria). The check must be performed at whichever is more frequent of the new lot or 300 cartridges used.

7.3.2 Condition the cartridge as described in Section 7.1, and then perform the cartridge cleanup starting with Section 7.2.1 using the aliquot of the performance check solution previously described (Section 6.6).

8. QUALITY CONTROL

8.1 The efficiency of each lot of Florisil cartridges must be verified using the Florisil check standard (Section 6.6). Cartridges from a given lot number may be used to process samples once a test of the performance check standard has yielded acceptable results. Up to 300 cartridges from a single lot can be used per successful lot check.

8.2 Acceptance criteria for Florisil cartridge performance check: the lot of Florisil cartridges is acceptable if all pesticides are recovered at 80-120%, the recovery of 2,4,5-trichlorophenol is less than 5%, and no peaks interfering with the target analytes are detected. The analytical group maintains records of each lot check that is performed. Documentation of each lot check may be required to be included in final data packages by some clients.

8.3 All quality control samples associated with the sample extracts that are cleaned using this procedure must also be processed through this cleanup method.

9. DEVIATIONS FROM THE METHOD

Concentrations of analytes in the lot check solution have been adjusted to be within the working range of the analytical instrument in use. Method SW3620C has acknowledged that the concentrations listed in SW3620B were in error. Acceptance criteria for

quantitative recovery of the target compounds suggested in the method is 80-110% recovery for a subset of target compounds. Paragon checks for quantitative recovery of all single component target and surrogate compounds and utilizes control limits of 80-120% recovery. No other deviations from the organochlorine pesticide cleanup portion of Method SW3620 are known.

10. SAFETY, HAZARDS AND WASTE DISPOSAL

10.1 SAFETY AND HAZARDS

10.1.1 Read the MSDSs before prior to preparing standards or using any solvents or reagents.

10.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

10.1.3 Chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Hexane and acetone have TLV <50ppm.

10.1.4 Non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

10.2 WASTE DISPOSAL

10.2.1 Any hexane, acetone, or other nonhalogenated organic solvents may be disposed of in the Acetonitrile/Nonhalogenated Waste Profile.

10.2.2 Extracts and the vials associated with the extracts are be disposed of by the analytical group in the appropriate waste extract stream.

10.2.3 Empty solvent bottles are disposed of appropriately. Please note that all labels and markings must be defaced prior to disposal.

11. REFERENCES

11.1 Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, US EPA SW-846, 3rd Edition, Final Update III, Method 3620B, December 1996.

11.2 Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, US EPA SW-846, Draft Update IVB, Method 3620C Revision 3, November 2000.

DOCUMENT REVISION HISTORY

11/12/07: Minor changes and clarifications throughout. Added DOCUMENT REVISION HISTORY and Form.

_____ A **PESTICIDES / PCBs -- EXTRACTION WORKSHEET** *Paragon Analytics*

WO #s _____ **Batch ID** _____ **Surr Code** _____ **Matrix Spike Code** _____
Ex Date/Time _____ (start) _____ (stop) **Matrix** Aq Solid Other _____ **Balance ID** _____ **Ex SOP** ____ **Rev**___ **Initials** ____
Ex Method: (3520C) CLE (3550B) SONC (3540C) SOX (3510) SEP (3580) Wdilute (SOP 673) Wipes **EX Code:** 8081B (pest) 8082 (PCB) 608 (pest) 8081B (TCLP pest)

Sample No.	Amount (g / mL)	pH	Surr. Spike Amt. (mL)	Matrix Spike Amt. (mL)	Spike Analyst / Witness	Date KD / Analyst	Final Solvent	Final Vol. (mL)	Cleanup Req. (y / n)	Comments
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Lots: $MeCl_2$ _____ Hexane _____ Na_2SO_4 _____ Form 616r13.xls (3/29/05)

_____ B **PESTICIDES / PCBs -- CLEANUP WORKSHEET** *Paragon Analytics*

WO #s _____ **Batch ID** _____ **Cleanup SOP** _____ **Rev**____ **Initials** _____
Cleanup Method: (3620B) Florisil (3665A) Sulfuric (3640A) GPC (See additional forms) Other _____

FLORISIL: Has lot check been done? y/n _____ **GPC** (Note: half the extract is lost during cleanup) **SULFURIC ACID**

Sample No.	Amount Extract (mL)/ Solvent	Date Cleanup / Analyst	Final volume (mL) / Solvent	**Date Vialed / Analyst**	Amount Extract (mL) / Solvent	**Date Cleanup / Analyst**	Date KD / Analyst	Final volume (mL) / Solvent	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Comments

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Sulfuric acid _____ Na_2SO_4_____ **Reviewed by / date** _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 651 REVISION 9

TITLE: SULFURIC ACID CLEANUP - METHOD SW3665A

FORM: 616 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11/14/07

QUALITY ASSURANCE MANAGER _____ DATE 11/14/07

LABORATORY MANAGER _____ DATE 11-14-07

HISTORY: Rev0, 5/15/92; Rev1, PCN #168, 3/14/94,; Rev2, PCN #278, 10/18/94; Rev3, PCN #453, 4/18/95; Rev4, 11/18/99; Rev5, 3/26/02; Rev6, 3/14/03; Rev7, 3/14/04; Rev8, 2/27/06.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references -- SW-846 3665A, describe the cleanup of sample extracts prior to analysis for polychlorinated biphenyls (PCBs) by method SW8082. This procedure is currently performed on all extracts to be subsequently analyzed by method SW8082. This procedure is not used to clean extracts for other analytical processes performed at Paragon, as it will oxidize most organic compounds to varying degrees. Method SW3665A states that the permanganate portion of the cleanup should be performed "if necessary". Paragon's experience has shown that permanganate cleanup is generally not necessary; hence it is not addressed in our procedures or this SOP.

2. SUMMARY

A sample extract from Paragon SOPs 617, 622, 625 or 626 is solvent exchanged from methylene chloride to hexane following Paragon SOPs 607 and 637 (extracts from SOP673, being extracted with hexane, do not require exchange). The extract is then vigorously mixed with concentrated sulfuric acid and subsequently centrifuged to separate the hexane extract from the sulfuric acid. This cleanup may be repeated if necessary. Batch QC elements (blanks, spikes, and replicates) must be subjected to the same cleanup as the samples associated with them.

3. RESPONSIBILITIES

3.1 It is the responsibility of the Technician to perform these procedures according to this SOP and to complete all documentation required for review. The Technician must demonstrate the capability to generate acceptable results utilizing these methods, this demonstration may come in the form of Supervisory/training review or the results of precision and accuracy tests performed.

3.2 It is the responsibility of all personnel who work with the samples or data involving this method to consult applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Any anomalies or out-of-control events must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, or other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by processing and successfully analyzing method blanks.

4.2 This technique will not remove chlorinated benzenes, chlorinated naphthalenes, and a number of chlorinated pesticides.

5. APPARATUS AND MATERIALS

5.1 glass Pasteur pipets

5.2 centrifuge, Fisher Scientific Marathon 10K or equivalent

5.3 vials, appropriate sizes, with PTFE-lined screw-top caps

6. REAGENTS - All reagents must be analytical reagent grade or better

6.1 concentrated sulfuric acid (H_2SO_4)

6.2 hexane

7. PROCEDURES

7.1 Bring the extract to a predetermined volume in hexane (typically 10mL).

7.2 Place the extract in a 40mL vial (other sized vials may also be used, as appropriate).

7.3 Add 20mL of H_2SO_4 (volume of acid should be twice that of extract, if final volume of extract varies from 10mL) to the extract. Cap tightly and shake each vial containing the extract and acid thoroughly for 1 to 2 minutes. A vortex mixer may be utilized, or the vials may be vigorously shaken by hand.

CAUTION: Avoid skin contact - sulfuric acid causes burns!

7.4 Centrifuge the mixture for 3-5 minutes at no higher than 1500rpm to separate the acid and extract layers. Alternatively, the mixture of hexane and acid can be left for 15-20 minutes to separation on its own.

7.5 Examine the hexane layer. It should not be highly colored, nor should it have a visible emulsion or cloudiness. If a clean hexane layer is achieved, proceed to Step 7.7. If the hexane layer is colored, or the emulsion persists, remove the hexane layer (and, if present, as much of the emulsion as possible) from the top of the vial and transfer the hexane to a fresh vial. The remaining acid layer can be disposed of properly at this point. Add another portion of concentrated sulfuric acid (2:1, v/v) to the hexane extract and perform Steps 7.3 and 7.4 again. Record

the number of cleanup steps in the logbook if any samples required repeated cleanups.

7.6 Normally, extracts do not require more than two acid washes, although oil samples or oily samples may require three. The method blank and laboratory control samples need only be acid washed once.

7.7 Use a disposable pipet to transfer the hexane layer into an appropriate size vial with PTFE-lined cap. Dispose of the acid layer into the concentrated acid waste.

No acid should be present in the extract to be delivered, as it can damage the analytical instrumentation used. Visually inspect for the presence of two phases after the transfer. If any acid is seen, carefully transfer the hexane phase to a fresh vial.

7.8 Re-extraction and notification of the Department Manager may be warranted if a large amount of the extract is lost during the acid cleanup (i.e. if less than 1mL is remaining). If re-extraction is not possible due to extenuating circumstances (e.g, no sample remaining, past holding time), the extract should be kept and notation made on the benchsheet.

7.9 Complete benchsheet (Form 616) and observe proper internal chain-of-custody procedures (SOP 318) to deliver the extracts to the appropriate analytical area.

8. QUALITY CONTROL

The associated quality control samples (blanks, spikes, duplicates, replicates) for sample extracts that are acid cleaned must also be processed through the same cleanup procedure. This is done in order to demonstrate that the compounds of interest are being quantitatively recovered after acid cleanup.

9. DEVIATIONS FROM THE METHOD

9.1 The referenced Method SW3665A suggests use of 1:1 sulfuric acid/water (v/v). Paragon uses concentrated sulfuric acid.

9.2 The permanganate oxidation step of the cleanup method is not utilized at this time by Paragon and is not described in this SOP.

9.3 Section 7.1.9 of Method SW3665A describes a post-cleanup "extraction" of the sulfuric acid with 1mL of clean hexane ("to ensure quantitative transfer of the PCB's"). This step is not performed at Paragon and is not described in this SOP. Historical recoveries of PCB's in LCS/D samples do not indicate significant negative bias as a result of omitting this step.

10. SAFETY, HAZARDS AND WASTE DISPOSAL

10.1 SAFETY AND HAZARDS

10.1.1 Applicable material safety data sheets (MSDSs) must be read prior to

using any solvents or reagents for the first time.

10.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

10.1.3 Chemicals with a Threshold Limit Value (TLV) of less than 50ppm must be worked with in a laboratory fume hood (e.g., solvents and acids). **As sulfuric acid TLV<50ppm and hexane TLV = 50ppm both fall in this category, the procedure must be done in a properly working fume hood.**

10.1.4 All flammable compounds must be kept away from ignition sources.

10.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, date prepared or transferred and the initials of the preparer.

10.2 WASTE DISPOSAL

10.2.1 Hexane wastes (that have contacted samples) may be disposed of in the TSCA PCB Waste.

10.2.2 The sample remainders, extract vials and associated extracts may be disposed of intact in the PCB Debris waste.

10.2.3 Aqueous corrosive waste that may contain PCBs in excess of 50ppm will be disposed of by lab packing for TSCA disposal.

10.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

11. REFERENCES

11.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3600C , December 1996.

11.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Method 3665A, December 1996.

DOCUMENT REVISION HISTORY

11/12/07: Added list of compounds NOT removed to INTERFERENCES. Augmented DEVIATIONS with 9.3 text. General word-smithing and clarification throughout. Added DOCUMENT REVISION HISTORY and Form.

___________ A **PESTICIDES / PCBs -- EXTRACTION WORKSHEET** *Paragon Analytics*

WO #s ______________________ **Batch ID** ____________________ **Surr Code** _______________ **Matrix Spike Code** _____________
Ex Date/Time ___________ (start) ____________ (stop) **Matrix** Aq Solid Other ________ **Balance ID** ______ **Ex SOP** ___ **Rev**___ **Initials** ___
Ex Method: (3520C) CLE (3550B) SONC (3540C) SOX (3510) SEP (3580) Wdilute (SOP 673) Wipes **EX Code:** 8081B (pest) 8082 (PCB) 608 (pest) 8081B (TCLP pest)

Sample No.	Amount (g / mL)	pH	Surr. Spike Amt. (mL)	Matrix Spike Amt. (mL)	Spike Analyst / Witness	Date KD / Analyst	Final Solvent	Final Vol. (mL)	Cleanup Req. (y / n)	Comments
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Lots: $MeCl_2$ ____________ Hexane ____________ Na_2SO_4 ____________ Form 616r13.xls (3/29/05)

___________ B **PESTICIDES / PCBs -- CLEANUP WORKSHEET** *Paragon Analytics*

WO #s ______________________ **Batch ID** ____________________ **Cleanup SOP** _____ **Rev**____ **Initials** _____
Cleanup Method: (3620B) Florisil (3665A) Sulfuric (3640A) GPC (See additional forms) Other ___________

FLORISIL: Has lot check been done? y/n _____ **GPC** (<u>Note</u>: half the extract is lost during cleanup) **SULFURIC ACID**

Sample No.	Amount Extract (mL)/ Solvent	Date Cleanup / Analyst	Final volume (mL) / Solvent	Date Vialed / Analyst	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Date KD / Analyst	Final volume (mL) / Solvent	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Comments

Lots: $MeCl_2$ ________ Hexane _________ Acetone _________ Florisil _________ Sulfuric acid _________ Na_2SO_4_________ **Reviewed by / date** _______________

CONFIDENTIAL

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 658 REVISION 7

TITLE: PAINT FILTER LIQUIDS TEST – SW9095A

FORMS: 648

APPROVAL:

TECHNICAL MANAGER _____ DATE 2-27-2006

QUALITY ASSURANCE MANAGER _____ DATE 2/28/06

LABORATORY MANAGER _____ DATE 2-28-06

HISTORY: Rev0, 9/15/92; Rev1, PCN #165, 3/14/94; Rev2, PCN #457, 4/18/95; Rev3, 10/27/99; Rev4, 3/26/02; Rev5, 3/14/03; Rev6, 5/12/04; Rev7, 2/27/06. **re-released w/o revision 11/9/07 DAS**

1. SCOPE AND APPLICATION

This procedure and the Method it references, SW-846 9095A, are used to determine the presence of free liquids in a representative sample of waste. Method SW 9095A can be used to determine compliance with 40 CFR 264.314 and 265.314. Free liquids, by definition, are any material that passes through the mesh portion of the filter.

2. SUMMARY

A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within five minutes, the material is deemed to contain free liquids.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the logbook pages, analytical review sheets or case narrative indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of measures taken to correct any errors that were found in the data during review.

3.4 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Filter media can separate from the filter cone upon exposure to alkaline materials. This development causes no problem if the sample is not disturbed.

4.2 Temperature can affect test results if the test is performed below the freezing point of any liquid in the sample. This procedure is performed at ambient temperature in the laboratory. Ambient temperature is generally 23±4°C in the laboratory.

5. APPARTUS AND MATERIALS

5.1 conical paint filters, mesh number 60±5% (fine meshed size) and available at local paint stores

5.2 ring stands and rings

5.3 beakers or graduated cylinders, 100mL

5.4 glass or steel funnels with wide bottom opening or fluted funnels

5.5 stop watch or timer

6. REAGENTS

None.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 Samples may be contained in any glass or plastic container.

7.3 No chemical preservation is required as part of this procedure.

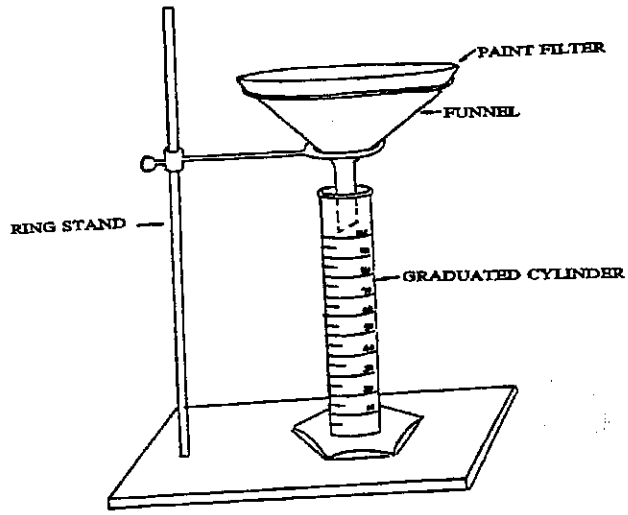
7.4 Refrigerated storage for samples submitted for this procedure is not required. However, refrigerated preservation may be required for other tests being performed on the samples.

8. PROCEDURE

8.1 Assemble the test apparatus as follows: secure a ring on a ring stand with sufficient height to allow a beaker or a graduated cylinder to be placed under it as

shown in Figure 1 below. A fluted funnel or a wide-opening funnel may be placed in the ring, and the paint filter into the glass funnel as shown in Figure 1.

Figure 1
PAINT FILTER TEST APPARATUS



8.2 A 100mL or 100g aliquot is required for this test. The aliquot must be representative of the sample. If it is not possible to obtain a sample of 100mL or 100g that is sufficiently representative of the waste, the analyst may use larger size samples in multiples of 100mL or 100g. However, when larger samples are used, analysts shall divide the sample into 100mL or 100g portions and test each portion separately.

8.3 Place sample aliquot in the filter. If the sample is of such light density that it overflows the filter, then the sides of the filter can be extended upward by taping filter paper to the inside of the filter and above the mesh. Settling the sample into the paint filter may be facilitated by lightly tapping the side of the filter as it is being filled. If the waste filled paint filter cannot sustain its weight on the ring stand, then a fluted funnel (Figure 1) or a funnel with a mouth that allows at least 1 inch of the filter mesh to protrude should be used to support the filter.

8.4 In order to ensure uniformity and standardization of the test, material such as sorbent pads or pillows that do not conform to the shape of the paint filter should be cut into small pieces and poured into the filter. The particles to be tested should be reduced to smaller than 1cm (i.e., should be capable of passing through

a 9.5mm, 0.375inch standard sieve). Sample size reduction may be accomplished by cutting the material with scissors, shears, knife, etc., so as to preserve the integrity of the sample as much as possible. *Grinding sorbent materials should be avoided as this may destroy the integrity of the sorbent and produce many "fine particles" that would not normally be present.*

8.5 For brittle materials larger than 1cm that do not conform to the filter, light crushing to reduce oversize particles is acceptable if it is not practical to cut the material. Materials such as clay, silica gel, and some polymers may fall into this category.

8.6 Allow sample to drain for 5 minutes into the beaker or graduated cylinder.

8.7 If any portion of the test material collects in the beaker or graduated cylinder in the 5 minute period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314. Record the volume or weight of sample that passed through the filter.

9. QUALITY CONTROL

9.1 Method blanks are not analyzed as part of this procedure.

9.2 Laboratory control samples are not analyzed as part of this procedure.

9.3 One sample should be analyzed in duplicate with each batch, if sample volume is adequate. Batches are defined as 20 or fewer field samples prepared and analyzed as a unit.

10. DEVIATION FROM THE METHOD

There are no known deviations from the referenced Method.

11. SAFETY, HAZARDS, AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.2 Particle size reduction as discussed above may produce fine particles that can be ingested. Any size reduction efforts must be performed in a manner that minimizes exposure to these fines.

11.1.3 This procedure should be conducted in an appropriately ventilated hood enclosure as the samples should be considered as potential hazards.

11.2 WASTE DISPOSAL

11.2.1 This test is nondestructive and the sample aliquots used for this procedure may be utilized in other procedures in the lab where appropriate.

11.2.2 Any non-radioactive solid sample residues should be disposed of in the Contaminated Soils and Solids waste stream.

11.2.3 Any radioactive solid sample residues shall be disposed of in the Radioactive Soils and Solids waste stream.

11.2.4 Any non-radioactive liquid sample residues should be disposed of in the Hazardous Aqueous Waste (if water) or if an organic liquid in the Oil and Grease Waste (non-PCB).

11.2.5 Any radioactive liquid sample residues should be disposed of in the Mixed Hazardous Radioactive Liquids waste stream.

11.2.6 Empty sample containers are defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Method 9095A, December 1996.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 663 REVISION 7

TITLE: **MONITORING TCLP TUMBLER REVOLUTIONS AND ROOM TEMPERATURE**

FORMS: **608, 623** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/27/07

QUALITY ASSURANCE MANAGER _____ DATE 2/27/07

LABORATORY MANAGER _____ Lance Steere for KDC DATE 2/27/07

HISTORY: NEW, Rev0, 3/9/93; Rev1, 4/18/95; PCN #663; Rev2, 2/12/99; Rev3, 4/10/02; Rev4, 3/19/03; Rev5, 4/16/04; Rev6, 2/27/06; Rev7, 2/27/07.

re-released without revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the monitoring of Toxic Characteristic Leaching Procedure (TCLP) tumbler revolutions per minute (RPM). This procedure also describes how Paragon monitors room temperature for all leaching procedures (SW1311, SW1312, and Cal-WET).

2. SUMMARY

Uniquely identified tumblers are loaded with samples and tumbling is initiated. At the beginning and the end of the tumbling process, the RPMs of the tumblers are measured and recorded on a benchsheet. TCLP room temperature s monitored throughout the entire leaching procedure using a min/max thermometer that is verified annually (SOP 923). The TCLP room temperature during tumbling is recorded on the benchsheet.

3. RESPONSIBILITIES

3.1 Organic Extractions personnel are responsible for monitoring and controlling the temperature of the TCLP room. To help keep temperature constant, use of outside and inside doors proximate to this area is limited. As necessary, Organic Extractions staff shall notify the Facilities Manager when thermostatic adjustment to control TCLP room temperature is necessary.

3.2 Organic Extractions personnel are responsible for ensuring that the electronic thermometer used to monitor TCLP room temperature is functioning properly (as needed, replacement batteries can be obtained from the QA Department), and that the correct thermometer is indicated in the laboratory logbook. A replacement thermometer is available from the Quality Assurance (QA) Department should malfunction occur.

3.3 The QA Department is responsible for managing thermometers (including their annual verification per SOP 923) and for providing temperature record logbooks, as needed.

3.4 It is the responsibility of the Technician to perform these tasks according to this SOP and to complete all documentation required for review. Any anomalies or out-of-control events must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

4.1 Tumbler, with 30±2 RPM capability, Associated Design and Manufacturing Model 3740 or equivalent

4.2 Stopwatch, VWR #62379-460 or equivalent

4.3 Electronic min/max thermometer, with external probe immersed in liquid, VWR #62379-549 or equivalent (NIST-traceable)

5. PROCEDURE

5.1 Note room temperature before tumblers are turned on. If room temperature is not 21-25°C, then do not start the tumbling. Bring room temperature to 21-25°C before tumbling samples.

5.2 Load samples onto tumbler and turn on tumbler. SOPs 608, 609, 666, 668 and 669 provide guidance on various leaching procedures.

5.3 Reset the min/max thermometer when tumbling starts.

5.4 Start the stopwatch and count the revolutions for 30 seconds, counting each time the orange dot on the moving part lines up with the orange dot on the stationary part. Record the revolutions (multiplied by 2) on the benchsheet.

The measured RPM for the units during tumbling must be 30±2. If the measured rate of revolution is out of this range, tag the tumbler "Out of Service" (SOP 317) and notify the Department Manager.

Also record on the benchsheet:

- numbers on the tumblers used (tumbler #)
- date and time the tumbling starts
- initials of the Technician taking initial readings

5.5 Just before the tumbling is complete, measure RPMs as described in Step 5.4; record on benchsheet.

Also record on the benchsheet:

- the minimum and maximum temperature of the TCLP room during the tumbling process
- date and time the tumbling stops
- initials of the Technician taking final readings

6. QUALITY ASSURANCE

6.1 If initial RPM is within specifications but final RPM measurement indicates the tumbler is out of specification, then this must be documented using a Non-Conformance Report (NCR, SOP 928).

6.2 The room temperature must be 23±2°C for Methods SW-846 1311 and 1312. Document on an NCR if temperature is outside of the acceptable range during tumbling process.

7. SAFETY AND HAZARDS

7.1 Always inspect electrical cords and switches prior to using electrical equipment.

7.2 Take care when operating moving machinery. Do not let long hair hang loose or wear ties and/or loose fitting clothing.

8. REFERENCES

8.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 1311, Rev 0, July 1992.

8.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 1312, Rev 0, September 1994.

8.3 California Code of Regulations: Title 22, Article 4, "Lists of RCRA Hazardous Wastes", Appendix II, effective 7-1-91 (Register 91, No.22).

DOCUMENT REVISION HISTORY

2/27/07: Republished to put on a better publication schedule. SUMMARY Section revamped. RESPONSIBILITIES Section expanded. Organizational changes made to PROCEDURE Section for clarity. DOCUMENT REVISION HISTORY Section and Forms added.

Paragon Analytics

ZHE PERCENT SOLIDS DETERMINATION & TUMBLING

Work Order # _____	**(Start) Date** _____ **Time** _____	**(Run) Temp. (min/max)** _____/_____ **°C**
Batch # _____	**(Start) RPM** _____ **Temp.** _____ **°C** *(from min/max* SN 21251556)	**(Stop) Date** _____ **Time** _____
Method _____ **SOP 608 Rev** _____	**(Start) PSI** _____ **Analyst** ____ RESET MIN/MAX AFTER READING OBTAINED	**(Stop) RPM** _____ **Temp. (min/max)** _____/_____ **°C**
Leaching Fluid ID		**(Stop) PSI** **Analyst**
Filtration Date _____ **Time** _____ **Initials** _____		**Reviewed by date** _____

		Percent Solids Determination						ZHE Aliquot					
Sample Number	**Sample Matrix**	Free Liquid? Y / N *	Initial Sample Weight (g)	Filter Weight (g)	Beaker Weight (g)	Sample Dry Weight (g)	% Solid (DRY/TOT)	Tumbler Number	Aliquot (g)	Fluid Volume (mL)	**Final pH**	**Leachate Number**	**Comments**

* If "No", percent solids are 100% by visual inspection (test not performed). **INTERNAL COC TRANSFER**: Relinquished by _____ (initials) to _____ (RU # & Location) _____ (Date & Time)

Form 608r10.doc (10/21/05)

Paragon Analytics

Logbook No./Page _______________ B

LEACHING PROCEDURE WORKSHEET

Work Order # _______________________
Batch ID # _________________________
Method **SOP** **Rev**

(Start) Date ________ **Time** ______
(Start) RPM _______ **Temp.** _____ **°C** *(from min/max* SN 21251556*)*
(Start) Analyst _____ RESET MIN/MAX AFTER READING OBTAINED

(Stop) Date _______ **Time** ______ **RPM** ______
(Stop) Temp. ____ **°C** **Tumble Min/Max** ___/___ **°C**
RESET AFTER EACH READING **(Stop) Analyst** _____

Extraction Fluid ID ____________________ **Filtration Date/Time/** ___________________ **Initials** ________

Reviewed By / Date ________________________

Preliminary Solids[a]	Particle Reduction[b]	Sample Number	Initial pH	Fluid Determination				Sample Weight (g)	Fluid (mL)	Final pH	Leachate No.	Comments
				HCl (mL)	Final pH	Fluid #	Fluid pH					
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
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I S M	Y N											

[a] I = insignificant (< 0.5%); S = 100%; M = Multiphasic (see attached % Solids Determination form).

[b] Y = Yes - reduction required / performed; N = no partical size reduction required.

INTERNAL COC TRANSFER: Relinquished by _______ (initials) to ______________________ (RU# & location) ____________________ (Date & Time)

Form 623r10.doc (1/17/2006)

Paragon Analytics

PERCENT SOLIDS (% SOLIDS) DETERMINATION

Logbook No./Page _____ A **(For Samples on Following Logbook Page)**

Units = grams	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
Sample No.	Weight of Beaker, Spatula & Sample	Weight of Beaker, Spatula & Residue	Total Sample Weight (a - b)	**Weight of Filter**	Weight of Collection Flask	Weight of Flask & Filtrate	Filtrate Weight (f - e)	Total Solids Weight (c - g)	% Solids (Wet) (h / c) * 100	Weight of Filter & Dried Solids	Weight of Dried Solids (j - d)	% Solids (Dry) (k / h) * 100

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Must Discard 30 Days from _____ (date printed)

Amended 3/17/08 to include Timer Operator Aid. DAS
Re-released w/o revision 3/14/09 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 664 REVISION 8

TITLE: **EXTRACTION AND DERIVATIZATION OF SAMPLES FOR HERBICIDE ANALYSIS BY GAS CHROMATOGRAPHY -- METHODS SW8151A, EPA 615, AND EPA 515.1**

FORMS: **604 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-2007

QUALITY ASSURANCE MANAGER _____ DATE 11/20/07

LABORATORY MANAGER _____ DATE 11-21-07

HISTORY: Rev0, 12/20/93; Rev1, PCN #385, 2/17/95; Rev2, 4/16/02; Rev3, 8/5/02; Rev4, 4/3/04; Rev5, 11/22/04; Rev6, 3/9/06; Rev7, 7/24/06; Rev8, 11/20/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references - Methods SW8151A, EPA 615 and EPA 515.1, are used to prepare liquid (all) and solid (SW8151A) matrices for subsequent analysis for chlorinated acid herbicides by gas chromatography. The following compounds typically comprise Paragon's herbicide target analyte list:

Dalapon	Silvex
Dicamba	2,4,5-T
MCPP	2,4-DB
MCPA	Dinoseb
Dichloroprop	2,4-Dichlorophenylacetic acid
2, 4-D	

Other compounds are listed in Methods EPA 515.1, EPA 615, and SW8151A; these compounds may be extracted using this procedure after successful completion of method detection limit (MDL) studies and initial demonstration of capability (DOC).

2. SUMMARY OF METHOD

Herbicides are produced and applied in several chemical forms (i.e., acids, salts, esters, etc.). This procedure addresses the preparation of liquid and solid matrix environmental field samples and quality control (QC) samples for total herbicide content analysis. Samples are extracted, hydrolyzed, concentrated by Kuderna-Danish (SOP 607), and then derivatized (to methyl esters) using diazomethane. The resultant methyl-esterified extracts are then solvent exchanged into hexane by a nitrogen evaporation procedure (SOP 637) before subsequent gas chromatographic (GC) analysis (SOP 434).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform this procedure according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work and documentation of the measures taken to correct the errors that were found.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that can lead to discrete artifacts or elevated baselines in chromatograms. All materials must be routinely demonstrated to be free from interferences under the conditions of the analysis.

4.2 Organic acids, especially chlorinated acids, cause the most direct interference with the subsequent analysis. One of the common target compounds, *dinoseb*, is a nitrophenol. As a class of compounds, phenols may be extracted, derivatized, and subsequently interfere with the analysis procedure if they respond to the electron capture detector used in the analysis (SOP 434).

4.3 Sodium sulfate must be acidified before use. After the hydrolysis step in the procedure, it is very important to maintain pH of aqueous solutions below the lowest pK_a of the desired target compounds to ensure successful recovery.

4.4 Ether extracts must be free of water and methylene chloride prior to the derivatization steps or poor recoveries will be obtained.

5. APPARATUS AND MATERIALS

5.1 separatory funnels with PTFE stopcock and stopper, 250-2000mL, as appropriate

5.2 soxhlet apparatus consisting of the following:

- 500mL round flat bottom flasks
- soxhlet extractors
- fritted glass thimbles
- condensers with circulating cooling water

5.3 phosphoric acid acidified glass wool, Supelco #2-0383 or equivalent

Alternatively, glass wool may be acidified in-house using 8µ Corning #3950 glass wool or equivalent as follows:

5.3.1 Pour 150mL of ether into a 1000mL beaker. Slowly add 2.5mL conc. sulfuric acid.

5.3.2 Submerge as much glass wool as possible in the acidified ether.

5.3.3 The ether is evaporated by placing the beaker on top of the S-Evap steam bath in a fume hood. Swirl occasionally as the ether evaporates.

5.3.4 After ether is completely evaporated, place acidified glass wool in labeled container, cap and store.

5.4 beakers and Erlenmeyer flasks, various sizes as appropriate

5.5 boiling chips, PTFE, Chemware #D1069103 or equivalent or silicon carbide.
Rinse first with methylene chloride, then with diethyl ether prior to use.

5.6 Pasteur pipets, glass or plastic, disposable

5.7 glass vials, with screw tops equipped with PTFE septa, 10mL, 40mL, or as appropriate

5.8 PTFE tubing

5.9 magnetic stir bar and stir plate

5.10 powder funnels

5.11 pH paper, narrow (acidic and basic) and wide range

5.12 peroxide test strips (0-25ppm): EM Science #10011-1 or equivalent

NOTE: Always check peroxide level of ether prior to use. Apply solvent to test strip and evaluate as compared to reference scale. If the level of peroxide in the ether is ≥10ppm, then ether is NOT suitable for use! Notify Supervisor immediately.

5.13 Kuderna-Danish (K-D) apparatus consisting of the following:
- concentrator tubes, graduated, 10mL or other appropriate size
- evaporation flasks, attached to the concentrator tube with a clip, 500mL or other appropriate size
- 3-ball macro Snyder columns

5.14 top-loading balance, capable of weighing to ±0.1g, verified per SOP 305

5.15 glass syringes, 0.5-1mL or as appropriate

5.16 graduated cylinders, 20-2000mL as appropriate

6. SOLVENTS AND REAGENTS

6.1 SOLVENTS - **All solvents must be pesticide residue grade or equivalent.**

6.1.1 methanol (CH_3OH, MeOH): Burdick & Jackson #230-4 or equivalent

6.1.2 methylene chloride ($MeCl_2$, DCM), Fisher, #D154-4 or equivalent

6.1.3 n-hexane (C_6H_{14}), Fisher #H300-4 or equivalent

6.1.4 methyl tert-butyl ether ($(CH_3)3(COCH_3)$), JT Baker #9043-02 or equivalent

6.1.5 diethyl ether ($C_2H_5OC_2H_5$), Burdick & Jackson #107-4 or equivalent.

Must be peroxide-free and stabilized with BHT (not ethanol) or unpreserved

6.1.6 organic-free reagent water, Paragon's deionized (DI) water passed through a Milli-Q Plus system for additional purification

6.2 REAGENTS - **All reagents must be ACS reagent grade or better.**

6.2.1 sodium chloride (NaCl), VWR #SX0420-5 or equivalent

6.2.2 hydrochloric acid (HCl), concentrated, EMD #HX0603-75 or equivalent

6.2.3 sulfuric acid (H_2SO_4), concentrated, EMD #SX1247-2 or equivalent.

Make a 1:2 (v/v) solution by adding 1 part acid to 2 parts DI water. Used for pH adjustment.

CAUTION: Always add acid to water. Prepare in Pyrex™ glass beaker or jar. Reaction produces heat.

6.2.4 acidified anhydrous sodium sulfate (Na_2SO_4), EMD #SX0760E–5 or equivalent.

Purify by heating at about 450ºC (kiln) for 3-6 hours in a shallow tray.

Acidify as follows:

6.2.4.1 Weigh 1kg of dried sodium sulfate into a 2L flask or beaker. Slowly add 8mL of concentrated sulfuric acid to 450mL of ether in a 1000mL beaker. Pour the acidified ether into the 1kg sodium sulfate and mix thoroughly. Place mixture on top of steam bath and stir with a glass rod every few minutes to evaporate the ether.

6.2.4.2 After the sodium sulfate is dry, mix 1g of the resulting solid with 5mL of organic-free reagent water and measure the pH of the mixture. The solution pH must be below 3. Place the dried acidified sodium sulfate in a labeled clean jar, cap and store.

6.2.5 Carbitol® Also known as di(ethylene glycol) ethyl ether or (2-ethoxyethoxy) ethanol. Aldrich Chemicals #E455-0 or equivalent

6.2.6 Diazald® (N-methyl-N-nitroso-p-toluenesulfonamide), Aldrich Chemicals, #D2800-0 or equivalent

6.2.7 potassium hydroxide (KOH), VWR #VW5040-1 or equivalent.

Make 37% (w/v) solution by dissolving 37g of potassium hydroxide pellets in 100mL DI water.

6.3 GASES

nitrogen gas, 99.999% purity. Used for diazomethane generation and for concentration and solvent exchange of final extract (SOP 637).

6.4 SPIKE SOLUTIONS

Laboratory control, matrix and surrogate spike solutions are prepared by the analytical group according to SOPs 434 and 300 and provided to the extractions group for use. These spike solutions are documented in Paragon's Standards and Reagents database. Currently, 2,4-dichlorophenylacetic acid (DCAA) is used as the surrogate for this procedure.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are generally not chemically preserved and must be collected in amber glass containers (generally 1000mL) with Teflon™-lined lids. Samples must be maintained at 4±2°C and be extracted within 7 days of collection. Sodium thiosulfate ($Na_2S_2O_3$) may be used to remove free chlorine present in liquid samples if obtained from a processed water source. This should be accomplished by the client in the field. The Project Manager may specify the need for residual chlorine check of the sample upon receipt. Additionally,

samples for Method EPA 608 may need to have pH adjusted upon receipt.

7.3 Solid samples are collected in wide-mouth glass containers with Teflon™-lined lids. Solid samples are not chemically preserved but must be maintained at 4±2°C. Solid samples must be extracted within 14 days of collection.

8. EXTRACTION AND DERIVATIZATION PROCEDURES

8.1 WASTE DILUTION (SW3580A)

Organic liquids are prepared for analysis using Paragon SOP 622 and the following notes:

8.1.1 An appropriate volume of surrogate (and matrix spike standard, where appropriate) is added to each sample prior to dilution.

8.1.2 Diethyl ether is used as the dilution solvent.

8.1.3 Depending on the required analysis, extracts may require further preparation before delivery to the appropriate analytical group. If the sample is to be analyzed for both herbicide esters and acids, then the extract must be hydrolyzed and derivatized. Proceed to Section 8.2.3. If the analysis is for acid herbicides only, proceed to Section 8.5 for derivatization. Consult Department Manager for further direction if necessary.

8.2 SOIL SAMPLES

Soil samples are first extracted under acidic conditions. The extracts are then hydrolyzed prior to further extraction, concentration, and derivatization.

NOTE: Paragon extracts solid samples for herbicide analysis by soxhlet extraction (Paragon SOP 625) after acidifying the sample/sodium sulfate matrix. Section 7.2 of SW8151A discusses sonication and shaker extraction. As the guidance of SW-846 states, alternative preparation methods are acceptable provided the laboratory establishes performance documentation, which shows the procedure employed provides appropriate performance for the intended application. Paragon has met this requirement (refer to REPORT: Soxhlet Extraction of Herbicides in Soils, J:\Audits and Corrective Actions\ Findings and Corrective Actions\Topical Corrective Actions\Sox_Herb_SO).

8.2.1 SOIL SAMPLE PREPARATION

8.2.1.1 Decant and discard any water layer present on a sediment sample. Take care to discard any foreign objects (e.g., sticks, leaves, rocks) or any portion of the sample that appears to ***not*** be representative of the sample. Mix sample thoroughly, especially composited samples, to

ensure that a representative sample is obtained. ***Consult Department Manager regarding difficult, unusual matrices.***

8.2.1.2 Homogenize sample and place 30g into a 400mL thick-walled beaker with enough sodium sulfate to dry the sample. Adjust to pH<2 using concentrated HCl, 2mL of acid is generally adequate. If a significant reaction occurs (evidenced by rapid fizzing) upon addition of HCl to the sample, more acid may be required to adjust the pH.

8.2.1.3 Mix the sample, sodium sulfate and acid thoroughly. The mixture should be free flowing when dried sufficiently. Additional sodium sulfate may be necessary. *Be careful that the mixture will not exceed the capacity of the glass thimble.*

8.2.2 SOIL SAMPLE EXTRACTION

8.2.2.1 Quantitatively transfer the dried sample mixture to a Soxhlet thimble. Add 1.0mL of a 2.0mg/kg herbicide surrogate spiking solution to all field and QC samples. To the LCS, LCSD, MS, and MSD samples, also add 1.0mL of the herbicide spiking solution (0.25mg/kg to 250mg/kg spike component concentrations).

8.2.2.2 Per Paragon SOP 625, extract the samples with methylene chloride for 16-24 hours. Allow extract and apparatus to cool to room temperature before disassembling.

8.2.3 SOIL SAMPLE HYDROLYSIS

8.2.3.1 Quantitatively transfer the extract from the flat bottom flask into a 500mL Kuderna-Danish (K-D) flask connected to a 10mL concentrator tube. Add boiling chips and attach a rinsed/pre-wetted macro Snyder column. Evaporate the extract in a steam bath to a volume of approximately 5mL following SOP 607.

8.2.3.2 Remove the flask from the bath and allow the extract to cool to room temperature.

8.2.3.3 Add 5mL 37% KOH and 25mL organic-free water to the extract contained in the K-D concentrator. Add a few boiling chips. Reflux in a steam bath (S-Evap) or water bath at 65-70°C until the hydrolysis step is complete (usually 1-2 hours). The methylene chloride will have completely evaporated when the hydrolysis is complete.

Remove flasks and cool to room temperature (approximately 1 hour).

8.2.3.4 Transfer the aqueous hydrolysate to a 250mL separatory funnel. Check that the pH of the hydrolysate is pH≥12. Extract 3 times with 60mL methylene chloride. Each extraction consists of vigorous agitation (approximately 2 minutes for the first extraction, 1.5 minutes for the second, and 1 minute for the third) with periodic venting followed by approximately 10 minutes of settling for separation of the organic and aqueous phases.

If an emulsion interface between the layers is more than one-third the volume of the solvent layer, further mechanical techniques (stirring, filtration, centrifugation, etc.) are required to achieve suitable separation. SOP 626 provides further guidance on how to break emulsions. Drain and discard methylene chloride (the bottom layer) after each clean-up extraction. **It is particularly important to make sure that as much methylene chloride as possible is removed after the third extraction** - residual methylene chloride remaining in the sample during acidification (Section 8.2.3.5) will lead to poor target recoveries.

NOTE: These three extractions with methylene chloride serve to clean up neutral or basic non-target compounds from the sample prior to extraction of the target compounds.

8.2.3.5 After the third clean-up extraction is completed, adjust the pH of the aqueous hydrolysate to pH<2 with sulfuric acid solution. Typically, 5mL acid or less is needed.

8.2.3.6 Extract the acidified aqueous hydrolysate 3 times with diethyl ether. Add 60mL of ether for the first extraction, and 40mL for the second and third. Each extraction consists of vigorous agitation (about 2 minutes for the first extraction, 1.5 minutes for the second, and 1 minute for the third) with periodic venting followed by about 10 minutes settling for separation of the organic and aqueous phases. The ether extract layer will be at the top.

Drain the aqueous layer into an Erlenmeyer flask or beaker. Drain the ether extract into a 250mL Erlenmeyer flask or 250mL round flat bottom flask containing 10-25g of acidified sodium sulfate. Return the aqueous portion to

the separatory funnel.

8.2.3.7 After all three portions of extract have been drained into the collection flask containing acidified sodium sulfate, cap and let the extract dry for at least two hours (preferably overnight). Make sure the sodium sulfate is still loose and friable. If not, add more acidified sodium sulfate and let extract dry for at least 2 more hours.

8.2.3.8 Proceed to Section 8.4 - EXTRACT CONCENTRATION.

8.3 AQUEOUS SAMPLES

Aqueous samples are first hydrolyzed, then extracted under acidic conditions by separatory funnel.

8.3.1 AQUEOUS SAMPLE PREPARATION

8.3.1.1 Assemble 1.5-2 liter separatory funnels and add 250g NaCl to each. Mark the volume of sample on the sample bottle. Decant 1 liter (or other volume as suitable) of sample into a separatory funnel. Retain the original sample container; refill the container up to the mark with tap water and measure volume of sample to be extracted using a graduated cylinder. Place cleaned stoppers in each funnel and gently shake to dissolve salt. General guidance for separatory funnel extractions is provided in SOP 626. .

8.3.1.2 Spike all blanks, field samples and QC samples with 1.0mL of a 2.0mg/kg surrogate spiking solution. Additionally, spike LCS, LCSD, MS, and MSD QC samples with 1.0mL of the herbicide spiking solution (0.25mg/kg to 250mg/kg spike component concentrations).

8.3.2 AQUEOUS SAMPLE HYDROLYSIS

8.3.2.1 Add enough base (KOH) to each separatory funnel to raise to pH>12 (about 15mL of KOH solution is generally adequate). Place stopper in each separatory funnel and shake for 10-20 seconds. Check the pH of the solution using narrow range pH paper. If the pH is not >12, then add more base and repeat this step.

NOTE: This is a critical step. The pH must be 12 or greater or target compounds may be lost in later steps of this procedure. This high pH is also necessary for complete hydrolysis of herbicide esters in the sample.

8.3.2.2 Let hydrolyzing samples sit for 1-2 hours at room temperature.

8.3.2.3 After the 1-2 hour hydrolysis step, extract 3 times with 60mL methylene chloride. Each extraction consists of vigorous agitation (approximately 2 minutes for the first extraction, 1.5 minutes for the second, and 1 minute for the third) with periodic venting followed by approximately 10 minutes of settling for separation of the organic and aqueous phases.

If an emulsion interface between the layers is more than one-third the volume of the solvent layer, further mechanical techniques (stirring, filtration, centrifugation, etc.) are required to achieve suitable separation. SOP 626 provides further guidance on how to break emulsions.

Drain and discard methylene chloride (the bottom layer) after each clean-up extraction. **It is particularly important to make sure that as much methylene chloride as possible is removed after the third extraction -** residual methylene chloride remaining in the sample during acidification (Section 8.3.2.1) will lead to poor target recoveries.

NOTE: These three extractions with methylene chloride serve to clean up neutral or basic non-target compounds from the sample prior to extraction of the target compounds.

8.3.3 AQUEOUS SAMPLE EXTRACTION

8.3.3.1 Add 5-15mL of cold (4±2°C) sulfuric acid solution, seal the separatory funnel and shake for 10-20 seconds to mix the acid with the sample, venting several times to release pressure. Check the pH. If the pH is ≤2, then proceed to the next step. If the pH is not ≤2, then adjust by adding more acid.

8.3.3.2 Extract the acidified aqueous hydrolysate 3 times with diethyl ether. Add 80mL of ether for the first extraction, and 60mL for the second and third. Each extraction consists of vigorous agitation (about 2 minutes for the first extraction, 1.5 minutes for the second, and 1 minute for the third) with periodic venting followed by about 10 minutes settling for separation of the organic and aqueous phases. The ether extract layer will be at the top.

Drain the aqueous layer into an Erlenmeyer flask. Drain the ether extract into a 250mL Erlenmeyer flask or 250mL round flat bottom flask containing 10-25g of acidified sodium sulfate. Return the aqueous portion to the separatory funnel.

8.3.3.3 After all three portions of extract have been drained into the collection flask containing acidified sodium sulfate, allow the combined extract to remain in contact with the drying agent for at least 2 hours (overnight is preferable). **Drying is critical to allow complete derivatization of any target compounds that may be present. Any moisture remaining in the extract will lessen the effectiveness of the diazomethane reagent, which can result in poor recovery.** Test to ensure that the drying capacity of the acidified sodium sulfate has not been exceeded. This can be done by swirling the flask and observing that the sodium sulfate is loose and friable versus caked. The amount of acidified anhydrous sodium sulfate is adequate if some free-flowing crystals remain. Add more acidified sodium sulfate if caking or clumping is evident, and allow to sit for at least more 2 hours.

8.4 EXTRACT CONCENTRATION

8.4.1 Plug a funnel with acidified glass wool and a few grams of acidified sodium sulfate; rinse with a few mL of ether and discard the rinse. Pour the dried extract through the prepared funnel and collect in a 500mL K-D flask with concentrator tube attached. Use a clean glass rod to crush any caked sodium sulfate and transfer the drying agent to the funnel.

8.4.2 Rinse the drying flask and funnel with 20-30mL of diethyl ether. Pour the rinse ether through the prepared funnel and into the K-D flask.

8.4.3 Place a few boiling chips into the K-D flask and attach a three-ball (macro) Snyder column that has been rinsed/pre-wetted with ether.

8.4.4 Reduce the volume to approximately 5mL per SOP 607. Allow the ether extract and the apparatus to cool to room temperature. Proceed to Section 8.5 (derivatization) for EPA 615 or SW8151A samples.

NOTE: For EPA 515.1 samples, reduce to an apparent volume of 0.5mL; the nitrogen-blow down technique (SOP 637) may be used. This volume must be solvent exchanged (SOP 637) to MTBE. Add 5mL of MTBE to the 0.5mL and reduce to 0.5mL again. Proceed to Section 8.5 (derivatization).

8.5 DERIVATIZATION BY IN SITU GENERATION OF DIAZOMETHANE
Prepared and concentrated extracts are derivatized (to methyl esters) using diazomethane. Diazomethane can be generated via a bubbler apparatus fabricated in-house or by using a diazald kit purchased from a suitable vendor. The bubbler method is suggested for all samples and is the technique described in this procedure because it is safer to use than the diazald kit.

8.5.1 Add 200µL of methanol to each extract to be derivatized.

8.5.2 Fabricate the diazomethane bubbler apparatus as shown in Figure 1.

8.5.3 Add 5mL of diethyl ether to the first 40mL vial.

8.5.4 Add the following to the second 40mL vial and immediately place the bubbler exit tube into the concentrator tube containing the sample extract:

2mL diethyl ether
4mL carbitol
5mL 37% KOH
4.5g Diazald

8.5.5 Apply nitrogen flow (1-2mL/min) to bubble diazomethane through the extract for up to 10 minutes, or until the yellow color of diazomethane persists. When the mix of reagents is optimum, many extracts will turn yellow in 30 seconds or less.

8.5.6 When the yellow color persists in the extract, remove the PTFE-tubing from concentrator tube. Seal the concentrator tube with a Teflon™ or Neoprene™ stopper. Allow to sit at room temperature in the hood for 20 minutes.

8.5.7 Remove the stopper from the concentrator tube after the 20 minute reaction time and allow the tube to stand open until the evolution of nitrogen gas has stopped. If not already present, a boiling chip may be added to aid the decomposition of excess diazomethane.

NOTE: Solutions of diazomethane decompose rapidly in the presence of solid materials (e.g., silicic acid, sodium sulfate or boiling chips).

8.5.8 The derivatized extracts are exchanged from ether to hexane per Paragon SOP 637.

9. QUALITY CONTROL

9.1 DEFINITION OF A PREPARATION BATCH

For this method, a preparation batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike (MS) sample and laboratory duplicate. An LCSD or MSD (or both) can serve as the laboratory duplicate. All quality control samples must be carried through all stages of the sample preparation and measurement steps.

9.2 METHOD BLANK

Method blanks (MB) are analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. For this procedure, the method blank consists of 30g of kilned Ottawa sand (solid matrix) or 1000mL organic-free DI water (aqueous matrix). See QC Table of SOP 434 for acceptance limits.

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method in a controlled matrix. A known amount of analyte is prepared and analyzed. For this method, 30g of kilned Ottawa sand (solid matrix) and 1000mL organic-free DI water (aqueous matrix) are used for the LCS. Results obtained are compared to results expected. See QC Table of SOP 434 for acceptance limits.

9.4 MATRIX SPIKE SAMPLE

The matrix spike (MS) sample is analyzed to assess the effect of matrix interferences upon the sample analysis. A known amount of analyte is spiked into a replicate aliquot of a selected sample and analyzed. Results obtained are compared to results expected. See QC Table of SOP 434 for acceptance limits.

9.5 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. The LCS, MS or both may be analyzed in duplicate to serve this purpose. Precision is expressed as Relative Percent Difference (RPD). RPD calculations are discussed in SOP 434.

10. DEVIATIONS FROM THE METHODS

This SOP meets the requirements of methods SW8151A, EPA 615 and EPA 515.1 except as noted:

10.1 Methods SW8151A and EPA 515.1 discuss the use of silicic acid to destroy the diazomethane present in the extract. Paragon removes excess diazomethane by streaming nitrogen on the extract during the solvent changeover and by the addition of a boiling chip.

10.2 Methods SW8151A and EPA 515.1 state that glassware used in this procedure

"must be acid-rinsed" prior to use to avoid analyte loss. Instead, Paragon kilns glassware at high temperature (approximately 450°C) prior to use. Historical data and internal studies have shown that kilning adequately addresses the problem of potential analyte loss due to residual alkaline substances.

10.3 Soxhlet extraction of solids is not referenced in method SW8151A. Paragon has shown that use of Soxhlet extraction as detailed in Paragon SOP 664 and documented in REPORT: Soxhlet Extraction of Herbicides in Soils (J:\Audits and Corrective Actions\ Findings and Corrective Actions\Topical Corrective Actions\Sox_Herb_SO) provides high performance and compliant results.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Special precautions must be taken when working with diazomethane. It is carcinogenic and can explode under certain conditions.

Carcinogenic: Avoid breathing vapors; use in well-ventilated hood.

Explosion hazard: Avoid ground surfaces (e.g., ground glass joints, glass stirrers). Do not heat above 90°C. Use of a safety screen is suggested.

11.1.2 Read the appropriate MSDS before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Methylene chloride, hexane, methyl tert-butyl ether, diethyl ether and methanol have TLV≤50ppm.

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Aqueous waste may be disposed of in the AQLW (separate radioactive and non-radioactive) waste streams.

11.2.2 Solid sample waste should be disposed of in the contaminated soils and solids waste streams (radioactive or non-radioactive, as appropriate).

11.2.3 Liquid waste left over from the diazomethane generation procedure is disposed of in the AQLW stream. Wait about an hour after the extracts are derivatized (to allow diazomethane generation to cease completely) before disposal of this waste.

11.2.4 Halogenated organic wastes may be disposed of in the Halogenated Organic Wastes satellite collection vessel.

11.2.5 Any ether, hexane or other nonhalogenated organic solvent that has not been potentially contaminated with PCBs may be disposed of in the Acetonitrile/Nonhalogenated Waste.

11.2.6 Disposal of extracts and extract vials is managed by the group responsible for the analysis.

11.2.7 All empty solvent bottles must be disposed of appropriately. Please note that all labels and markings must be removed or defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, "Method 8151A", Revision 1, December 1996.

12.2 US EPA Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with Electron Capture Detector".

12.3 US EPA Method 615, "The Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater".

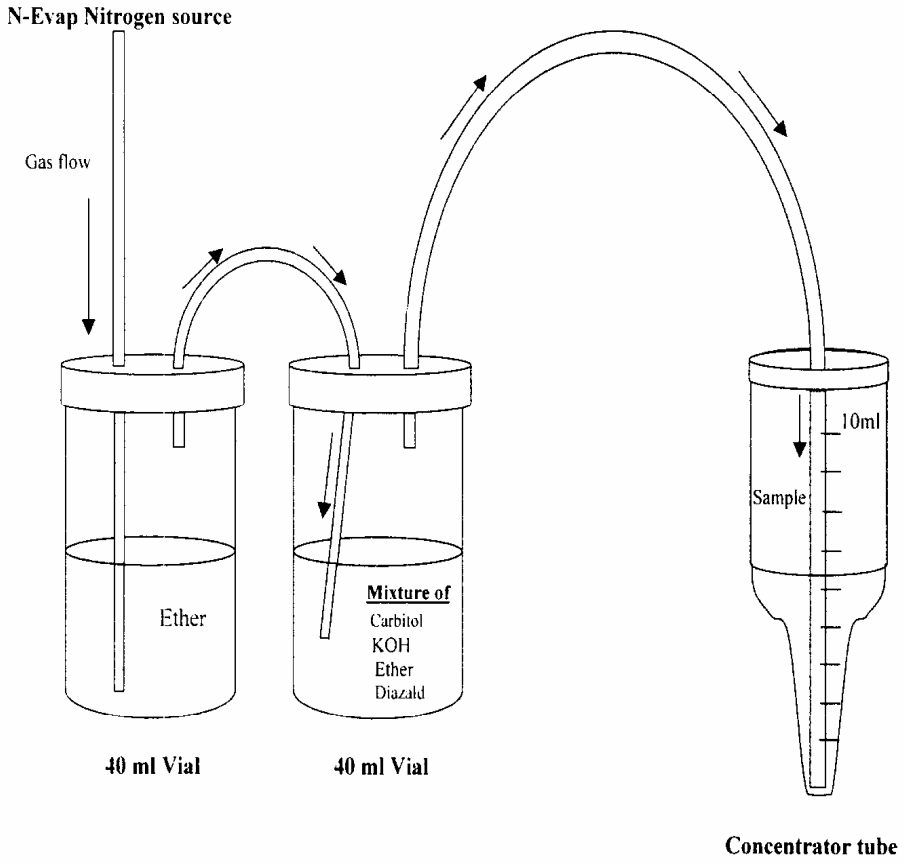
DOCUMENT REVISION HISTORY

7/7/06: Format updated. Augmented RESPONSIBILITIES. Updated DEVIATIONS to include reference to Soxhlet performance report. Added DOCUMENT REVISION HISTORY and Form.

11/20/07: Removed acceptance criteria from Section 9 and referenced determinative SOP 434 instead.

FIGURE 1

DIAZOMETHANE GENERATION APPARATUS



Paragon Analytics

HERBICIDE EXTRACTION / CLEANUP BENCHSHEET

WO #s _____ **Matrix** AQ Solid Other _____ **Batch ID** _____ **Sur Code** _____ **M Spike Code** _____

Extraction: Code 8151A E615 E515 **Method** (3540C)SOX (3510C)SEP (3580A)WDilute **SOP** ___ **Rev** ___ **Initials** _____ **Was glass wool & Na_2SO_4 acidified?** Y N

Balance ID ____ **Cleanup Code** (3640A)GPC (see other forms) (3620B)Florisil **SOP** 641(GPC) 648(Florisil) **Rev** ___ **Florisil Lot No.** _____ **Initials** _____

Extraction Start Date _____ **Time** _____ **Extraction End Date** _____ **Time** _____ **Reviewed by / date** _____

$MeCl_s$ _____ **Hexane** _____ **NaCl** _____ **Acidified Na_2SO_4** _____ **H_2SO_4** _____ **Form 604r9.frm (12/7/2002)**

NaOH _____ **KOH** _____ **Diazald** _____ **Carbitol** _____ **Diethyl Ether** _____ **HCl** _____

SAMPLE							EXTRACT							
Sample No.	Amount (g / mL)	pH (≥12)	pH (≤2)	Surrogate (mL)	Matrix Spike (mL)	Initials Spike Witness	Date KD (Initial)	Date Hydrolysis (SO only)	Date KD (Final)	Date Partitioning (SO only)	Date Hexane Exchange	Final Volume (mL)	Date Vialed	Type of Cleanup

Comments:

Timer Operation

1) **CLLE only** - check that the plugs connected to the power strip correspond to the heating mantles you wish to use.

   Soxhlet only - unplug the Variac(s) power cord(s) from the 3-outlet heavy-duty extension cord. Variac cords are marked with either the Variac # or "aqua" colored tape, or both. **MAKE SURE** the Variac(s) you are using correspond to the six-position set-up you want to run. Then, plug the Variac cord(s) into either (or both) of the 2 outlets on the digital timer. Each Variac is labeled as to which digital timer it should be plugged into. Check that the timer # on the Variac matches the timer # you are plugging it into. After plugging the Variac(s) into the timer, turn the Variac(s) on, using either the toggle or circular switch, depending on the model. Flip the appropriate toggle switches on the soxhlet heating mantle bank, to activate the position(s) you want to run.

2) Check that the **day-of-week**, **time**, and **AM/PM** on the timer are correct (press "CLOCK" on the timer). If any of the date/time display is incorrect, reset the clock as described in **Appendix A**.

3) Program the timer as follows:

   a: Press "PROG" button on the timer once. The left-hand side of the timer display should look like this:

```
   MO TU WE TH FR SA SUN
|ON
|          __ __ : __ __
```

   b: Press "DAY" button until the day of the week you want the timer to start (i.e., begin extraction) is indicated at the top of the display screen.

   c: Press "HOUR" button until the hour you want the timer to start is displayed. **MAKE SURE** that the hour selected is correct, with respect to AM/ PM, as timer does not display or run on "military" time.

   d: Press "MIN" button until the minute you want the timer to start is displayed. Holding down the "MIN" button will cause it to scroll.

   e: Once date/time to turn **ON** is established, press "PROG" again. The left-hand side of the timer display should now look like this:

```
   MO TU WE TH FR SA SUN
|OFF
|          __ __ : __ __
```

   f: **Repeat steps b-d** to program what time you want the timer stop (i.e., stop extraction). When complete, press "CLOCK" to return to the current date/time display.

   g: Check/confirm program **ON** date and time, by pressing "PROG" once. Check/ confirm program **OFF** date and time, by pressing "PROG" again. Press "CLOCK" to go back to the current date and time display.

   h: Lastly, press the "MODE" button until "**AUTO**" is displayed to the left on the date/ time display. **MAKE ABSOLUTELY SURE** that timer is set to "AUTO" mode, and not "OFF," "ON," or "RDM;" as these other modes will either cause timer to not turn on, turn on immediately, or turn on at a semi-random time.

4) The timer is now ready to run your program!

Important Notes:

- While the timer(s) will accept up to 7 different event programs, it is **not advised** that you use this feature. Rather, reprogram the timer under Event 1 (indicated by the little number "1" in the Program display) each time you want to program start / stop dates and times.
- When you are done using timer (i.e., your extraction is complete and you are finished using the timer to run samples) **it is important that you unplug the Variac cord** from the timer and plug it back into the 3-outlet heavy-duty extension cord; **as well as turning off the Variac power switch**. If you leave the Variac(s) plugged into the timer, the set program will run again in 1 week (if timer is on AUTO mode), regardless of whether CLLEs/Soxhlets are actually set up. This is a potential fire hazard, as the heating mantles get hot enough to scorch paper. Also, **press "MODE" on timer until "OFF" is displayed to the left of the date/ time display**. This turns the set program off, preventing the timer from re-running the program in seven days.
- The timer's clock runs on one "AA" battery. The battery in each timer should be replaced approximately every June and December to ensure performance of the timers. To replace, use a small Phillips-head screwdriver to remove the battery cover on the back of the timer, and install a fresh battery in the correct orientation.

APPENDIX A

SETTING CLOCK

1) Press "CLOCK" to view the currently programmed date and time. If it is not correct… while holding down "CLOCK":
   a: Press "DAY" until correct day-of-week is displayed.
   b: Press "HOUR" until correct hour is displayed, **remember to set correct hour by AM/ PM.**
   c: Press "MIN" until correct minute is displayed.
2) Release "CLOCK" button. The display should now give the correct date and time. As an example, if it is three-o-clock in the afternoon on Wednesday, the display should read:

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 665 REVISION 7

TITLE: **EXTRACTION OF EXPLOSIVES FROM WATER AND SOIL -- SW-846 METHODS 8330 AND 8332**

FORMS: **635** **(use current iteration)**

APPROVAL:

TECHNICAL MANAGER _____ DATE 11-14-07

QUALITY ASSURANCE MANAGER _____ DATE 11/2/07

LABORATORY MANAGER _____ DATE 11-14-07

HISTORY: NEW, PCN #464, 4/24/95; Rev1, 2/09/96; Rev2, 9/26/01; Rev3, 3/01/02; Rev4, 3/14/03; Rev5, 4/28/04; Rev6, 2/27/06; Rev7, 11/12/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references (SW-846 Methods 8330 and 8332) are intended for the extraction of explosive residues from water (surface or ground) and soil/sediment samples for subsequent analysis by HPLC using an ultraviolet (UV) detector.

2. SUMMARY

Aqueous samples are extracted by a salting-out procedure with acetonitrile (ACN) and sodium chloride (NaCl). The small volume of ACN that remains undissolved above the salty water is drawn off and transferred to a concentrator tube. The ACN is then concentrated to a final volume, typically 1.5mL, by nitrogen blowdown (SOP 637). As described in SOP 404 (SW-846 Method 8330) and SOP 408 (SW-846 Method 8332), extracts from aqueous samples are mixed with acidified water prior to analysis. Aqueous samples known to contain more than 10µg/L of explosives may be better analyzed by direct aqueous injection. Soil and sediment samples are extracted using ACN in a cooled ultrasonic bath. A portion of the extract is mixed with an aqueous calcium chloride ($CaCl_2$) solution to aid flocculation, then centrifuged, and finally filtered.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the logbook pages, analytical review sheets or case narrative indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of measures taken to correct any errors that were found in the data during review.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated chromatographic baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences.

4.2 Tetryl can decompose rapidly in acetonitrile/water solutions. The decomposition of tetryl proceeds more rapidly at temperatures above room temperature; therefore, samples and extracts should not be exposed to temperatures above room temperature. Acetonitrile extracts from aqueous samples are mixed with acidified water prior to analysis to minimize the base-catalyzed degradation of tetryl during analysis. The appropriate analytical SOPs are referenced previously.

5. APPARATUS AND MATERIALS

5.1 Volumetric flasks, appropriate sizes

Water samples are extracted in 500mL volumetric flasks because of the ease of removing the extract from the thin neck. These flasks are not used for volumetric purposes; therefore, they may be placed in the kiln for cleaning and they need not be Class A glassware. **The flasks must be permanently marked or segregated as unsuitable for volumetric use if they have been kilned or if the extraction vessels are not Class A glassware.**

5.2 magnetic laboratory stirrer, and PTFE stir bars

5.3 scintillation vials, glass, with Teflon-lined caps, 20mL

5.4 vials, glass, with screw caps, 2mL and 4mL sizes

5.5 ultrasonic bath with chiller coil and adequate circulating cooling water

5.6 concentrator tubes, 10mL

5.7 nitrogen evaporation apparatus (NEVAP)

5.8 balance, capable of accuracy to ±0.01g

5.9 graduated cylinders- appropriate sizes

5.10 syringes, 5mL, glass or plastic disposable

5.11 pipettes, 5mL

5.12 Pasteur pipettes

5.13 centrifuge

5.14 desiccating cabinet

5.15 pH test paper, acidic

6. REAGENTS – Only reagent grade or better chemicals shall be used.

6.1 acetonitrile (CH_3CN), HPLC grade

6.2 sulfuric acid (H_2SO_4), concentrated

6.3 calcium chloride ($CaCl_2$): prepare an aqueous solution of 5g/L and adjust pH to approximately 3 or slightly less with a few drops of concentrated sulfuric acid.

6.4 sodium chloride (NaCl): the NaCl may need to be pre-rinsed with acetonitrile (CH_3CN), dried and purified at approximately 450°C (kilned) for four (4) hours, if necessary.

6.5 organic-free reagent water - HPLC grade water may be purchased for this process or deionized organic free water produced in the lab may be used if proven to be suitable.

6.6 Ottawa sand

6.7 indicating Drierite®

6.8 standard solutions - these are purchased from a vendor and diluted for surrogate and matrix spiking solutions by the analytical group.

CAUTION: Do not let explosive standards evaporate to dryness, as they may present an explosion hazard.

6.8.1 Water matrix spike -- generally contains all target analytes or those required by the client. The concentration of each analyte is typically 1.5µg/mL.

6.8.2 Soil matrix spike -- typically contains all target analytes or those required by the client. The concentration of each analyte in the soil matrix spike is typically 10µg/mL.

6.8.3 Water Surrogate -- 1,4-dinitrobenzene (0.75µg/mL) is currently utilized, but other surrogates and concentrations may be used.

6.8.4 Soil Surrogate -- 1,4-dinitrobenzene (5.0µg/mL) is currently utilized, but other surrogates and concentrations may be used.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 Water samples should be collected in amber glass containers with PTFE-lined caps. Soil samples should be collected in glass containers, preferably amber glass.

7.3 Samples and sample extracts must be stored in the dark at 4±2ºC (refrigerated). From the time of collection, sample holding times are 7 days for waters and 14 days for soils.

8. PROCEDURE

8.1 PREPARATION OF WATER SAMPLES (LOW-LEVEL EXTRACTION)

8.1.1 Typically only a portion of the sample is used for this extraction, thus care must be taken to mix the sample thoroughly before the aliquot is taken. Aqueous samples with sediment present are generally not mixed prior to decanting because the particles may cause emulsions during the extraction process.

8.1.2 Add 115g of sodium chloride and a solvent-rinsed stir bar to each of the volumetric flasks. Decant 350mL of sample into the 500mL flask. Volumetric flasks provide a thin neck that aids in removal of the acetonitrile layer after mixing; these flasks are not used for quantitative measurement of volumes. Stir to dissolve salt.

8.1.3 Spike 1.0mL of water surrogate into all field and quality control (QC) samples and 1.0mL of water matrix spike solution into the MS/MSD and LCS/(LCSD) samples.

8.1.4 Stir on the magnetic laboratory stirrer, maintaining a strong vortex at all times. After the salt is completely dissolved, add 80mL of

acetonitrile and continue stirring. Reagent water may be added at any time to bring the acetonitrile layer into the neck of the flask.

8.1.5 Continue to stir for at least 10 minutes. Tap the side of the flask frequently to prevent the acetonitrile from sticking to the sides of the flask.

8.1.6 Stop the stirring and allow the phases to separate for five minutes minimum. The acetonitrile layer should be 3-5mL. If the acetonitrile layer is less than 2mL, then add a few mL of acetonitrile and stir again. If the acetonitrile layer is greater than 5mL, then add a few mL of water and repeat the stirring.

8.1.7 After the phases have separated, remove the acetonitrile extract with a minimal amount of water (typically no more than 50-100µL) using a Pasteur pipette and place in a 10mL concentrator tube or similar size glass container.

8.1.8 Add 2-3mL of acetonitrile to the flask and repeat Steps 8.1.5 through 8.1.7 **twice more**, placing the acetonitrile into the appropriate collection vial.

8.1.9 If there is water present in the combined extracts (visible as a bottom layer), use a Pasteur pipette or a syringe to carefully remove as much of the water from the concentrator tube as possible. The acetonitrile and water may separate better if drawn up into the pipette and then used to rinse the tube. Several repetitions of this step usually turn the acetonitrile milky and leave the water clear.

8.1.10 Concentrate the acetonitrile to ~1.5mL on the NEVAP per SOP 637 with the following exception - the water bath should be turned **off** and extracts should not come in contact with a heat source.

8.1.11 Adjust the final volume to 1.5mL and transfer the acetonitrile extract to a 2mL screw-cap vial. Complete the internal chain-of-custody process (SOP 318), and place the extracts in the HPLC extract refrigeration, unit for storage.

8.1.12 One method blank (MB) and laboratory control sample (LCS), consisting of aliquots of organic-free reagent water, are to be prepared per each batch of samples. One matrix spike/matrix spike duplicate (MS/MSD) is also to be prepared per each batch of samples, as sample volume permits. In some cases, a laboratory control sample duplicate (LCSD) may also be prepared, particularly if MS/MSD samples cannot be prepared.

8.1.13 Preparation of water samples for high level analysis by direct aqueous injection consists of filtering the water sample, and is performed by the HPLC analyst following the appropriate analytical SOP.

8.2 PREPARATION OF SOIL SAMPLES

8.2.1 Decant and discard any water layer on a sediment sample. Discard any foreign objects (e.g., sticks, leaves, rocks) or any portion of the sample that appears to not be representative of the sample. Mix sample thoroughly to ensure that a representative sample is obtained, especially composited samples. *Consult the Department Manager for difficult, unusual matrices.*

8.2.2 Dry an aliquot of the solid sample in air at room temperature or colder until completely dry, insuring that the samples are not exposed to direct sunlight. To speed up the drying process, place a homogenized aliquot of the sample into an appropriately labeled aluminum weighing dish. The dish and sample are then placed in the extraction hood or desiccating cabinet until dry.

Under no circumstances may soil samples for explosives analysis be placed in the oven to hasten the drying process.

8.2.3 Because soil samples are completely dried before extraction is performed, there is no need to determine percent moisture for samples undergoing this procedure. Moisture determinations of samples suspected to contain high concentrations of explosives should be discouraged to prevent accidentally placing samples containing explosives in the oven.

8.2.4 Weigh approximately 2g of air-dried soil into a 20mL vial with Teflon-lined cap. Record the weight of the sample to the nearest 0.01g in the logbook (Form 635). Smaller aliquots of sample may be used for difficult matrices such as tissues or if high concentrations of explosives are expected.

8.2.5 Select a sample from which to prepare the MS/MSD. A 6g aliquot of this sample should be homogenized prior to sub-sampling the three aliquots (i.e., unspiked native, MS, MSD).

8.2.6 Prepare a method blank and an LCS using aliquots of Ottawa sand. An LCSD may also be prepared.

8.2.7 Spike 1.0mL of soil surrogate into all client samples and quality control (QC) samples.

8.2.8 Spike 1.0mL of soil matrix spike solution into the MS, MSD, LCS, and LCSD.

8.2.9 Add 9.0mL of acetonitrile and cap each vial -- **with the following exceptions** -- to the MS, MSD, LCS, and LCSD, add 8.0mL of acetonitrile. Cap. The volume of solvent in the extraction vessel should be 10mL after spiking and solvent addition takes place.

8.2.10 Place the vials in the sonic bath. As the sonic bath operates, the temperature of the water will rise and may cause degradation of the explosive analytes. To prevent degradation, be sure the copper cooling coil is in the sonic bath and the cold water is running continuously. Extract for 18±2 hours, ensuring that the water level in the bath is at or above the solvent level in the 20mL vials. *The 18±2 hour extraction time may cause degradation of nitroglycerin as documented in Method SW8332. A shorter sonication time (2hr) may be used when analysis of this target compound alone is requested.*

8.2.11 **Note: To minimize the possibility of introducing non-target (chromatographically interfering) contaminants to the sample extracts, syringes should be pre-rinsed with acetonitrile prior to being used to aliquot extracts.** Remove a 5.0mL aliquot of prepared extract, and combine it with a 5.0mL volume of the acidified 5g/L $CaCl_2$ solution in a glass scintillation vial. Record the $CaCl_2$ volume on the benchsheet. Let the solution sit for 10-15 minutes so that flocculation can occur. Centrifuge the extract/$CaCl_2$ solution at a setting of no higher than 1500rpm for 3-10 minutes.

8.2.12 After centrifugation, filter through a 0.45µm PTFE filter into a 4mL screw cap glass vial and record the final volume as 20mL.

8.2.13 Complete the internal chain-of-custody process (SOP 318), and place the extracts in the HPLC extract refrigeration, unit for storage.

9. QUALITY CONTROL

The laboratory must extract a method blank(MB), a laboratory control sample (LCS), a matrix spike and a matrix spike duplicate (MS/MSD) for each analytical batch (up to a maximum of 20 samples/batch). Laboratory control duplicate samples may be required and may be used instead of MS/MSD if insufficient sample volume is available for an MS/MSD pair or at the request of the client. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of matrix spike samples.

10. DEVIATIONS FROM THE METHOD

This procedure conforms to the referenced method (SW-846 8330) with the following exception -- Aqueous extracts are not back-extracted as suggested in the method. This back-extraction is performed to minimize potential interferences with HMX determination on the C18 column. The interference presumably is from nitrate ions, which absorb strongly at 254nm. Paragon has not observed this interference, and thus back-extraction is not performed.

11. SAFETY, HAZARDS, AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 **This procedure is designed for the extraction of environmental levels of explosives from soils and waters. The procedure is not intended for operations involving pure product explosives or non-environmental levels of explosives.**

11.1.2 **Samples containing explosive material may under no circumstances be heated in any fashion (e.g., boiling a solution or drying a sample in an oven). Also, all operations in the sonic bath must be performed with cooling coil in place and operational, and the cold water must be turned on.**

11.1.3 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.4 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.5 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). **Acetonitrile (TLV< 50ppm) must be used in a properly ventilated fume hood.** Flammable solvents shall be kept away from ignition sources.

11.1.6 Finely divided soils should be handled in fume hood.

11.1.7 Any non original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name; NFPA Health, Flammability, and Reactivity ratings; and date.

11.2 WASTE DISPOSAL

11.2.1 The non-radioactive solid sample residues shall be disposed of in the Contaminated Soils and Solids Waste. Radioactive sample residues are placed in Radioactive Solids Waste stream.

11.2.2 Acetonitrile solvent wastes are disposed of in the Non-Halogenated Solvent Waste stream.

11.2.3 Extracted non-radioactive waters are disposed of in the Aqueous Laboratory Waste. Radioactive aqueous sample residues are placed in Radioactive Aqueous Waste stream.

11.2.4 Extract vials and their contents are disposed of in an appropriate waste stream by the analytical group they were delivered to.

11.2.5 All empty solvent or reagent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

11.2.6 Radioactive sample disposal - the extracted solid sample residues shall be disposed of in the Radioactive Soils and Solids container. Mixed waste solids shall be disposed of in the appropriate mixed waste container.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Method 8330, Revision 0, December 1996.

12.2 US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Method 8332, Revision 0, December 1996.

DOCUMENT REVISION HISTORY

11/12/07: General clarification and wordsmithing throughout. Cleaned up Section 1, updated LIMS program specification language Section 3.3. Added “pre-rinsing” of syringes w/ACN Section 8. Added DOCUMENT REVISION HISTORY and Form.

Paragon Analytics

EXPLOSIVES (8330) / NITROGLYCERIN (NG) and/or PETN (8332) -- EXTRACTION WORKSHEET Form 635r7.doc (4/22/04)

Batch # _____ **WO #s** _____ **Initials** _____ **Matrix:** AQ SO Other _____ **Sur Code** _____ **MSpike Code** _____ **Balance ID** ___

SOP 665 Rev__ **Extr Code:** 8330 (AQ) 8330 (SO-SONC) 8332 (AQ) 8332 (SO-SONC) **Extraction: Start Date/Time** _____ **End Date/Time** _____

Reagent Lots: MeCl, _____ Acetonitrile _____ NaCl _____ $CaCl_2$ _____ HPLC Water _____ **Reviewed by / date** _____

SAMPLE					EXTRACT			
Sample Number	Amount (g / mL)	Amount Surrogate (mL)	Matrix Spike (mL)	Initials Surrogate and Matrix Spike Witness	Volume $CaCl_2$ (mL)	Final Volume (mL)	**Date Vialed**	**Comments**

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Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 666 REVISION 6

TITLE: WASTE EXTRACTION TEST (Cal-WET) FOR THE ANALYSIS OF METALS AND SEMIVOLATILE ORGANIC COMPOUNDS

FORMS: 623, 825, 345 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-12-07

QUALITY ASSURANCE MANAGER _____ DATE 11/12/07

LABORATORY MANAGER _____ DATE 11-12-07

HISTORY: Rev0; PCN # 501, 6/12/95; Rev1, 11/27/96; Rev2, 10/27/99; Rev3, 4/23/02; Rev4, 2/13/04; Rev5, 2/27/06; Rev6, 11/12/07.

1. SCOPE AND APPLICATION

The Waste Extraction Test (WET) described in this Standard Operating Procedure (SOP) is used to determine the amount of extractable metals and semivolatile substances in a waste or other material. The procedure follows the guidelines found in Title 22, Division 4.5, Chapter 11, Article 5, Section 66261.126, Appendix II of the California Code of Regulations.

2. SUMMARY

The extraction procedures outlined in this SOP are the initial steps in determining the metals, semivolatile organics, and other inorganics that can be leached from a sample. Analysis of the leachate is performed after digestions and extractions of the leachate are completed in accordance with additional Paragon SOPs. The leaching solution for semivolatile organics and most metals and inorganics such as fluoride, is a citrate buffer (pH=5). Deionized water is the leaching solution for hexavalent chromium determination.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 This procedure is performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful analysis of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the

laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the bench sheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the Technician/Analyst who performed the work and documentation of measures taken to correct any errors that were found in the data.

3.5 All personnel who use this procedure have a responsibility to note any anomalies or out-of-control events associated with processing the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks (see Quality Control Section).

5. APPARATUS AND MATERIALS

5.1 rotary tumbler with 30±2rpm capability, Associated Design and Manufacturing Model 3740 or equivalent

5.2 pH meter, accurate to ±0.05 pH units @ 25°C
Meter must be calibrated prior to use (see Form 825)

5.3 magnetic stir plate, and PTFE stir bars

5.4 polyethylene (metals) and/or glass (semivolatile organics) containers with lids, wide mouth, 1000-2500 mL. **Rinse containers with 1:1 nitric acid followed by several rinses with deionized water before use.**

5.5 polyethylene bottles, 4oz

5.6 glass bottles, amber, 1L

5.7 0.45µm filters

5.8 pressure filtration device, Associated Design and Manufacturing Model 3750-LHWF or equivalent. A.K.A. "lunar lander"

5.9 centrifuge tubes, glass and polyethylene

6. REAGENTS - Only reagent grade or better chemicals shall be used.

6.1 interferent-free laboratory deionized (DI) water

6.2 citric acid monohydrate

6.3 sodium citrate dihydrate

6.4 sodium hydroxide (NaOH), 4N

6.5 **sodium citrate buffer, 0.2M , pH = 5.0±0.1**: For each 500mL needed, add 29.4g sodium citrate dihydrate to DI water, mix thoroughly and bring to 500mL final volume. Adjust fluid pH by adding 4N NaOH drop-wise until the pH reaches 5.0±0.1. Alternatively, for each 500mL needed, add 21g citric acid monohydrate to water, mix thoroughly and bring to 500mL final volume. Add 4N NaOH dropwise until the pH reached stabilizes between 5.0±0.1.

6.6 nitric acid (HNO_3), concentrated

6.7 **nitric acid solution, 1:1 (v:v):** Prepare by slowly adding 500mL of concentrated acid to 500mL of reagent water in a Pyrex™ beaker or flask while stirring. Do not add water to concentrated acid.

6.8 N_2 (99.999% purity)

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Soils to be leached for semivolatile organic compounds should be leached within 14 days of sampling. Soils to be leached for metals should be leached within 6 months of sampling.

7.2 Chemical preservation is not generally utilized for solids samples. Refrigeration to 4±2°C may be needed for some samples submitted for this procedure. Room temperature storage may be adequate for samples to be leached and analyzed for metals only.

7.3 Portions of WET leachates for subsequent organic or fluoride analysis are not chemically preserved. Extraction or analysis must start within 24hrs of collection unless the leachate is frozen as a means of preservation. Portions of WET leachates for metals analysis are chemically preserved with nitric acid as described in Section 8.10.

8. SAMPLE COLLECTION, PRESERVATION AND HANDLING

8.1 Categorize samples to be leached as follows:

Type i = a solid

Type ii = a liquid-solid mixture with more than (≥) 0.5% filterable solids

Type iii = a non-filterable sludge, slurry, or oily, tarry resinous material

8.2 Inspect samples to ensure they will pass through a No.10 (2mm) sieve, keeping in mind that rocks, glass, etc, that are extraneous, are irrelevant as hazardous

constituents to the waste, and shall be removed and discarded. Samples that will not pass through a No.10 standard sieve will need to be milled or crushed. Due to safety concerns, such as dust control, this milling is not generally done at Paragon (see 11.1.7).

8.3 The filterable liquid portion of a ***type ii*** sample is considered part of the leachate. The volume of liquids obtained after pressure filtration using a 0.45µm filter shall be recorded on the benchsheet. The filterable liquids shall be retained. The solids retained on the 0.45µm filter are leached in the same manner as ***type i*** and ***iii.*** After leaching, the retained filtered liquids are combined with the filtered leachate to create the final leachate.

8.4 Label each 1000mL wide mouth container with a sample number. **Rinse containers before use with 1:1 nitric acid followed by several rinses with deionized water.** Use polyethylene containers for metals only extractions; use glass containers when both metals and semivolatiles are to be extracted and analyzed (unless other containers are approved by the client - consult the applicable LIMS program specification). Consult with Supervisor for sample's scheduled tests and final extract volumes needed.

8.5 Prepare the leaching fluid (0.2M sodium citrate for semivolatile organics and metals, deionized water for hexavalent chromium). The ratio of leaching fluid to sample should be maintained at 10 mL/g. If 50g of sample are not available for leaching, adjust leaching fluid volume to maintain this ratio. **Flush extraction fluid with N_2 gas for 15 minutes to remove O_2 immediately prior to adding extraction fluid to samples.**

8.6 Add the appropriate volume of leaching fluid (as discussed above) to the weighed samples. Rapidly seal the container and tumble per Step 8.7 below.

8.7 Place samples on a rotating tumbler for 48±2 hours. **Record the time tumbling was initiated on the benchsheet. Record the room temperature per Paragon SOP 663.** The room temperature must be maintained between 20° and 40°C during the tumbling. Tumbler revolutions per minute are not specified in the Cal-Wet procedure, but Paragon follows the guidelines of 30±2 rpm from SW-846 Method 1311. Actual rpms are measured and recorded on the benchsheet per SOP 663.

8.8 Reactions in the tumbling vessel may cause a pressure buildup in the vessel. The extraction bottles may need to be vented frequently when tumbling is initiated. Vent every 15 minutes or as necessary, until pressure buildup stops.

8.9 Stop tumbler and remove samples from tumbler after 48±2 hours, and allow solids to settle. Record time tumbling was halted on benchsheet. Record the

minimum and the maximum temperature during the 48±2hr tumbling on the benchsheet.

8.10 The leachate must be filtered before analysis for metals or organics (0.45µm). For many samples, it may be necessary or advisable to centrifuge or pre-filter using a larger pore size filter, before final filtration at 0.45µm. Acidify a portion of the filtrate with HNO3 acid (5% v/v) if metals analysis is required. For example, 50mL of filtered leachate is acidified with 2.5mL of concentrated HNO_3.

8.11 Store the WET leachates for metals analysis in labeled 4oz plastic bottles. The WET leachates for organics or fluoride analysis need to be preserved by freezing (**Caution**: glass bottles are used to store leachates for semivolatile organic analysis; polyethylene bottles are used to store leachates for fluoride analysis), or extracted in preparation for analysis within 24 hours of filtration.

9. QUALITY CONTROL

One method blank (MB) consisting of an aliquot of laboratory DI water will be processed with each batch of samples, containing up to twenty (20) samples per batch.

10. DEVIATIONS FROM THE METHOD

This procedure meets the requirements of the California Title 22 WET procedure with the exception of particle size reduction. Because of safety concerns, particle size reduction is not performed at Paragon (see Section 11.1.7).

11. SAFETY, HAZARDS AND WASTE

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs before prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals, or within a laboratory area.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.1.5 Any venting operations that are carried out on the sample container during the initial phase of the tumbling must be performed in a fume hood.

11.1.6 All compressed gas cylinders must be secured at all times. The cylinder cap must be installed immediately after removing the regulator and before removing the tie down strap or chain from the cylinder. The cylinder shall be secured to a gas cart for transport.

11.1.7 Safety concerns such as dust control may preclude the grinding of samples for particle size reduction. These safety concerns must *always* be addressed before attempting to grind any sample. Generally, due to health and safety concerns, grinding to reduce particle size is not practiced in the extractions area. Samples requiring particle size reduction have been sent to an appropriate facility before an extraction was performed.

11.2 WASTE DISPOSAL

11.2.1 Corrosive only wastes such as the citric acid buffer used in this procedure are disposed of by discharging into the Paragon wastewater treatment facility. These materials that are corrosive only (e.g., no hazardous components or characteristics other than corrosivity) may be neutralized in the water treatment facility.

11.2.2 The aqueous samples or supernatant of solid samples shall be disposed of in the Aqueous Laboratory Waste stream.

11.2.3 The non-radioactive soil/solid samples and sediments of solid samples shall be disposed of in the Contaminated Soils and Solids .

11.2.4 Radioactive sample disposal - the extracted solid sample residues residue shall be disposed of in the Radioactive Soils and Solids container. Mixed waste solids shall be disposed of in the appropriate mixed waste container.

11.2.5 All empty solvent bottles or sample containers must be disposed of appropriately. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

California Code of Regulations, Title 22, Division 4.5, Chapter 11, Article 5, 66261.126 Management of Special Wastes, Appendix II Waste Extraction Test Procedures.

DOCUMENT REVISION HISTORY

11/12/07: Minor clarifications throughout. Expanded APPARATUS AND MATERIALS Section. ADDED DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

Corning Model 320 pH Meter Calibration & Maintenance Log

Result Units = pH units

Date	Time	Analyst	4.01 Solution Lot No./ Result	10.01 Solution Lot No./ Result	% Slope	7.00 Solution Lot No./ Result	Check Solution Result
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Comments/Maintenance Notes:

Form 825r0.xls (4/18/2003)

Paragon Analytics

PERCENT SOLIDS (% SOLIDS) DETERMINATION
(For Samples on Following Logbook Page)

Logbook No./Page _____ A

Units = grams	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
Sample No.	Weight of Beaker, Spatula & Sample	Weight of Beaker, Spatula & Residue	Total Sample Weight (a - b)	**Weight of Filter**	Weight of Collection Flask	Weight of Flask & Filtrate	Filtrate Weight (f - e)	Total Solids Weight (c - g)	% Solids (Wet) (h / c) * 100	Weight of Filter & Dried Solids	Weight of Dried Solids (j - d)	% Solids (Dry) (k / h) * 100

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Logbook No./Page ________________ B

LEACHING PROCEDURE WORKSHEET

Work Order # ___________________________

Batch ID # ______________________________

Method **SOP** **Rev**

(Start) Date ________ **Time** ______

(Start) RPM _______ **Temp.** _____ **°C** *(from min/max* SN 21251556*)*

(Start) Analyst _____ RESET MIN/MAX AFTER READING OBTAINED

(Stop) Date _______ **Time** ______ **RPM** ______

(Stop) Temp. ____ **°C** **Tumble Min/Max** ___/___ **°C**

RESET AFTER EACH READING **(Stop) Analyst** _____

Extraction Fluid ID ______________________ **Filtration Date/Time/** ____________________ **Initials** ________

Reviewed By / Date __________________________

Preliminary Solids[a]	Particle Reduction[b]	Sample Number	Initial pH	Fluid Determination				Sample Weight (g)	Fluid (mL)	Final pH	Leachate No.	Comments
				HCl (mL)	Final pH	Fluid #	Fluid pH					
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
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I S M	Y N											
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I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											

[a] I = insignificant (< 0.5%); S = 100%; M = Multiphasic (see attached % Solids Determination form).

[b] Y = Yes - reduction required / performed; N = no partical size reduction required.

INTERNAL COC TRANSFER: Relinquished by _______ (initials) to _______________________ (RU# & location) _____________________ (Date & Time) **Form 623r10.doc (1/17/2006)**

Paragon Analytics

TEMPERATURE LOGBOOK

ORGANIC EXTRACTIONS - TCLP ROOM

Acceptable Range 23 ± 2 °C

A current temperature reading must be recorded at the onset of TCLP tumbling, and the min/max memory must be reset. DO NOT initiate tumbling if temperature is not within acceptable limits. The current temperature and min/max information must be recorded at the completion of tumbling. Both the Department and QA Managers must be notified in a timely manner if an excursion occurs.

		Thermometer: 41406316 (min/max)				
DATE	TIME	Current Temp. (°C)	Temp. Min (°C) Date/Time Occurred	Temp. Max (°C) Date/Time Occurred	INITIALS	COMMENTS

Reviewed by / date _____ **Form 345r1.doc (7/10/06)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 668 REVISION 4

TITLE: **SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP) FOR THE ANALYSIS OF METALS AND SEMIVOLATILE ORGANICS -- METHOD SW1312**

FORMS: **623, 646, 825, 345 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3-4-08

QUALITY ASSURANCE MANAGER _____ DATE 3/4/08

LABORATORY MANAGER _____ DATE 3-4-08

HISTORY: Rev0, 10/28/99; Rev1, 8/23/02; Rev2, 3/6/04; Rev3, 3/9/06; Rev4, 3/4/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW-846 Method 1312 -- are designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. Application of these procedures to matrices other than those specified will be handled individually to simulate the leaching procedure as best as possible.

Procedures for ZHE SPLP extractions are described in SOP 669.

2. SUMMARY

For liquid wastes (i.e., <0.5% solids), the sample is filtered through a 0.7µm glass fiber filter, and the filtrate is defined as the SPLP leachate.

For samples containing ≥0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solid phase is reduced. The solids are then leached with an amount of extraction fluid (the extraction fluid employed is a function of the region of the country where the sample site is located, and of the type of matrix and analyses required), equal to twenty (20) times the weight of the solid phase. Following the SPLP extraction, the leachate is separated from the solids by filtration through a 0.7µm filter.

If a liquid phase was present in the sample and set aside as described above, then this liquid is combined with the leachate from the solid phase, if the two are miscible, before metals or semivolatile organic preparation for analysis. If the liquid and the leachate are not miscible, the liquid and the leachate are analyzed separately, and the results are mathematically combined to yield a volume-weighted average concentration.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the bench sheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of measures taken to correct the errors that were found.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by processing and analyzing method blanks.

5. APPARATUS AND MATERIALS

Extraction vessels and filtration devices shall be made of inert materials that will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) are to be used only when evaluating the mobility of metals.

5.1 rotary tumbler with 30±2rpm capability, Associated Design and Manufacturing Model 3740 or equivalent

5.2 pH meter, accurate to ±0.05 pH units @ 25°C
Meter must be calibrated prior to use (see Form 825).

5.3 pressure filtration device, Associated Design and Manufacturing Model 3750-LHWF or equivalent. A.K.A. "lunar lander".

5.4 fiber filters, borosilicate glass, Gelman™ #66256, 0.7µm nominal or equivalent

NOTE: The glass fiber shall contain no binder materials and shall have an effective particle size of 0.6 to 0.8µm. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1.0M HNO_3, followed by three consecutive rinses with deionized water (a minimum of 1000mL per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

5.5 bottle extraction vessel, 2L or slightly larger. Borosilicate glass, 2200mL Kontes™ #332100-021 or equivalent. If PVC coated for safety, do not place in kiln. HDPE plastic, 2000mL Eagle Picher #EP150-02WM or equivalent

Paragon typically uses disposable HPDE extraction bottles for metals and semivolatile organics. The use of HDPE extraction bottles has been demonstrated to generate leachates that are free of contaminants for the analyses being conducted.

5.6 balance, accurate to within ±0.01g

5.7 beakers or Erlenmeyer flasks, glass 500mL (or 4.5oz plastic cups)

5.8 watch glass, appropriate diameter to cover beaker or Erlenmeyer flask (or cap for plastic cup)

5.9 carboys for containerizing extraction fluids

5.10 stirring hot plate, with magnetic stir bar

5.11 graduated cylinders, sized as appropriate

5.12 centrifuge

5.13 drying oven, capable of maintaining 100±20°C

6. REAGENTS - Only reagent grade or better chemicals shall be used.

6.1 water, of sufficient purity that target analytes or interferences are not observed at levels of interest for the analytes of interest. For semivolatile organics and metals analysis, laboratory deionized (DI) ASTM Type II water meets the definition of reagent water. Prior to being used for this procedure, this water is filtered through a Millipore Synergy 185® filtration system for further purification.

6.2 sulfuric acid (H_2SO_4), used in combination with nitric acid to adjust pH of leaching solution.

6.3 nitric acid (HNO_3), used in combination with sulfuric acid to adjust pH of leaching solution, as well as to prepare 1N HNO_3 for rinsing metals from containers and filters.

6.4 sulfuric acid/nitric acid (60/40% w/w). Carefully mix 60g of concentrated sulfuric acid with 40g of concentrated nitric acid. If preferred, a more dilute acid mixture may be prepared and used to more easily adjust pH of the extraction fluids.

6.5 **SPLP Extraction fluid 1**: Make by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to water until the pH is 4.20 ±0.05. *This fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.*

6.6 **SPLP Extraction fluid 2**: Make by adding the 60/40 weight percent mixture of sulfuric acid and nitric acids (or a suitable dilution) to water until the pH is 5.00 ±0.05. *This fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.*

6.7 **SPLP Extraction fluid 3**: This fluid is laboratory deionized water and is used to determine cyanide leachability.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 All samples should be collected using an appropriate sampling plan. Since samples that are predominantly liquid may not have enough solids to obtain 100g by filtration, several hundred grams of sample may be necessary to properly conduct this procedure.

7.2 Chemical preservatives are not added to solid samples. Some liquid samples may contain residual chlorine and the free chlorine should be deactivated with sodium thiosulfate or another dechlorinating reagent while in the field. Preservatives shall <u>not</u> be added to samples before extraction.

7.3 Samples should be collected in Teflon-lined septum capped bottles and stored at

4±2°C. Samples may be refrigerated unless refrigeration results in irreversible physical change of the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

7.4 SPLP leachate should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH<2, unless precipitation occurs. Refrigeration is generally the only preservation technique applied to the leachates intended for semivolatile organic analysis. Maximum hold times are:

MAXIMUM HOLD TIMES (DAYS)

Leachate Analysis	From Field Collection to SPLP Leaching	From SPLP Leaching to Preparation for Analysis	From Preparation to Analysis
Semivolatile organics (including Pesticides, Herbicides)	14	7	40
Mercury (Hg)	28	NA	28
Metals (except Hg)	180	NA	180

NA=Not Applicable

8. PROCEDURES

8.1 PRELIMINARY EVALUATION

Preliminary evaluation includes: (1) determination of the percent solids (8.1.1); (2) determination of whether the sample contains insignificant solids and is, therefore, its own leachate after filtration (8.1.2); (3) determination of whether the solid portion of the sample requires particle size reduction (8.1.3) and (4) determination of which extraction fluid is to be used for the nonvolatile SPLP extraction of the waste (8.1.4).

Select samples to be analyzed and record on benchsheet. Perform preliminary SPLP evaluations on a minimum 100g aliquot of sample, assuming adequate volume of sample has been provided (notate on benchsheet if otherwise); this aliquot may not actually undergo SPLP extraction.

8.1.1 DETERMINATION OF PERCENT SOLIDS
PHASE SEPARATION

8.1.1.1 Percent solid is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out under applied pressure, as described below. Visual inspection may be sufficient for this determination.

If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., it is 100% solids), then proceed to Section 8.1.3 - Particle Size Reduction Determination.

8.1.1.2 **Phase Separation**. If the sample is liquid or multiphasic, liquid/solid separation is required to make a preliminary determination of percent solids. Phase separation involves the filtration device discussed in Section 5.3, and is accomplished per the procedure outlined below:

8.1.1.2.1 Weigh the filter paper for each sample and record this weight on the benchsheet (Form 623). Weigh the collection flask for each sample and record this weight on the benchsheet. Acid wash the filter if evaluating the mobility of metals (5.4).

Place the filter on the support screen. Assemble the filtration device.

8.1.1.2.2 Transfer an aliquot of the waste (100g minimum) into a beaker. Record the combined weight of the sample, beaker and spatula on the benchsheet.

8.1.1.2.3 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If centrifugation is used, then the liquid should be decanted and filtered, followed by filtration of the solid portion of the waste through the same filtration system.

8.1.1.2.4 Quantitatively transfer the waste sample to the filtration device (liquid and solid phases).

8.1.1.2.5 After transferring the sample to the filtration device, place the spatula in the beaker and record the combined weight of both. Then continue with the calculations prompted on the benchsheet.

8.1.1.2.6 Spread the waste sample evenly over the

surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature before filtering.

8.1.1.2.7 Gradually apply vacuum or gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If gas or air does not move through the filter at this range of pressures and if no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10psi increments to a maximum pressure of 50psi. **Note that instantaneous application of high pressure can rupture the glass fiber filter and may cause premature plugging.**

If after each incremental increase of 10psi, the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in a 2-minute interval, proceed to the next 10psi increment.

When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

8.1.1.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. However, even after applying vacuum or pressure filtration as outlined previously, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. **Do not replace the original filter with a fresh filter under any circumstances; use only one filter.**

8.1.1.2.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (8.1.1.1) from the total weight of the filtrate-filled container; record on benchsheet.

8.1.1.2.10 Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase (8.1.1.9) from the weight of the total waste sample; record on benchsheet.

8.1.1.3 Calculate the percent solids as follows:

$$\%\ \text{solids} = 100 * \frac{\text{weight of solids (8.1.1.10)}}{\text{total weight of waste (from benchsheet)}}$$

8.1.2 DETERMINATION OF INSIGNIFICANT SOLIDS

If the percent solids as determined above (8.1.1.3)is equal to or greater than (≥) 0.5%, then proceed either to Section 8.1.3 (particle size reduction determination) or continue as outlined below (8.1.2.1), if it is noticed that a small amount of the filtrate is entrained in the wet filter.

If the percent solids determined (8.1.1.3) is less than (<) 0.5%, then proceed to Section 8.2 (Aliquots for Leaching).

8.1.2.1 Remove the solid phase and filter from the filtration apparatus.

8.1.2.2 Dry the filter and solid phase at 100±20°C until two successive weighings yield the same value (±1%). Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. If it is suspected that the material is flammable, drying in the hood overnight is recommended. When the filter paper is dry, re-weigh and calculate the % solids with the new value. This Step is performed when it is suspected that the weight from the moisture in the filter paper has caused the % solids value to rise above 0.5%. Perform this Step only in borderline cases.

8.1.2.3 Calculate the percent dry solids as follows:

$$\%\,\text{dry solids} = 100 * \frac{(\text{dry waste} + \text{filter}) - (\text{initial weight of filter})}{\text{initial weight of waste (8.1.1.6 or 8.1.1.8)}}$$

8.1.2.4 If the percent dry solid is < 0.5%, then proceed to Section 8.2 if the nonvolatile SPLP is to be performed.

If the percent dry solid is ≥0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 8.1.3). **The portion of sample that has been dried is not to be used in the leaching procedure.**

8.1.3 PARTICLE SIZE REDUCTION DETERMINATION

8.1.3.1 Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1cm^2, or is smaller than 1cm in its narrowest dimension (i.e., is capable of passing through a 9.5mm [0.375 inch] standard sieve). If the particle size is larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above.

8.1.3.2 Note that the surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

8.1.3.3 Safety concerns such as dust control may preclude the grinding of samples for particle size reduction. These safety concerns must always be addressed before attempting to grind any sample. Generally due to health and safety concerns, grinding to reduce particle size is not practiced in the extractions area. Samples requiring particle size reduction have been sent to an appropriate facility before an extraction was performed.

8.1.3.4 If a particle size reduction of the solid portion of the waste is required, continue as follows:

8.1.3.4.1 Prepare the waste for extraction by crushing, cutting or grinding the solid portion of the waste to a suitable surface area or particle size.

8.1.3.4.2 *Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4±2°C prior to particle size reduction.*

8.1.3.4.3 *The means used to effect particle size reduction must not generate heat in and of itself.*

8.1.3.4.4 *Work carefully and quickly, as exposure of the waste to the atmosphere should be avoided to the extent possible.*

8.1.3.4.5 Note that sieving of the waste is not normally required. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth and similar) waste materials. Actual measurement of surface area is not recommended.

If the waste as received passes a 9.5mm sieve, quantitatively transfer the solid material into an extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to 8.4 - Tumbling.

8.1.3.4.6 When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into the extractor bottle. Include the filter used to separate the initial liquid from the solid phase. Then proceed to 8.3 - Filtration..

8.1.4 EXTRACTION FLUID DETERMINATION

If the solid content of the waste is ≥0.5%, then determine the appropriate fluid for the nonvolatiles extraction as follows:

8.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, Extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, Extraction fluid #2 should be used.

8.1.4.2 For wastes and wastewater, Extraction fluid #1 should be used.

8.1.4.3 For cyanide-containing wastes and/or soils, Extraction fluid #3 (reagent water) must be used, because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

8.2 DETERMINATION OF ALIQUOTS FOR LEACHING

8.2.1 Label a 2000mL container with work order number, sample number, and fluid number (for metals, rinse the container with 0.1N HNO_3, followed by a rinse with deionized water). For each reagent blank, label a container with the date of tumbling, reagent blank number and fluid number.

8.2.2 Determine the number of analyses to be performed upon each sample: Herbicides, organochlorine pesticides, and semivolatiles analysis each require 100mL of tumbled fluid. Metals analysis requires 50mL of tumbled fluid. Each analysis also requires one (1) matrix spike sample/fluid/day tumbled, so these amounts may be doubled to ensure sufficient amount of fluid for all analyses and matrix spike quality control samples.

Each analysis also requires a reagent blank/fluid/day tumbled, which consists of the appropriate fluid placed in a container (no solid added) and tumbled with the samples. The reagent blank should also be put on the benchsheet and carried through the tumbling/filtering/extracting (and analysis) process.

The amount of fluid added to the sample is equal to 20 times the weight of the solid (e.g., 20g of sample requires 400mL of fluid).

8.2.3 If the aliquot of the sample used for the preliminary evaluation was determined to be 100% solid (8.1.1.1), then that aliquot can be used for the nonvolatile extraction (assuming that aliquot is sufficient to generate enough leachate to support the requested analyses).

Do not use leach solid that was dried in the oven.

8.2.4 The amount of solid necessary is dependent upon whether a sufficient

amount of leachate will be produced to support the required analyses. If an adequate amount of solid remains, proceed with the nonvolatile SPLP extraction (Section 8.4).

A minimum sample size of 100g (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content (8.1.1.3) of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous leachate of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough SPLP solids should be generated for extraction such that the volume of leachate will be sufficient to support all of the analyses required.

If the amount of leachate generated by a single SPLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed, and the leachates from each combined and aliquoted for analysis

8.2.5 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a subsample of the waste (100g minimum) and proceed to Section 8.3 – Filtration.

8.2.6 If the sample is liquid or multiphasic, liquid/solid separation is required as outlined in Section 8.1.1.2..

8.2.7 Weigh out an aliquot of the sample (100g minimum) and record the weight. If the waste contains <0.5% dry solids (Section 8.1.2.3), the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required.

8.2.8 For wastes containing $\geq$0.5% solids, use the percent solids information obtained in Section 8.1.1.3 to determine the optimum sample size (100g minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP leachate.

8.2.9 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered, followed by filtration of the solid portion of the waste through the same filtration system.

8.3 FILTRATION

8.3.1 Pre-weigh the container that will receive the filtrate; record weight.

8.3.2 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 5.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

8.3.3 Quantitatively transfer the sample (liquid and solid phases) to the filter holder. Spread the sample evenly over the surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 8.3.6, to determine the weight of the waste sample that will be filtered.

8.3.4 Gradually apply vacuum or gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10psi increments to a maximum of 50psi. **Note Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.**

8.3.5 When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

8.3.6 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in the Section 8.2, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. **Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.**

8.3.7 Weigh the filtrate; record weight.

8.3.8 If the sample contains <0.5% dry solids, proceed to Section 8.5 - Preparation for Analysis.

If the sample contained no initial liquid phase, the filtrate is defined as the SPLP leachate; proceed to Section 8.5 - Preparation for Analysis.

8.3.9 EXTRACTION FLUID ALIQUOT DETERMINATION
Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (8.1.1.3)} \times \text{weight of waste filtered (8.3.3)}}{100}$$

8.4 EXTRACTION (TUMBLING)

8.4.1 Slowly add the calculated amount of appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal).

8.4.2 Secure the extractor bottle in the rotary tumbler, and rotate at 30±2 rpm for 18±2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23±2°C during the extraction period. SOP 663 describes the procedures for monitoring tumbler revolutions and room temperature.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically vented (e.g., after 15 minutes, 30 minutes, and 1 hour), into a hood.

8.4.3 Following the 18±2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter.

8.4.4 For final filtration of the SPLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration.

Filter(s) shall be acid-washed (see Section 5.4) if evaluating the mobility of metals.

8.4.5 Following collection of the SPLP leachate, the pH of the leachate should be recorded. Immediately aliquot and preserve the leachate for analysis.

8.4.6 The liquid phase may now be either analyzed (8.5) or stored at 4±2°C until time of analysis. If miscible, the initial liquid phase may be combined with the SPLP leachate. If the initial liquid phase of the waste is not or may not be compatible with the filtrate, do not combine these liquids. Although they are collectively defined as the SPLP leachate, they are to be analyzed separately, and their analysis results combined mathematically (8.5.2).

8.5 PREPARATION FOR ANALYSIS

8.4.1 Metals aliquots must be acidified with nitric acid to pH<2. If precipitation is observed upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate for metals analyses shall not be acidified, and the leachate shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4±2°C) until analyzed.

8.4.2 The SPLP leachate shall be prepared and analyzed according to appropriate analytical methods. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ±0.5%), conduct the appropriate analyses, and combine the results mathematically by using a volume-weighted average as shown below:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = volume of the first phase (L)

C_1 = concentration of the analyte of concern in the first phase (mg/L)

V_2 = volume of the second phase (L)

C_2 = concentration of the analyte of concern on the second phase (mg/L)

9. QUALITY CONTROL

9.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel. No more than 20 field samples may be included in a batch.

9.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.). A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

9.2.1 Matrix spikes are to be added after filtration of the TCLP leachate and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

9.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP leachate as that which was analyzed for the unspiked sample.

9.2.3 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%\ Recovery) = 100\ (Xs - Xu)/K$$

where:

Xs = measured value for the spike sample
Xu = measured value for the unspiked samples
K = known value of the spike in the sample

10. DEVIATIONS FROM THE METHOD

There are no known deviations from the SW-846 Method 1312 with the following exception: Paragon allows for the use of HDPE bottles for metals and semivolatile organics leaching, if approved by the client (see LIMS program specifications), and if this type of container can be shown to meet the criteria discussed in Section 5.5 (i.e., inert and does not adsorb or release target analytes).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses and a lab coat when working with chemical materials (e.g., standards, solvents, reagents, or samples).

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.2 WASTE DISPOSAL

11.2.1 Unused sample leachate may be disposed of in the Aqueous Laboratory Waste.

11.2.2 Unused non-radioactive sample solids may be disposed of in the Contaminated Soils and Solids Waste.

11.2.3 Unused radioactive sample solids may be disposed of in the appropriate Radioactive Waste stream (consult with Waste Compliance Officer).

11.2.4 All empty solvent bottles shall be disposed of appropriately. Note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, US EPA SW-846, 3rd Edition, Final Update III, Volume 1c, Method 1312, Rev 0, September 1994.

DOCUMENT REVISION HISTORY

3/4/08: Updated LIMS language 3.3. Reformatted Section 8, included temperature monitoring and SOP 663 reference. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

LEACHING FLUIDS LOG

Lot Nos.: Sodium Hydroxide _____ Glacial Acetic Acid _____

Solution Name	Date Prepared	Initials	Volume NaOH Used (mL)	Volume Glacial Acetic Acid Used (mL)	Total Volume Made (mL)	Final pH	Comments

Reviewed by _____ Date _____

FORM 646r1.doc (4/17/02)

Paragon Analytics

PERCENT SOLIDS (% SOLIDS) DETERMINATION

Logbook No./Page _____ A

(For Samples on Following Logbook Page)

Units = grams	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
Sample No.	Weight of Beaker, Spatula & Sample	Weight of Beaker, Spatula & Residue	Total Sample Weight (a - b)	**Weight of Filter**	Weight of Collection Flask	Weight of Flask & Filtrate	Filtrate Weight (f - e)	Total Solids Weight (c - g)	% Solids (Wet) (h / c) * 100	Weight of Filter & Dried Solids	Weight of Dried Solids (j - d)	% Solids (Dry) (k / h) * 100

Paragon Analytics

Logbook No./Page ________________ B

LEACHING PROCEDURE WORKSHEET

Work Order # ___________________________
Batch ID # ______________________________
Method **SOP** **Rev**

(Start) Date ________ **Time** ______
(Start) RPM _______ **Temp.** _____ **°C** *(from min/max* SN 21251556*)*
(Start) Analyst _____ RESET MIN/MAX AFTER READING OBTAINED

(Stop) Date _______ **Time** ______ **RPM** ______
(Stop) Temp. ____ **°C** **Tumble Min/Max** ___/___ **°C**
RESET AFTER EACH READING **(Stop) Analyst** _____

Extraction Fluid ID ______________________ **Filtration Date/Time/** _____________________ **Initials** ________

Reviewed By / Date __________________________

Preliminary Solids[a]	Particle Reduction[b]	Sample Number	Initial pH	Fluid Determination				Sample Weight (g)	Fluid (mL)	Final pH	Leachate No.	Comments
				HCl (mL)	Final pH	Fluid #	Fluid pH					
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
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I S M	Y N											
I S M	Y N											

[a] I = insignificant (< 0.5%); S = 100%; M = Multiphasic (see attached % Solids Determination form).

[b] Y = Yes - reduction required / performed; N = no partical size reduction required.

INTERNAL COC TRANSFER: Relinquished by _______ (initials) to ________________________ (RU# & location) ______________________ (Date & Time) **Form 623r10.doc (1/17/2006)**

Paragon Analytics

Corning Model 320 pH Meter Calibration & Maintenance Log

Result Units = pH units

Date	Time	Analyst	4.01 Solution Lot No./ Result	10.01 Solution Lot No./ Result	% Slope	7.00 Solution Lot No./ Result	Check Solution Result
			/	/		/	
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Comments/Maintenance Notes:

Form 825r0.xls (4/18/2003)

Paragon Analytics

TEMPERATURE LOGBOOK

ORGANIC EXTRACTIONS - TCLP ROOM

Acceptable Range 23 ± 2 °C

A current temperature reading must be recorded at the onset of TCLP tumbling, and the min/max memory must be reset. DO NOT initiate tumbling if temperature is not within acceptable limits. The current temperature and min/max information must be recorded at the completion of tumbling. Both the Department and QA Managers must be notified in a timely manner if an excursion occurs.

		Thermometer: 41406316 (min/max)				
DATE	TIME	Current Temp. (°C)	Temp. Min (°C) Date/Time Occurred	Temp. Max (°C) Date/Time Occurred	INITIALS	COMMENTS

Reviewed by / date _____ **Form 345r1.doc (7/10/06)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 669 REVISION 4

TITLE: **SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP) OF SAMPLES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOCs) BY ZERO HEADSPACE EXTRACTION (ZHE) -- METHOD SW1312**

FORMS: **608, 825, 345 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3.4.08

QUALITY ASSURANCE MANAGER _____ DATE 3/4/08

LABORATORY MANAGER _____ DATE 3-4-08

HISTORY: Rev0, 10/28/99; Rev1, 9/19/02, Rev2, 2/13/04; Rev3, 3/9/06; Rev4, 3/4/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW-846 Method 1312 -- are designed to determine the mobility of volatile organic compounds (VOCs) present in liquids, soils, and wastes (including multiphasic samples). Application of these procedures to matrices other than those specified will be handled individually to simulate the leaching procedure as best as possible.

2. SUMMARY OF PROCEDURE

For liquid samples (i.e., those containing less than 0.5% dry solid material), the sample, following filtration through a 0.6 to 0.8µm glass fiber filter, is defined as the SPLP extract (leachate).

For samples containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis. The particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid (reagent water) equal to twenty (20) times the weight of the solid phase. A special extractor vessel for volatile compounds is used in this procedure. Following extraction, the liquid extract (leachate) is separated from the solid phase by filtration through a 0.6 to 0.8µm filter.

If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is typically added back to the solid phase prior to addition of reagent water and leaching. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the logbooks, analytical review sheets or case narratives indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work and documentation of the measures taken to remedy any errors found in the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Possible contaminant sources are volatile solvents used in the laboratory. Analyses of reagent blanks provide information about the presence of these contaminants. The ZHE vessels are thoroughly cleaned between uses. The vessel number used for each sample or blank is recorded in the logbook. The same vessel is not to be used repeatedly for the blank - all vessels must be used for the blank on a rotating basis.

5. APPARATUS AND MATERIALS

5.1 **Zero-Headspace Extraction vessel (ZHE)**: ADAM 3745 ZHE or equivalent. These devices are used when the mobility of VOCs are of concern. The ZHE allows for liquid-solid separation (within the device), extraction, and final extract filtration without opening the vessel. Thus, headspace and potential loss of volatiles from this closed system is effectively precluded. The ZHE have an internal volume of 500-600mL and are equipped to accommodate a 90-100mm diameter filter. The devices utilize Viton™ o-rings to form a seal. These o-rings should be inspected before each use and may need to be replaced if they show signs of wear or damage.

For the ZHE vessel to be acceptable for use, the piston within the ZHE should be mobile with approximately 15psi or less (it is helpful to first moisten the piston o-rings slightly with extraction fluid). If it takes more pressure to move the piston, the o-rings in the device should be replaced. If replacing the o-rings does not solve the problem, the ZHE is unacceptable for SPLP analyses and the manufacturer should be contacted for re-machining.

Each ZHE device contains a built-in pressure gauge. The gauge should be frequently monitored to ensure that the ZHE is free of leaks throughout the extraction process. If the gauge indicates that the ZHE is not holding pressure correctly, or if the device shows other signs of a leak, pressurize the device to 50psi, allow it to stand unattended for 1 hour, and recheck the pressure. The ZHE can also be submerged in water after pressurization to check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace o-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted. If new ZHE are purchased, they must successfully pass this pressurization test prior to being used for sample analysis.

The ZHE vessel is used for filtration of the final ZHE extract. The ZHE vessel must be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50psi). When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE vessel.

5.2 **Pressure filtration device**, Associated Design and Manufacturing Model 3750-LHWF or equivalent. A.K.A. “lunar lander”.

5.3 pH meter, accurate to +0.05pH units @ 25 °C
Meter must be calibrated prior to use (see Form 825).

5.4 **Fiber filter**, borosilicate glass, free of binder materials, 0.6 to 0.8µm particle size. *Pre-filters must not be used.* Glass fiber filters are fragile and should be handled with care. Use Gelman #66256, 90mm or equivalent, and/or Whatman #6890-2507, 25mm or equivalent.

5.5 VOA vials, 20mL or 40mL, septum seal, certified ‘clean’.

5.6 laboratory balance, accurate to ±0.01g

5.7 centrifuge

5.8 drying oven, capable of maintaining 100±20°C

5.9 apparatus for pressurizing ZHE's: Ultra high-purity Nitrogen tank, regulator (set to around 60psi), hose, and adapter for attachment to ZHE and pressure filtration device ("lunar lander").

5.10 rotary tumbler with 30±2rpm capability, Associated Design and Manufacturing Model 3740 or equivalent

5.11 **ZHE Extract Collection Devices**, used to collect the initial liquid phase and the final extract of the waste. Plastic gas-tight syringes (50-60mL with Luer-Lok® fitting) or TEDLAR® bags may be used. Following collection, the extract is filtered during transfer to a 'VOA' vial (20 or 40mL volume) to meet the method requirements for storage in minimal headspace conditions until time of analysis. The devices listed are recommended for use under the following conditions:

5.11.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), a syringe should be used to collect and combine the initial liquid and solid extract.

5.11.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the Tedlar® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

5.11.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the Tedlar® bag or the syringe may be used. If the syringe is used, discard the first 5mL of liquid expressed from the device. The remaining aliquots are used for analysis.

6. REAGENTS

reagent water: defined as water in which an interferent is not observed at or above the method's detection limit of the analyte(s) of interest. Paragon's laboratory deionized water is suitable for use. This DI (reagent) water is used as the ZHE extraction fluid.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 All samples should be collected using an appropriate sampling plan.

7.2 There may be requirements on the minimal size of the field sample, depending upon the physical state of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of percent solids and particle size. Another aliquot may be needed to actually conduct the nonvolatile extraction. An additional aliquot is needed for the volatile organics extraction. Quality control (QC) samples may require additional aliquots. Further, it is wise to collect

additional sample in case something goes wrong with the initial attempt to conduct the test.

7.3 Preservatives shall not be added to samples before extraction.

7.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

7.5 Because the samples are to be analyzed for volatiles, care shall be taken to minimize their loss; samples shall be collected and stored accordingly. Samples should be collected in glass jars with Teflon®-lined lids and stored at 4±2°C. (although EnCore® samplers may also be used for sample collection, their limited sampling capacity makes them less desireable for this procedure). Samples should only be opened immediately prior to extraction.

7.6 SPLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for volatile organic analyses shall be exposed to the atmosphere for as short a time as possible to minimize losses.

7.7 SPLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Maximum hold times are:

Sample Holding Times [days]

	Time from field collection to SPLP leaching	Time from ZHE-SPLP leaching to determinative analysis
Volatiles	14 days	14 days

8. PROCEDURE

8.1 PRELIMINARY EVALUATION

Preliminary evaluation includes: (1) determination of percent solids; (2) determination of whether or not the waste contains insignificant solids and is, therefore, its own extract after filtration; and (3) determination of whether or not the solid portion of the waste requires particle size reduction (if required, procedure is described in SOP 609).

NOTE: Even if only the volatile SPLP extraction is being done, it is often useful to perform the (initial) phase separation in order to determine the optimum sample aliquot with which to charge the ZHE. The experienced prep analyst may, however, choose to forego this procedure, as percent solids determination is also conducted as part of the procedure in determining the amount of extraction fluid to add (Steps 8.2.3 through 8.2.5).

Select samples and record on benchsheet (Form 608). Perform preliminary SPLP evaluations on a minimum 100g aliquot of waste (if there is insufficient sample or it is impractical to use 100g, notate on benchsheet).

8.1.1 DETERMINATION OF PERCENT SOLIDS
PHASE SEPARATION

8.1.1.1 Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample), from which no liquid may be forced out by an applied pressure, as described below. Visual inspection may be sufficient for this determination.

If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids), then proceed to Section 8.1.3 - Particle Size Reduction Determination.

8.1.1.2 **Phase Separation**. If the sample is liquid or multiphasic, liquid/solid separation is required to make a preliminary determination of percent solids. This involves the filtration device described in Section 5.2, and performance of the procedures outlined below:

8.1.1.2.1 Pre-weigh the filter, spatula, and beaker that will receive the filtrate. Record the weights in the appropriate boxes on the TCLP % solid benchsheet (Form 608). Foil dishes may be used to collect solids from sample with very low solids content and the foil dish weight must be recorded before solids are placed on the foil.

8.1.1.2.2 Assemble the filtration device and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

8.1.1.2.3 Weigh out a subsample of the waste (100g minimum) and record the weight. If sufficient sample is not available, record such on benchsheet.

8.1.1.2.4 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered

followed by filtration of the solid portion of the waste through the same filtration system.

8.1.1.2.5 Quantitatively transfer the waste sample to the filtration device (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature before filtering.

8.1.1.2.6 After transferring the waste sample to the filtration device, place the spatula in the beaker, weigh, and record the initial sample weight on the TCLP % solids benchsheet.

8.1.1.2.7 Gradually apply gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If gas or air does not move through the filter at this range of pressures and if no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10psi increments to a maximum pressure of 50psi. **Note that instantaneous application of high pressure can rupture the glass fiber filter and may cause premature plugging.**

When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

8.1.1.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration as outlined above, this material may not filter. If this is the case, the material within the filtration

device is defined as a solid as is carried though the SPLP extraction. **Do not replace the original filter with a fresh filter under any circumstances.** Use only one filter.

8.1.1.3 Determine the weight of the liquid phase by subtracting the weight of the empty beaker (8.1.1.2.1) from the total weight of the filtrate-filled beaker syringe; record weight on TCLP % solids benchsheet (Form 608).

Determine the weight of the solid phase (8.1.1.2.8) of the waste sample by subtracting the weight of the liquid phase (above) from the weight of the total waste sample (8.1.1.2.3); record weight on TCLP % solids benchsheet.

8.1.1.4 Calculate the percent solids as shown below:

$$\text{Percent Solids} = \frac{\text{Weight of solid (8.1.1.3)}}{\text{Total weight of waste (8.1.1.2.3)}} \times 100$$

8.1.2 DETERMINATION OF INSIGNIFICANT SOLIDS

If the percent solids as determined above (8.1.1.4) is equal to or greater than (≥) 0.5%, then proceed either to Section 8.1.3 (particle size reduction determination) or continue as outlined below (8.1.2.1), if it is noticed that a small amount of the filtrate is entrained in wetting of the filter.

If the percent solids determined (8.1.1.4) is less than (<) 0.5%, then proceed to Section 8.2 (ZHE procedure), with a fresh portion of the waste.

8.1.2.1 Remove the solid phase and filter from the filtration apparatus.

8.1.2.2 Dry the filter and solid phase at 100±20°C until two successive weighings yield the same value (±1%). Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. If it is suspected that the material is flammable, drying in the hood overnight is recommended. When the filter paper is dry, re-weigh and calculate the % solids with the new value. This Step is performed when it is suspected that the weight from the moisture in the filter paper has

caused the % solids value to rise above 0.5%. Perform this Step only in borderline cases.

8.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent Dry Solids} = \frac{\text{Wt dry sample + filter - Tared wt of filter}}{\text{Initial weight of sample (8.1.1.2.3)}} \times 100$$

8.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 8.2.

8.1.3 PARTICLE SIZE REDUCTION DETERMINATION

8.1.3.1 Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than $3.1cm^2$, or is smaller than 1cm in its narrowest dimension (i.e., is capable of passing through a 9.5mm [0.375 inch] standard sieve). If the particle size is larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above.

8.1.3.2 Note that the surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

8.1.3.3 Safety concerns such as dust control may preclude the grinding of samples for particle size reduction. These safety concerns must *always* be addressed before attempting to grind any sample. Generally due to health and safety concerns, grinding to reduce particle size is not practiced in the extractions area. Samples requiring particle size reduction have been sent to an appropriate facility before an extraction was performed.

8.1.3.4 Particle size reduction prior to leaching for volatile organics may lead to loss of target compounds, compromising the analytical results.

8.1.3.5 If a particle size reduction of the solid portion of the waste is required, continue as follows:

8.1.3.5.1 Prepare the waste for extraction by crushing, cutting or grinding the solid portion of the waste to a suitable surface area or particle size.

8.1.3.5.2 *Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4±2°C prior to particle size reduction.*

8.1.3.5.3 *The means used to effect particle size reduction must not generate heat in and of itself.*

8.1.3.5.4 *Work carefully and quickly, as exposure of the waste to the atmosphere should be avoided to the extent possible.*

8.1.3.5.5 **Note that sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth and similar) waste materials. Actual measurement of surface area is not recommended.**

8.1.3.5.6 When the surface area or particle size has been appropriately altered, proceed to Section 8.2.3 - Filtration.

8.2 ZHE PROCEDURE

Use the ZHE vessel to obtain SPLP leachate for analysis of VOCs only. Leachates resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, semivolatiles). The ZHE vessel has an internal capacity of 500-600mL, and can thus accommodate a maximum of approximately 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

8.2.1 EQUIPMENT SET-UP

8.2.1.1 Charge the ZHE with sample only once and do not open the device until the final leachate (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

8.2.1.2 **Do not allow the sample, the initial liquid phase, or the leachate to be exposed to the atmosphere for any more time than is absolutely necessary. Manipulation of the sample to be leached should be done when cold (4±2°C) to minimize loss of volatiles. Leaching fluids are added at room temperature. After filtration, leachates should be cooled to 4±2°C by placing the 'VOA' vial into a suitable refrigeration unit as soon as practical.**

8.2.1.3 Pre-weigh the (evacuated) filtrate collection container (5.11) and set aside. If using a Tedlar™ bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis.

8.2.1.4 Place the ZHE piston within the body of the ZHE (it is helpful to first moisten the piston o-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move after the ZHE is charged with sample (based upon sample size requirements as discussed previously). Secure the gas inlet/outlet (bottom) flange (with the valve open) onto the ZHE body per the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set the liquid inlet/outlet flange (top flange) aside.

8.2.2 ALIQUOT DETERMINATIONS

8.2.2.1 If the sample is 100% solid (8.1.1.1), weigh out a subsample (25g maximum – care should be taken to choose a sample weight that will yield sufficient leachate to support the analysis) of the waste, record weight, and proceed to Step 8.2.3 - Filtration.

8.2.2.2 If the waste contains <0.5% dry solids (8.1.2.3), the liquid portion of waste, after filtration, is defined as the ZHE extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required (weigh out a 100-500g subsample, record weight). Proceed to Step 8.2.3 - Filtration.

8.2.2.3 If the waste contains ≥0.5% dry solids, use the percent solids information obtained in Step 8.1.1.4 to determine the optimum sample size to charge into the ZHE vessel as follows:

$$\text{Wt of waste to charge ZHE} = \frac{10}{\text{percent solids (8.1.1.4)}} \times 100$$

Weigh out the appropriate size of waste subsample as determined and record the weight on the ZHE benchsheet (Form 608).

8.2.3 FILTRATION

8.2.3.1 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

8.2.3.2 Quickly and quantitatively transfer the entire sample (liquid and solid phases) of the waste aliquot to the ZHE vessel.

NOTE: If waste material (>1% of original subsample weight) has obviously adhered to the container used to transfer the sample to the ZHE vessel, determine the weight of this residue and subtract it from the sample weight (8.1.1.2.3) to determine the actual weight of the waste subsample that will be filtered.

8.2.3.3 Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings, and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the leachate collection device to the top plate.

8.2.3.4 Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10psi (or more if necessary) to force all headspace *slowly* out of the ZHE vessel.

At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4±2°C reduces the amount of expressed liquid beyond what would be expressed at room temperature, then allow the sample to warm to room temperature before filtering.

If the waste is 100% solid (8.1.1.1), slowly increase the pressure to a maximum of 50psi to force most of the

headspace out of the device, then proceed to Section 8.2.6 - Extraction (Tumbling).

8.2.3.5 Attach the evacuated pre-weighed 60mL plastic Luer-Lok® syringe to the liquid inlet/outlet valve of the ZHE and open the valve. Begin applying gentle pressure of 1-10psi to force the liquid phase of the sample into the filtrate collection container. **Note that instantaneous application of high pressure can rupture the glass fiber filter and may cause premature plugging.**

If no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10psi increments (and waiting a 2-minute interval with no additional liquid passing) to a maximum of 50psi.

When liquid flow has ceased such that continued pressure filtration at 50psi does not result in any additional filtrate within a 2-minute period, stop the filtration.

8.2.3.6 Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container; record weight on ZHE benchsheet. Using the information recorded on the benchsheet, calculate the amount of solid waste left inside the ZHE.

8.2.4 PHASE DISCUSSION

The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase. Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the SPLP extraction as a solid.

If the original waste contained <0.5% dry solids (8.1.2.3), this filtrate is defined as the SPLP leachate and is analyzed directly. Proceed to Section 8.2.7 - Preparation for Volatile Analysis.

The liquid phase may now be either analyzed immediately (8.2.7), stored at 4±2°C under minimal headspace conditions until time of analysis, or recombined (if miscible) with the sample prior to tumbling.

8.2.5 EXTRACTION FLUID ALIQUOT DETERMINATION

Determine the weight of reagent water to add to the ZHE as follows:

$$\text{Weight of reagent water} = \frac{20 \times \text{percent solids (8.1.1.4)} \times \text{weight of waste filtered (i.e., the solid waste left inside the ZHE, 8.2.3.6)}}{100}$$

8.2.6 EXTRACTION (TUMBLING)

8.2.6.1 Fill a clean beaker of appropriate volume with reagent water, then fill a clean 60mL gas-tight Luer-Lok® syringe from the beaker. Vent residual air from the syringe so that it only contains the measured amount of fluid.

With the ZHE vessel in the vertical position, attach the syringe to the liquid inlet/outlet valve. Release gas pressure on the ZHE piston (open the gas inlet/outlet valve), open the liquid inlet/outlet valve, and depress the syringe plunger to transfer extraction fluid into the ZHE vessel. Close the liquid inlet/outlet valve and remove the syringe.

Continue to add reagent water to the ZHE in this manner until the appropriate amount (8.2.5) has been introduced into the device.

8.2.6.2 After the reagent water has been added, immediately close both the liquid inlet/outlet valve and the gas inlet/outlet valve.

8.2.6.3 Reposition the ZHE vessel in the vertical position with the liquid inlet/outlet valve on top. Pressurize to 5-10psi and slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of reagent water. *This bleeding should be done quickly - stop at the first appearance of liquid from the valve.* Re-pressurize to 5-10psi and check all ZHE fittings to ensure that they are closed.

8.2.6.4 Place the ZHE in the rotary extractor apparatus and rotate at 30±2 rpm for 18±2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23±2°C during agitation. SOP 663 describes the procedures for monitoring tumbler revolutions and room temperature.

8.2.6.5 Following the 18±2 hour agitation period, check the pressure gauge on the ZHE vessel to see that pressure has

been maintained. If the pressure has not been maintained, the device has leaked. Check the ZHE vessel for leaking as specified in Section 5.1, and correct the problem. Perform the extraction again with a new aliquot of waste sample.

8.2.6.6 If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases.

8.2.6.6.1 If the waste contained an initial liquid phase that has been stored, the leachate may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) that holds the initial liquid phase. *A separate filtrate collection container must be used if combining would create multiple phases, or if there is not enough volume left within the filtrate collection container.*

8.2.6.6.2 After attaching the filtrate collection container (TEDLAR® bag or clean syringe) slowly open the liquid inlet/outlet valve (top flange) to collect the filtered leachate. Note that an in-line glass fiber filter may be used to filter the material within the ZHE vessel if it is suspected that the internal glass fiber filter has ruptured. *All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase that was NOT recombined with solids prior to tumbling.*

8.2.6.6.3 If the original sample contained no initial liquid phase, the filtered liquid material obtained from Section 8.2.3 is defined as the SPLP leachate. If the sample contained an initial liquid phase, the filtered liquid material obtained from Section 8.2.3 and the initial liquid phase (8.1.1.2) are collectively defined as the SPLP leachate.

8.2.7 PREPARATION FOR VOLATILE ANALYSIS
Following collection of the SPLP leachate, immediately prepare the

leachate for analysis, by transferring to a septum-sealed "VOA" vial, and store with minimal headspace at 4±2°C until analyzed.

The SPLP leachate is analyzed according to the appropriate determinative method. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L)

C_1 = The concentration of the analyte of concern in the first phase (mg/L)

V_2 = The volume of the second phase (L)

C_2 = The concentration of the analyte of concern in the second phase (mg/L)

9. QUALITY CONTROL

9.1 A minimum of one method blank (MB), using the same extraction fluid (reagent water) as used for the samples, must be analyzed for every 20 extractions that have been conducted in an extraction vessel. No more than 20 field samples may be included in a batch.

9.2 Matrix spikes and laboratory control samples are prepared at the time of analysis by the volatiles analysis group.

10. DEVIATIONS FROM METHOD

This SOP meets the requirements of SW-846 Method 1312. There are no known deviations from this method.

It should be noted that, when only the volatile TCLP extraction is being done (i.e., no semivolatile or metals), the initial percent solids determination (using the "lunar lander") may be skipped, as the percent solids can be determined after the sample is loaded into the ZHE (Steps 8.2.3.4 through 8.2.3.6). Experience of the prep analyst weighs heavily here, as (in the case of a very wet sample matrix), too small of an aliquot into the ZHE may not yield an adequate volume of leachate for analysis.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses and a lab coat when working with chemical materials (e.g., standards, solvents, reagents, or samples).

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.2 WASTE DISPOSAL

11.2.1 Unused sample liquids may be disposed of in the Aqueous Laboratory Waste.

11.2.2 Unused sample leachate solids may be disposed of in the Contaminated Soils and Solids.

11.2.3 Waste from processing radioactive samples shall be disposed of in the appropriate radioactive waste stream.

11.2.4 All empty solvent bottles shall be disposed of according to the appropriate SOPs. All labels and markings must be defaced prior to disposal.

12. REFERENCES

Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, US EPA SW-846, 3rd Addition, Final Update III, Method 1312, December 1996.

DOCUMENT REVISION HISTORY

3/4/08: Minor clarifications throughout. Augmented LIMS program specification language Section 3.3. Added detail re: ZHE vessels Section 5.1. Added rotary tumbler to APPARATUS AND MATERIALS. Reformatted Section 8, included temperature monitoring and SOP 663 reference. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

ZHE PERCENT SOLIDS DETERMINATION & TUMBLING

Work Order # _____	**(Start) Date** _____ **Time** _____	**(Run) Temp. (min/max)** _____/_____ **°C**
Batch # _____	**(Start) RPM** _____ **Temp.** _____ **°C** *(from min/max* SN 21251556)	**(Stop) Date** _____ **Time** _____
Method _____ **SOP 608 Rev** _____	**(Start) PSI** _____ **Analyst** _____ RESET MIN/MAX AFTER READING OBTAINED	**(Stop) RPM** _____ **Temp.** _____ **°C**
Leaching Fluid ID		**(Stop) PSI** **Analyst**
Filtration Date _____ **Time** _____ **Initials** _____		**Reviewed by date** _____

		Percent Solids Determination						ZHE Aliquot					
Sample Number	**Sample Matrix**	Free Liquid? Y / N *	Initial Sample Weight (g)	Filter Weight (g)	Beaker Weight (g)	Sample Dry Weight (g)	% Solid (DRY/TOT)	Tumbler Number	Aliquot (g)	Fluid Volume (mL)	**Final pH**	**Leachate Number**	**Comments**

* If "No", percent solids are 100% by visual inspection (test not performed). **INTERNAL COC TRANSFER**: Relinquished by _____ (initials) to _____ (RU # & Location) _____ (Date & Time)

Form 608r11.doc (10/25/07)

Paragon Analytics

Corning Model 320 pH Meter Calibration & Maintenance Log

Result Units = pH units

Date	Time	Analyst	4.01 Solution Lot No./ Result	10.01 Solution Lot No./ Result	% Slope	7.00 Solution Lot No./ Result	Check Solution Result
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Comments/Maintenance Notes:

Form 825r0.xls (4/18/2003)

Paragon Analytics

TEMPERATURE LOGBOOK

ORGANIC EXTRACTIONS - TCLP ROOM

Acceptable Range 23 ± 2 °C

A current temperature reading must be recorded at the onset of TCLP tumbling, and the min/max memory must be reset. DO NOT initiate tumbling if temperature is not within acceptable limits. The current temperature and min/max information must be recorded at the completion of tumbling. Both the Department and QA Managers must be notified in a timely manner if an excursion occurs.

		Thermometer: 41406316 (min/max)				
DATE	TIME	Current Temp. (°C)	Temp. Min (°C) Date/Time Occurred	Temp. Max (°C) Date/Time Occurred	INITIALS	COMMENTS

Reviewed by / date _____ **Form 345r1.doc (7/10/06)**

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 670 REVISION 12

TITLE: ANALYSIS OF TOTAL ORGANIC CARBON BY METHODS EPA 415.1, SW9060, AND SM5310 C

FORMS: 647 **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-14-07

QUALITY ASSURANCE MANAGER _____ DATE 11/13/07

LABORATORY MANAGER _____ DATE 11-14-07

HISTORY: **SOP 803:** Rev0, PCN #182, 3/1/94; Rev1, 4/11/96; Rev2, 3/13/97; Rev3, 6/15/99; Rev4, 3/3/00; Rev5, 2/11/02; Rev6, 4/3/02. **SOP 670:** Rev7, 8/13/02; Rev8, 3/14/03; Rev9, 5/26/04; Rev10, 8/23/04; Rev11, 2/27/06; Rev12, 11/12/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the methods it references -- EPA 415.1, SW9060 and SM5310 C -- describe procedures for the analysis of Total Organic Carbon (TOC) in water. These procedures are applicable to the measurement of organic carbon contained in drinking, surface, ground, and saline waters, as well as domestic and industrial wastes. Exclusions are noted under Inferferences (Section 4).

This procedure is applicable only to homogenous samples that can be injected into the instrument reproducibly by the autosampler.

The forms of carbon that can be measured by this procedure include the following:

- soluble, nonvolatile organic carbon (e.g., natural sugars)
- soluble, non-purgeable volatile organic carbon (e.g., mercaptans, alkanes, low molecular weight alcohols)
- insoluble, partially volatile carbon (e.g., low molecular weight oils)
- insoluble, particulate carbonaceous materials (e.g., cellulose fibers)
- soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter (e.g., oily matter adsorbed on silt particles).

Because of purging, most volatile organic solvents may be lost.

2. SUMMARY

TOC concentration in water is measured by the use of an automated TOC analyzer. The sample is acidified (if not preserved prior to receipt) and sparged with nitrogen (N_2) gas to remove inorganic carbon. Organic carbon is then oxidized to carbon dioxide (CO_2) by persulfate ($S_2O_8^{-2}$) in the presence of ultraviolet (UV) light. The resultant CO_2 is sparged from the sample and carried in a stream of N_2 gas to a non-dispersive infrared detector

(NDIR). TOC concentration in the sample is calculated as a function of CO_2 peak area by use of a linear equation generated from a previously analyzed multipoint initial calibration. Sample aliquots, reagents and waste are transferred through the system by means of the autosampler apparatus.

Dissolved Organic Carbon (DOC) can also be measured by this procedure. Although Paragon prefers that samples be filtered prior to receipt at the laboratory, this filtering can be done after receipt.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of a proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating logbooks, analytical review sheets and/or the case narrative indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of measures taken to correct these errors.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Any inorganic carbon (e.g., dissolved CO_2, HCO_3^-, and CO_3^{-2}) present in the sample at the oxidation step will contribute to the CO_2 reaching the detector and consequently give a high bias to the measured TOC concentration. Inorganic

carbon must either be removed from the sample prior to the oxidation step, or be accounted for in the final calculation. When the Phoenix 8000 instrument is operating in the TOC mode, the sample is routinely acidified and sparged to remove inorganic carbon prior to oxidation of organic carbon. Note that volatile organic compounds may be lost when inorganic carbon is sparged from the sample.

4.2 A study published by the instrument vendor (Tekmar-Dohrmann) indicates that sulfuric acid (H_2SO_4) could form SO_3 gas in the UV reaction cell. Because SO_3 has similar absorption in the infrared region as CO_2, the SO_3 can cause a positive interference in the NDIR detector of the instrument. Therefore, it is recommended that phosphoric acid (H_3PO_4) be used instead of H_2SO_4 where acid preservation is designated for aqueous TOC samples.

Acidification to pH$\leq$2 at time of collection is desirable for unstable samples, however, it should be noted that acid preservation invalidates any inorganic carbon determination on the samples.

4.3 Chloride (Cl^-) ions can react with persulfate in the reaction cell to form Cl_2 (gas). If the Cl^- concentration in a sample is high (≥ 1000mg/L) this reaction can compete with the oxidation of organic C for persulfate. This reaction can lead to excessive peak tailing of the signal from the NDIR detector. At very high Cl^- concentrations (common to brines, seawater, and some chemical wastewaters) the effect can be severe and low TOC recovery can result because some of the organic matter will not be oxidized in the established analysis time. Therefore, hydrochloric acid (HCl) should not be used as a preservative for water samples designated for TOC analysis. As noted previously, the instrument manufacturer recommends the use of phosphoric acid as a preservative for aqueous samples.

4.4 Because solid particles can plug or damage the 8-port valve in the instrument, it may be necessary to filter samples that contain particulates or to allow the solids to settle out prior to analysis.

5. APPARATUS AND MATERIALS

5.1 Phoenix 8000 TOC analyzer (Tekmar-Dohrmann), or equivalent

5.2 pH paper, narrow-range, acidic

5.3 vials, glass, 40mL VOA-type

5.4 syringe filters, Life Sciences IC Acrodisc®, 25mm, 0.45um Supor® (PES) membrane, or equivalent, for filtering samples prior to DOC analysis (Section 12)

6. REAGENTS - Only reagent grade or better chemicals shall be used

6.1 nitrogen (N_2), 99.999% purity, used as carrier and purge gas

6.2 reagent water, (HPLC grade or Milli-Q ASTM Type II)

6.3 phosphoric acid, H_3PO_4, concentrated, reagent grade

6.4 acid reagent for IC sparging: Add 100mL conc. H_3PO_4, to 500mL of reagent water.

6.5 potassium hydrogen phthalate (KHP), used to create the in-house first-source TOC stock solution.

6.6 copper (Cu) granules

6.7 tin (Sn) granules

6.8 sodium persulfate reagent: transfer 100g of sodium persulfate ($Na_2S_2O_8$) to a large beaker. To the beaker add 850mL of reagent water and 36mL of conc. H_3PO_4. Place a magnetic stir bar into the beaker and stir on a magnetic stir plate until all of the solid particles are dissolved. (expiration date = 1 year).

6.9 STANDARDS

6.9.1 TOC stock solution, 1000mg/L TOC, first source: Prepared in-house by adding 2.13g of KHP ($C_8H_5KO_4$) to a 1L Class A volumetric flask half-filled with reagent water. Place a magnetic stir bar into the flask and stir on a magnetic stir plate until all of the solid particles are dissolved. Carefully add 1.0mL of phosphoric acid to acidify the solution to pH $\leq$2, let cool to room temperature. Bring to near full volume with reagent water and verify solution pH as $\leq$2. Bring to full volume with reagent water. **Refrigerate.** The expiration date of this solution is 1 year or less as described in SOP 300. Discard the solution if a precipitate forms or degradation is suspected.

6.9.2 Initial calibration standards: Prepared at a minimum of 5 levels to bracket the linear range of the detector. Prepared by diluting aliquots of the 1000mg/L TOC stock solution with reagent water. Calibration standards with concentrations of 10mg/L or greater can be stored for 1 year or as described in SOP 300. Standards with concentrations of less than 10mg/L are made daily upon use.

6.9.3 "Demand" TOC reference standard, second source: This is a stock standard solution obtained from a commercial vendor that is used to prepare the ICV/LCS standard. Alternately, the standard can be prepared in-house from sources independent of the calibration solutions, per the directions contained in the referenced method. The expiration date of this standard is the manufacturer's expiration date or 1 year from preparation ($\geq$10mg/L), whichever is shorter.

6.9.4 ICV/LCS (Initial Calibration Verification and Laboratory Control Sample): An aliquot of the "Demand" TOC reference stock standard is diluted with reagent water according to instructions provided by the vendor. The reference concentration of the prepared standard is

provided by the vendor and may vary from lot number to lot number. The concentration of the ICV is typically different from the CCV and between 20-40mg/L.

6.9.5 CCV (Continuing Calibration Verification) standard: An aliquot of the TOC stock solution is diluted with reagent water to a concentration at or below the mid-point of the calibration range. The concentration of the CCV is typically 30mg/L for a calibration range of 0.5-60mg/L. This standard expires in the shorter of 6 months or the expiration date of the standard it was prepared from.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 All samples should be collected according to an approved sampling plan.

7.2 Sampling and storage of samples in amber glass bottles is preferable. Plastic containers, such as conventional polyethylene and cubitainers, are permissible if it is established that the containers do not contribute contaminating organics to the sample or adsorb organics from the sample.

7.3 Methods EPA 415.1 and SW9060 provide for chemical preservation of samples using either hydrochloric (HCl) or sulfuric (H_2SO_4) acid. Method SM5310 C provides for chemical preservation of samples using either sulfuric or phosphoric acid (H_3PO_4). As discussed in Section 4.2, a technical note released by the instrument manufacturer (Tekmar-Dohrmann) recommends use of phosphoric acid to avoid possible instrumental interferences. Although Paragon can accept and process samples preserved with any of the three acids, it is Paragon's preference and practice to provide for phosphoric acid preservation to pH$\leq$2.

7.4 The referenced methods do not prescribe a maximum holding time allowance. Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between collection of samples and analysis should be minimized. Paragon's policy is to analyze samples within 28 days of collection.

7.5 Samples should be kept cool (4±2°C) and protected from sunlight and atmospheric oxygen.

8. PROCEDURE

8.1 INSTRUMENT SET UP

Prior to analyis, check to see each of the following are adequate for the amount of samples to be analyzed:

8.1.1 N_2 carrier gas, 500^+psi from cylinder.

8.1.2 Ample supplies of persulfate reagent, sparging acid, and reagent water.

8.1.3 Halogen scrubber, ample life.

8.1.4 Carrier gas flow rate (200cc/min, ±10%).

8.1.5 Gas/liquid separator water level filled to waste outlet.

8.1.6 Mist trap is empty, drain if necessary.

8.1.7 Thumbscrews of 8-port valve are hand tightened.

8.2 INITIAL CALIBRATION

8.2.1 Prepare calibration standards as described in Section 6.9 above. Typical concentrations comprising the calibration curve are 1.0, 4.0, 10, 20 and 40ppm.

8.2.2 Analyze the calibration standards on the instrument using the instrument software (TOC Talk™).

8.2.3 After analyzing the standards, the instrument software will calculate a linear equation to fit concentration with instrument response. To be acceptable, the coefficient of variation (r^2 or "r-squared" value on the output) must be 0.99 or greater.

8.3 CALIBRATION VERIFICATION

8.3.1 ICV: After an acceptable initial calibration has been established, an initial calibration verification (ICV) check standard must be analyzed. The ICV must be prepared from a parent source that is independent from that used to prepare the calibration standards. The ICV is typically prepared at a concentration near the midpoint of the calibration range, although other concentrations should be analyzed occasionally. See Section 6.9.4 above for preparation guidance, and QC Table following for acceptance criteria and corrective measures to be taken if necessary.

Since there is no sample preparation step involved in this analysis, the ICV check standard can serve a dual role as the laboratory control sample (LCS) for a quality control (QC) batch of 20 or fewer samples.

8.3.2 CCV: A CCV check standard is run at the beginning and conclusion of each analytical sequence and after every 15 or fewer injections in the sequence. **If running samples by SW9060 protocol, this CCV should be prepared from a source other than that used to prepare the ICAL (i.e., a second source)**. Preparation of the CCV is described in Section 6.9.5. Refer to QC Table following for acceptance criteria and corrective measures to be taken if necessary.

8.4 SAMPLE ANALYSIS

8.4.1 Samples must be analyzed for TOC in QC batches of 20 or fewer samples. See Section 9 for QC requirements (type and frequency).

Confirm that pH is ≤2 for each sample prior to analysis and record the pH test result on Form 647.

8.4.2 Prior to aliquoting, all samples should be homogenized by thorough shaking or agitation of the sample bottle.

8.4.3 For samples analyzed per Method SW9060 protocol, quadruplicate analyses must be performed for all field samples. Report the average result of the four (4) analyses and the RSD (Relative Standard Deviation). The range of values may be obtained from the raw data.

8.4.4 If the TOC concentration of a sample exceeds the calibration range (i.e., exceeds the concentration of the highest calibration standard), the sample must be diluted and reanalyzed as necessary until the concentration is within range.

9. QUALITY CONTROL (QC)

See QC Table following for acceptance criteria and corrective measures to be taken if necessary.

9.1 METHOD BLANK

One method blank (MB) must be analyzed with every QC batch of 20 or fewer samples to demonstrate that potential contaminants within the analytical system are in control. The MB consists of an aliquot of reagent water.

9.2 LABORATORY CONTROL SAMPLES

One laboratory control sample (LCS) must be analyzed with every QC batch of 20 or fewer samples to demonstrate the effectiveness of the analytical system. The LCS composition is identical to that of the ICV check standard (see Section 6.9.4). Since there is no preparation step in this analysis, the ICV check standard at the beginning of an analytical sequence can serve a dual role as the LCS for a QC batch.

9.3 MATRIX SPIKES

Matrix spike (MS) samples consist of field samples into which known concentrations of target analytes have been introduced. Analysis of matrix spikes provides information on the effect of sample matrix on target analyte detection. A matrix spike duplicate (MSD) is typically run with the MS.

Sample volume permitting, one pair of matrix spike/matrix spike duplicate (MS/MSD) analyses must be performed for every 20 samples. The matrix spiked samples are prepared by spiking aliquots of a selected field sample in the preparation batch with aliquots of the 1000mg/L stock standard.

Analyte recovery for the MS and MSD is calculated as shown below:

$$\%R = \frac{(Conc._{Found} - Conc._{.Sample})}{Conc._{Target}} \quad X \quad 100$$

where:

$Conc_{Found}$ = analyte concentration found in the MS or MSD sample

$Conc_{Sample}$ = analyte concentration found in the field sample

$Conc_{Target}$ = target (anticipated) analyte concentration based on amount spiked

As a measure of precision, the relative percent difference (RPD) of the laboratory duplicate sample pair (or MS/MSD or LCS/LCSD pair) is calculated as shown below:

$$RPD\ (\%) = \frac{(Result_{MS} - Result_{MSD})}{(Result_{MS} + Result_{MSD}) / 2} \quad X \quad 100$$

9.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. The LCS, MS, or both may be analyzed in duplicate to serve this purpose. Precision is expressed as Relative Percent Difference (RPD) (see above).

SW9060 protocol requires a "spike duplicate sample for every 10 samples". If analyzing samples by SW9060 protocol, include either an LCSD or (if sufficient sample volume is provided) an MSD *for every 10 samples analyzed*. If there is insufficient sample for the MSD, then either a second LCS/D pair can be analyzed in the latter half of the prep batch, or prep batches may be limited to 10 samples. **Note that this requirement does not apply to samples being analyzed by Method 415.1.**

9.5 METHOD DETECTION LIMIT STUDY

A method detection limit (MDL) study shall be conducted in the manner prescribed by SOP 329. The MDL study shall be performed as needed and at a minimum, annually.

10. DEVIATIONS FROM METHOD

See discussion in Sections 4.2 and 7.4 regarding acid preservation of samples. Methods 415.1 and SW9060A both describe the homogenization of samples by means of a blender. In order to protect the instrument from being clogged by particulate matter, this approach is not utilized at Paragon (see Section 8.4). This SOP contains no other known deviations from the promulgated methods.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The laboratory facilities are equipped with safety shower, eyewash station, fire extinguisher, fire blanket, and first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

11.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.6 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL
The aqueous solution left over from the Potassium Hydrogen Phthalate (KHP) standard preparations as well as all of the acidified aqueous sample waste should be disposed of in the Aqueous Laboratory Waste stream.

12. REFERENCES

12.1 USEPA, EPA-600/4-79-020, Methods for the Chemical Analysis of Water and Wastes, Method 415.1, "Total Organic Carbon by Combustion or Oxidation", 1983.

12.2 USEPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Chapter 5, Method 9060, "Total Organic Carbon", Revision 0, September 1986.

12.3 Standard Methods for the Examination of Water and Wastewater, 18th Ed., 1992. "Total Organic Carbon, Persulfate-Ultraviolet Method", 5310 C.

12.4 Phoenix 8000 User Manual, Tekmar-Dohrmann, 1998.

12.5 Application Note, "TOC Analysis: The Acid Preservation Debate", Tekmar-Dohrmann, 2001.

12.6 "Method Development Study: Dissolved Organic Carbon (DOC)", Darryl Patrick, 2007. J:\QAOffice\Demonstrations\

DOCUMENT REVISION HISTORY

11/12/07: Extensive reworking and clarification. Added DOC language Section 2, updated LIMS program specification language Section 3.3, added sample homogenization text Section 8 and spike duplicate analysis verbiage Section 9.4. Removed Section 8 language about acidifying MB with phosphoric acid (samples arrive already acidified). Removed QC acceptance criteria in body and referenced QC Table instead, added LIMS program specification limits reference as footnote to QC Table. Removed references to drinking water analyses throughout. Added reference to internal study of syringe filters and network location to REFERENCES 12.6. Added DOCUMENT REVISION HISTORY.

Analytical Method: EPA 415.1; SW9060, SM5310 C	**Parameter:** Total Organic Carbon (TOC) by Oxidation		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria **	Corrective Action
Initial Calibration, minimum 5-point	As needed (i.e., at on-set of analyses or when continuing calibration does not meet criteria)	r^2 must be ≥ 0.99	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze initial calibration to obtain acceptable curve.
Initial Calibration Verification (ICV), second source check standard run near mid-point of calibration curve (Because no sample preparation steps are involved, the ICV can also serve as the LCS for the initial QC batch of samples analyzed)	Once after each initial calibration	For Method 415.1 and SW9060 analyses, the ICV result must be within ±15% of the expected concentration	Prepare another ICV and analyze. If ICV still fails, system must be recalibrated.
Continuing Calibration Verification (CCV), run at or below midpoint of calibration; CCV concentration must be different from ICV concentration	Run after every 15 or fewer sample injections and to begin and end an analytical sequence	For Method 415.1 and SW9060 analyses, the CCV result must agree within ±15% of the expected concentration	Check that calculations and preparation are correct, evaluate/ correct instrument malfunction; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after the last acceptable CCV must be reanalyzed.
Laboratory Control Sample (LCS), second source standard run near mid-point of calibration curve (The ICV can also serve as the LCS for the initial QC batch of samples analyzed)	One LCS in every QC batch of 20 or fewer samples	For Method 415.1 and SW9060 analyses, the LCS result must be within ±15% of the expected concentration	Check calculations, spike preparation, and freshness of the standard used for spiking. Prepare another LCS and analyze. If LCS still fails, samples in QC batch must be reanalyzed.
Laboratory Duplicate (DUP)	For Method 415.1 and SW9060, the LCSD & MSD both can serve as a laboratory duplicate analysis	For both Method 415.1 and SW9060, the RPD between the duplicate pair should be ≤20%	For RPDs outside of QC limits, check all calculations for errors. Narrate.
Method Blank (MB)	One MB per every QC batch of 20 or fewer samples	For Method 415.1 and SW9060 analyses, the MB result must not exceed RL (usually 1mg/L TOC)	Prepare another MB and analyze. If MB still fails, samples in QC batch must be reanalyzed.
Matrix Spike and Matrix Spike Duplicate (MS/MSD)	Volume permitting, one MS/MSD pair per batch of ≤ 20 field samples	For Method 415.1 and SW9060 analyses, MS/MSD recoveries should meet advisory limits of ±20% (80-120% of the expected values)	Check for documentable errors (e.g., calculations and spike preparation). For Method 415.1 and SW9060 analyses, sample matrix effects are

Analytical Method: EPA 415.1; SW9060, SM5310 C	**Parameter:** Total Organic Carbon (TOC) by Oxidation		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria **	Corrective Action
		and RPD should be $\leq$ 20	analyses, sample matrix effects are the most likely cause if no errors are found. Document and note in case narrative.
Method Detection Limit (MDL) Study; run per guidance in SOP329	As needed and, at minimum, annually	Positive result < analyte reporting limit (usually 1.0PPM for both Method 415.1 and SW9060 analyses)	Determine the reason for failure and correct problem with system; then repeat study. If MDL study still not acceptable, discuss with Department and QA Managers, RL may be adjusted, if necessary.

**** Acceptance Limits are as stated within Table, or as otherwise specified in the applicable LIMS program specification.**

Paragon Analytics

Documentation of Preservation / Acidification and Filtration of Water Samples for TOC / DOC SOP 670 rev. __

Workorder ID/ Sample ID	DOC							TOC / DOC			Comments
	Date	Initials	Samples Filtered by PAI or Client	Filtered Through 0.45um? (Y/N)	Filter Spec's LOT #	Volume of H_3PO_4 Added (mL)	Conc. H_3PO_4 LOT #	Date	Initials	pH at Time of Analysis	

Filter Blanks = Milli Q Double Deionized Water. **Reviewed by/date _____** Instrument SN 01-011007 **Form 647r0.xls**

Must Discard 30 Days from _____ (date printed)

Amended 3/17/08 to include Steam Generator Operator's Aid. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 671 REVISION 6

TITLE: **DETERMINATION OF N-HEXANE EXTRACTABLE MATERIAL (HEM) AND SILICA GEL TREATED HEXANE EXTRACTABLE MATERIAL (SGT-HEM) BY EXTRACTION AND GRAVIMETRY FOR AQUEOUS SAMPLES -- METHODS EPA 1664A AND SW9070A**

FORMS: **603 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/20/07
QUALITY ASSURANCE MANAGER _____ DATE 2/20/07
LABORATORY MANAGER _____ DATE 2-20-07

HISTORY: Was previously SOP 1115. As SOP 671, Rev2, 9/19/02; Rev3, 12/9/02; Rev4, 2/23/04; Rev5, 2/27/06; Rev6, 2/9/07.

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- EPA 1664A and SW9070A -- are used to determine the content of n-hexane extractable material (HEM) in environmental water samples. Extractable materials that may be analyzed are relatively non-volatile hydrocarbons, vegetables oils, animal fats, waxes, soaps, greases and related materials. This method is not applicable to measurement of materials that volatilize at temperatures below approximately 85°C. The typical reporting limit is 5.0mg/L, which is equivalent to the Minimum Level (ML) required in Method 1664A. Note that SW-846 Method 9070A directs the reader to EPA Method 1664A, Publication No. EPA-821-R-98-002, for the method procedure. The suffix "A" and the method title were inadvertently omitted during the last promulgation as part of SW-846 Update IIIA.

2.0 SUMMARY

A 1L sample is acidified to pH ≤2 and serially extracted three times with n-hexane in a separatory funnel. The extract is dried over sodium sulfate. The solvent is ~~distilled~~ evaporated DAS from the extract and the HEM is desiccated and weighed. If the HEM is to be used for determination of SGT-HEM, the HEM is re-dissolved in n-hexane, then an amount of silica gel proportionate to the amount of HEM is added to remove polar materials. The solution is filtered to remove the silica gel, the solvent ~~distilled~~ evaporated DAS, and the SGT-HEM is desiccated and weighed.

3.0 RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of

Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this procedure to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing equipment are possible sources of contamination. Thorough cleaning of glassware is necessary. Materials used in the analysis must be demonstrated to be free of interferences by analyzing laboratory blanks.

4.2 Fine particulates suspended in the sample, as well as the sodium sulfate used in this procedure, could cause a positive interference by passing through the filter paper. If the filter paper is inadequate for removal of the fine particulates, then use of a 0.45µm filter is recommended.

4.3 Some crude oils and heavy fuel oils contain a significant percentage of materials that are not soluble in n-hexane (e.g., asphaltenes). Accordingly, recoveries of these materials may be low.

5.0 APPARATUS AND MATERIALS

5.1 boiling flasks, 500mL

5.2 PTFE-boiling chips: pre-clean by rinsing with methylene chloride, then dry

5.3 desiccator

5.4 indicating Drierite™

5.5 lint-free wiping cloths (e.g., KimWipes™), used to keep boiling flasks free of external contamination

5.6 analytical balance, 0.0001g sensitivity, calibration verified per SOP 305

NOTE: A 2mg weight is used in addition to the standard (SOP 305) calibration verification. This 2mg calibration verification is recorded on the benchsheet.

5.7 separatory funnels, with PTFE stopcock and stopper, 1500mL

5.8 graduated cylinder, 1L

5.9 Erlenmeyer flasks, 1500mL, or as appropriate

5.10 funnels, glass, for holding filter paper

5.11 filter paper, Whatman Glass Fiber Filter, GF/F, 142mm, #1825-142 or equivalent

5.12 steam generator and S-Evap unit or equivalents

5.13 Pasteur pipets, disposable

5.14 drying oven capable of maintaining 130-150ºC, and monitored per SOP 320

5.15 vacuum pump, with inlet hose

5.16 stirring hot plate

5.17 PTFE-coated magnetic stir bars

6.0 SOLVENTS

6.1 n-hexane, 85% purity, 99% minimum saturated C_6 isomers, residue less than 1mg/L.

6.2 acetone, ACS grade, residue less than 1mg/L.

7.0 REAGENTS

7.1 organic-free reagent water: laboratory deionized (DI) water is suitable.

7.2 hydrochloric acid (HCL) or sulfuric acid (H_2SO_4), 1:1 Solution: Mix equal volumes of ACS grade concentrated HCl or H_2SO_4 into DI water.

7.3 anhydrous sodium sulfate (Na_2SO_4), ACS grade, granular: Kiln for a minimum of 4 hours; cool to room temperature before use.

7.4 silica gel, anhydrous, 75-150µm, Davisil Grade 923, Supelco #21447-7a or equivalent. Dry at 130-150ºC for a minimum of 24 hrs. This material is stored in the drying oven until use.

8.0 STANDARDS

8.1 stearic acid, 98% minimum purity.

8.2 hexadecane, 98% minimum purity.

8.3 All standards are maintained per PAR SOP 300. Unopened stock standards are valid until the manufacturer's expiration date and may be stored at room temperature in flame-sealed ampules or as otherwise recommended by the manufacturer. After opening ampules, the stock solution may be stored at room temperature in a tightly capped vial and retained for up to six months, however, the unused stock remaining after opening and initial use is typically discarded. Intermediate standards (e.g., OPR Spiking Solution) may also be stored in a tightly sealed container at room temperature and retained for up to six months. Standards may be replaced sooner if laboratory quality control (QC) analyses or other factors indicate deterioration.

Target analyte stock standards are generally purchased as certified solutions, and used to create calibration and spike standards. **Note that for this analysis, only *one* source of standard is required, a check standard from an independent (2^{nd}) source is *not* required for this procedure.**

8.4 On-going Precision and Recovery (OPR) Spiking Solution (Hexadecane/Stearic acid): The OPR Spiking Solution is used to create laboratory control samples (LCSs), and is either purchased as a 4.0mg/mL in acetone commercial standard, or prepared as follows: Place 200±2mg of stearic acid and 200±2mg of hexadecane in a 100mL volumetric flask and fill to the mark with acetone. After the hexadecane and stearic acid have dissolved, transfer the solution to a 100-150mL glass container with a Teflon-lined cap; label appropriately. Verify concentration of spiking solution by removing 10.0mL of the solution and placing it in a tared weighing pan. Evaporate to dryness in a fume hood, then weigh. The mass of the residual materials in the pan must be 40±1mg.

8.5 All stock and intermediate standards are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials, and also documents the concentration of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis are maintained by the applicable laboratory Department.

9.0 SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

9.1 Samples should be collected according to an approved sampling plan.

9.2 A minimum of 1L of representative sample collected in a clean glass bottle is needed for analysis. If selected samples are to be used for matrix spike/matrix spike duplicate analysis, then additional aliquots must be collected accordingly.

9.3 If a sample is known or suspected to contain greater than 1,000mg/L of HEM, then a smaller volume of sample may be utilized for this analysis. **Note that this**

analysis does not allow subsampling of a water sample from the collection bottle at the laboratory. If smaller sample aliquots are desired, then they must be collected in the field, then shipped to the laboratory for analysis.

9.4 The pH of the sample is adjusted to ≤2 with hydrochloric or sulfuric acid, at the time of collection. If a sample when checked for pH at the laboratory upon receipt yields a pH >2, the Paragon Project Manager (PM) is notified, and will contact the client for instructions as to whether or not sample analysis should proceed.

9.5 Samples are stored at 4±2°C until analysis. No holding time has been established for this determination; Paragon observes a 28-day holding time to extraction for this procedure.

10.0 PROCEDURE

10.1 A sufficient number of boiling flasks must be prepared to accommodate all field and QC samples (e.g., MB, LCS/LCSD, MS/MSD) in the batch. Label, add 3-5 boiling chips, wipe and weigh each flask on the analytical balance to the nearest 0.1mg. Record the weight on the benchsheet.

NOTE: Because the flasks are cleaned (SOP 334) and dried in a kiln, they do not need to be rinsed with hexane and dried prior to use. Store the flasks in a desiccator until needed.

One method blank (MB) and one OPR spike sample (LCS, see Section 8 above), must be prepared with each batch of twenty or fewer field samples. Though not required by the Methods, it is Paragon's policy to prepare and analyze a duplicate laboratory control sample (LCSD), with each batch. Use a 1000mL aliquot of DI water for the MB, LCS and LCSD sample (place each DI water aliquot into an appropriately labeled separatory funnel). If the client provided sufficient sample volume, also prepare a matrix spike/matrix spike duplicate (MS/MSD) with each batch. Acidify all QC samples to pH<2. Spike LCS/LCSD and MS/MSD samples with OPR Spiking Solution to yield a target value of 40mg HEM/sample.

10.2 EXTRACTION

10.2.1 Using a marking pen, mark the sample's water level on the side of the sample container. Carefully pour the sample into a clean 1500mL separatory funnel.

10.2.2 Add 15mL of n-hexane to the emptied sample bottle, and re-cap with the container's lid. Shake the bottle to rinse the interior surfaces well with hexane. Pour the solvent rinse into the separatory funnel containing the sample. Repeat this Step.

10.2.3 For the MB, LCS/LCSD and MS/MSD QC samples, add 30mL hexane to each separatory funnel.

10.2.4 Re-fill the sample bottle to the mark with tap water, then pour the tap water into a graduated cylinder and measure what the volume of the original sample was. Record the volume (Vs in liters) on the benchsheet.

10.2.5 Extract the sample in the separatory funnel by shaking for two minutes, vent as needed to minimize pressure buildup.

10.2.6 Allow the organic phase (top solvent layer) to separate from the aqueous phase for a minimum of 10 minutes.

If an emulsion forms between the two phases, that is greater than ⅓ the volume of the solvent layer, break the emulsion using one of the following mechanical techniques:

- gentle stirring
- addition of sodium chloride
- filtration through glass wool
- drain emulsion into a glass centrifuge tube, spin to break emulsion
- use an ultrasonic bath cooled with ice

The optimum technique to employ depends on the extent of the emulsion formed. Consult Supervisor for details as to how a particular technique should be performed.

10.2.7 Place approximately 10g of anhydrous sodium sulfate into a filter funnel with filter paper and rinse with a small portion of n-hexane. Discard the rinsate appropriately. Place a pre-weighed boiling flask containing boiling chips under the filter funnel.

10.2.8 Drain the water (aqueous phase) from the extracted sample in the separatory funnel, into a 1500mL Erlenmeyer flask and momentarily set aside.

Then, suspend the separatory funnel over the filter funnel containing the pre-wetted sodium sulfate, and drain the n-hexane layer (solvent phase) through the sodium sulfate (drying agent) and into the boiling flask.

Rinse the tip of the separatory funnel with a few mL of hexane, allowing the rinse to pass through the sodium sulfate and into the boiling flask.

10.2.9 Return the sample aqueous phase that was momentarily set aside to the separatory funnel; add 30mL of hexane.

Extract as before by shaking for two minutes, venting as needed to minimize pressure buildup.

Allow the phases to separate for a minimum of 10 minutes; treat emulsion, if formed, as necessary.

Drain the water phase from the separatory funnel into the same 1500mL Erlenmeyer flask and momentarily set aside.

Suspend the separatory funnel over the same filter funnel containing sodium sulfate, and drain the solvent phase through the sodium sulfate into the same boiling flask containing the first extracted solvent portion.

Rinse the tip of the separatory funnel with a few mL of hexane, allowing the rinse to pass through the sodium sulfate and into the boiling flask.

10.2.10 Repeat Step 10.2.8 again, resulting in a total of three extractions of the aqueous sample using 30mL portions of n-hexane, passing the post-extraction solvent portions through the sodium sulfate drying agent, and combining the dried solvent phases into the same pre-weighed boiling flask.

10.2.11 To ensure quantitative transfer of the HEM from the drying column (filter funnel with sodium sulfate), rinse the sodium sulfate with 10mL of hexane, collecting the rinse in the same boiling flask..

10.2.12 A milky extract (i.e., contents of the boiling flask) indicates the presence of water. If the extract is milky, allow the solution to stand for up to one hour to allow the water to settle. Decant the solvent (upper) layer through sodium sulfate (use funnel and filter paper setup as previously described) to remove any excess water. Collect in a clean pre-weighed boiling flask. Rinse the initial boiling flask, filter paper and sodium sulfate, with small portions of n-hexane to ensure a quantitative transfer.

10.3 DETERMINATION

10.3.1 Evaporate the hexane extract contained in the boiling flask on top of the S-Evap unit. The temperature of the S-Evap should be maintained at <85°C to ensure that the more volatile components extracted into the hexane are not lost (note that stearic acid begins to volatilize at 90°C).

10.3.2 Bring flask to dryness. Evacuate remaining hexane vapors using a vacuum pump with hose.

10.3.3 Move the boiling flasks to a desiccator and store for several hours.

10.3.4 Weigh each flask and record on benchsheet. Return flask to desiccator, store again for several hours, then re-weigh. Repeat this step until a constant weight is achieved.

10.3.5 If the residue does not look typical (i.e., affected by watery extract or contaminated with sodium sulfate), then re-dissolve the residue in n-hexane, filter though a fresh drying funnel containing sodium sulfate, ensuring a quantitative transfer, and repeat evaporation process.

10.3.6 Calculate HEM per Section 11 below.

10.4 SILICA GEL TREATED HEM (SGT-HEM)

Silica gel cleanup is generally not performed unless the client specifies the need for separate data for HEM and SGT-HEM analytes. Also, if no HEM is detected, then there is no reason to proceed with the silica gel treatment.

10.4.1 If silica gel treatment is needed, then the MB and LCS (LCSD) must also be carried through the silica gel treatment. If the sample associated with the MS/MSD does not require silica gel treatment, then there is also no need to perform the silica gel treatment on the MS/MSD.

10.4.2 Re-dissolve the HEM in 80-90mL of n-hexane; swirl as necessary.

10.4.3 The amount of silica gel to use for treatment can be adjusted (up to 30g) based on the known weight of HEM. A 3.0g amount of silica gel can adsorb approximately 100mg of HEM. Add 3.0±0.3g of silica gel to the boiling flask for every 100mg of HEM measured. Add a PTFE-coated stir bar and stir on a magnetic stirrer for approximately 5 minutes.

10.4.4 Filter the solution through hexane-rinsed filter paper, into a pre-weighed boiling flask containing a few boiling chips. Rinse the sample flask, filter paper and funnel with a few aliquots of hexane (up to about 15mL total); evaporate the hexane on the S-Evap unit as described previously.

10.4.5 Cool in desiccator and determine constant weight as described previously (Steps 10.3.3. and 10.3.4).

10.4.6 Calculate SGT-HEM per Section 11 below.

11.0 CALCULATIONS

11.1 Calculate HEM as follows:

$$\text{SampleHEMConc.}(\text{mg/L}) = \frac{W_h\,(\text{mg})}{V_s\,(\text{L})}$$

where:

W_h = weight of extractable material (Step 10.3.4)

Vs = sample volume (Step 10.2.3)

11.2 Calculate the recovery of the OPR QC spike using the following equation:

$$\text{Recovery (\%R)} = \frac{\text{measuredconc.of HEM}}{\text{spikedconc.of HEM}} \text{ X } 100$$

See attached QC Table. Note that Method EPA 1664A provides different ongoing precision and recovery limits for the HEM vs SGT-HEM laboratory control sample.

11.3 Calculate the recovery of the MS/MSD QC samples as follows:

$$\text{Recovery (\%R)} = \frac{HEM_{Found} - HEM_{Sample}}{HEM_{Target}} \text{ X } 100$$

where:

HEM_{Found} = calculated HEM concentration in the MS or MSD

HEM_{Sample} = calculated HEM concentration in the field sample

HEM_{Target} = the target concentration of the added HEM spike

11.4 Calculate the Relative Percent Deviation (RPD) of the MS/MSD QC samples using the following equation:

$$\text{RPD (\%)} = \frac{\left|HEM_{MS} - HEM_{MSD}\right|}{\left(\frac{HEM_{MS} + HEM_{MSD}}{2}\right)} \text{ X } 100$$

where:

HEM_{MS} = calculated HEM concentration in the MS

HEM_{MSD} = calculated HEM concentration in the MSD

11.5 Calculate the concentration of SGT-HEM as follows:

$$\text{Sample SGT} - \text{HEM Conc.}(\text{mg} / \text{L}) = \frac{W_h\,(\text{mg})}{V_s\,(\text{L})}$$

where:

W_h = weight of silica gel treated extractable material (Step 10.4.5)

Vs = sample volume (Step 10.2.3)

12.0 QUALITY CONTROL

12.1 DEFINITION OF BATCH

A batch is defined as a group of ≤20 field samples of like matrix that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the MB, LCS (LCSD) and matrix spike and duplicate (MS/MSD). All QC samples must be carried through all stages of the sample preparation and measurement steps.

12.2 METHOD BLANK

Method blanks are aliquots of clean matrix (i.e., laboratory DI water) that have been prepared and analyzed in the same manner as the associated field samples. To be acceptable, concentrations of analytes of interest detected (if any) in the MB must be below the analyte reporting limit, or as otherwise specified in the LIMS program specification. If this criterion is not met, analyses should be halted and the source of the contamination found and corrected. See also attached QC Table.

12.3 OPR QC SAMPLE

This sample is comprised of a known concentration of target analyte contained in a clean matrix. This laboratory control sample (LCS) is analyzed to measure the accuracy of the analytical system. LCS recovery is calculated as shown in Section 11. See QC Table for evaluation criteria.

12.4 MS AND DUPLICATE

Matrix spikes consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection and recovery. MS recovery is calculated as shown in Section 11, see QC Table for evaluation criteria.

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this analysis, either a field sample may be analyzed in duplicate (DUP), or the laboratory control sample (LCSD) or matrix spike analysis (MSD) can be performed in duplicate. Recovery is calculated as

shown in Section 11, and precision (see Section 11 for calculation) is evaluated in terms of RPD. See QC Table for acceptance limits.

Possible causes for matrix spiked failure include:

- sample heterogeneity
- a sample matrix which inhibits extraction of spiked compounds
- high levels of HEM that "swamp out" the small amount of extractable materials added with the OPR spike.

NOTE: Typically, one MS and MS Duplicate pair is analyzed per batch. In the event that not enough sample volume is provided to generate MS and duplicate analyses, the requirement to perform these analyses is waived and an explanatory notation is made in the data package narrative.

For projects in which the client designates the MS/MSD samples, an analysis batch may not contain an MS/MSD pair because the required spikes were included in another batch. Where this occurs, a notation will be made in the data package narrative.

12.5 A METHOD DETECTION LIMIT (MDL) STUDY shall consist of the analysis of a minimum of seven replicate analyses for a target analyte at a concentration level near to the capabilities of the method. The MDL study is performed as needed, at a minimum, annually, following the guidance of SOP 329.

13.0 DEVIATIONS FROM METHOD

This procedure complies with the requirements of Methods EPA 1664A and SW9070A. There are no known deviations from the Methods.

14.0 SAFETY, HAZARDS AND WASTE DISPOSAL

14.1 SAFETY AND HAZARDS

14.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

14.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

14.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

14.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

14.1.5 All flammable compounds (i.e., hexane) must be kept away from ignition sources.

14.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

14.1.7 Food and drink are prohibited in all lab areas.

14.2 WASTE DISPOSAL

14.2.1 The aqueous solution left over from the original sample container shall be disposed of in the Aqueous Laboratory Waste or Radioactive Aqueous Lab Waste, as appropriate.

14.2.2 All empty solvent bottles shall be disposed of appropriately; note that all labels and markings must be defaced or the bottle labeled as empty prior to disposal.

15.0 REFERENCES

15.1 US EPA, EPA 821-R-98-002, February 1999, "N-Hexane Extractable Material (HEM: Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons)", Method 1664A, Revision A.

15.2 US EPA SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, "Method 9070", Update III, December 1996.

15.3 US EPA SW-846, Test Methods For Evaluating Solid Waste Physical/Chemical Methods, "Method 9070A", Update IIIA, April 1998.

DOCUMENT REVISION HISTORY

2/9/07: Minor clarifications added, format updated. Added form and DOCUMENT REVISION HISTORY.

Analytical Method: EPA 1664A; SW 9070A	**Parameter:** n-Hexane Extractable Material (HEM)		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
Method Blank (MB)	One per each batch of ≤20 field samples; one each time a reagent is changed	MB must not yield HEM content above the 5.0 mg/L reporting limit (RL)	Check all calculations. If no computation errors are found, prepare a fresh MB and analyze, associated samples must also be re-extracted and re-analyzed (if possible).
On-going Precision and Recovery (OPR) Sample; Laboratory Control Sample (LCS)	One per batch of ≤20 field samples	Results obtained must be within 79-114% of expected (known) concentration of HEM, and 64-132 % for SGT-HEM	Check calculations and preparation for documentable errors. If no errors are found, reanalyze OPR, associated samples must also be re-extracted and re-analyzed (if possible). If samples cannot be re-extracted, narrate.
Matrix Spike (MS)	One per batch of ≤20 field samples	Results obtained should be within 79-114% of expected concentration of HEM, and 64-132 % SGT-HEM	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, and associated OPR is within control limits, then sample matrix effects are the most likely cause. Note in narrative.
Matrix Spike Duplicate (MSD)	One per batch of ≤20 field samples	(See MS recovery criteria above) HEM RPD should be ≤18%; SGT-HEM RPD ≤34%	See MS recovery corrective actions above. For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/Project/QA Managers.
Method Detection Limit (MDL) Study; run at an analyte concentration near to but lower than the reporting limit (RL)	As needed; at a minimum annually	Must yield a positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with the analytical system. Repeat the MDL study. Consult with the Department/Project/ QA Managers (the Managers may determine that an adjustment to the RL is needed).

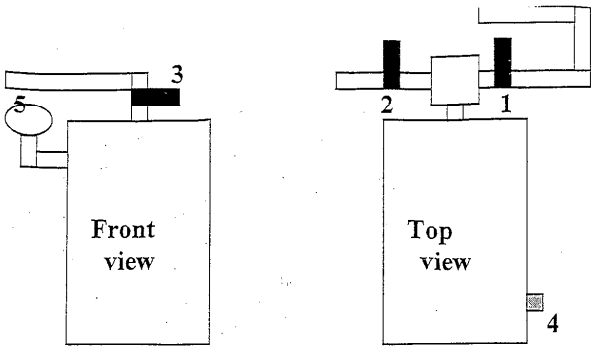
Paragon Analytics.

OIL & GREASE -- PREPARATION / ANALYSIS / CLEANUP – BENCHSHEET Form 603r9.frm (9/23/2003)

WO _____ AQ Solid _____ **Batch ID** _____ **M Spike Code** _____ **Analysis Code:** 9070A 9071 1664 **Balance ID** ____ **SOP** _____ **Rev** ___
Ex. Date/Time _____ (start) **Date/Time** _____ (stop) **Initials** _____ **Cleanup Code:** (3630C)Silica Gel **Cleanup Date/Time** _____ **SOP 644/Rev** __ **Initials** ____

SAMPLE					EXTRACT					
Sample No.	Amount (g / mL)	Matrix Spike (mL)	Matrix Spike Witnessed	Acidified? If so, amount used? (mL)	Date Evaporated to Final	Silica Gel (g)	Beaker Initial (g)	Beaker Final (g)	Difference (g)	Balance #5 2 mg weight check yielded result between 0.0019 – 0.0021 g ? Y / N Comments

Reagent Lots: HCl _____ H_2SO_4 _____ Silica Gel _____ Hexane _____ $NaSO_4$ _____ Reviewed by / Date _____



1. Water inlet valve
2. Steam blowout valve
3. Steam valve
4. Boiler switch knob
5. Steam pressure gauge

Steam Generator Start up

1. Check to see if steam blowout valve[2] is closed. (perpendicular to pipe) If not close it.
2. Open water inlet valve[1]. (parallel to pipe)
3. Turn boiler switch knob[4] on to 250. If boiler switch light does not come on re-check in five minutes. Light should be on. If light is not coming on contact supervisor.
4. After approximately 30 minutes Steam pressure gauge[5] should read between 20-60 psi. If not, wait until desired pressure is reached.
5. Open steam valve[3]. (parallel to pipe)

Steam Generator Shutdown

Caution: Pipes and Generator will be hot!

1. Turn boiler switch knob[4] to OFF
2. Close water inlet valve[1]. (perpendicular to pipe)
3. Close steam valve[3]. (perpendicular to pipe)
4. <u>SLOWLY</u>* open steam blowout valve[2]. (parallel to pipe)

**Caution: Do not open blowout valve fully until a majority of the steam is released. The tubing carrying the steam outside may come out of the wall.*

Must Discard 30 Days from _____ (date printed)

Amended 3/17/08 to include Steam Generator Operator's Aid. DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 672 REVISION 3

TITLE **EXTRACTION AND GRAVIMETRIC DETERMINATION OF LIPIDS IN TISSUES**

FORMS: **603** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8.17.07

QUALITY ASSURANCE MANAGER _____ DATE 8/16/07

LABORATORY MANAGER _____ DATE 8-20-07

HISTORY: Rev0, 1/8/03; Rev1, 3/6/04; Rev2, 2/27/06; Rev3, 8/16/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes procedures for determining the lipid content of tissues. This SOP is applicable to the determination of animal fats, vegetable oils, relatively nonvolatile hydrocarbons, waxes, soaps, greases, and related matter.

2. SUMMARY

A representative portion of solid tissue sample is mixed with a drying agent. The sample is then extracted with methylene chloride using a Soxhlet apparatus. The methylene chloride is evaporated from the sample and the dry residues recovered are measured gravimetrically and reported as the "lipids" from the tissue sample.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this procedure. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful analysis of an unknown proficiency test sample.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the analytical review sheets, logbook or case narrative indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Organic residues on glassware, as well as dust or other particulate matter can interfere with this procedure - tongs or clean gloves should be used at all times when handling flasks. This method is strictly empirical, and meaningful results can be obtained only by strict adherence to all details of the process.

The presence of non-oily extractable substances such as sulfur compounds, organic dyes, and chlorophyll may result in a positive bias. For the purpose of this method, all materials extracted and retained during this procedure are defined as lipids.

5. APPARATUS AND MATERIALS

5.1 analytical balance, 0.0001g sensitivity; verified per SOP 305

5.2 desiccating cabinets with viable Drierite® desiccant

5.3 steam generator and evaporator, Organomation S-Evap Model 120 or equivalent

5.4 laboratory tongs

5.5 Soxhlet apparatus consisting of the following:

- 500mL round flat-bottom flasks
- Soxhlet extractors
- fritted glass thimbles
- condensers with circulating cooling water

5.6 boiling chips, Teflon®, pre-cleaned with methylene chloride

5.7 beakers, sized as appropriate

5.8 lint-free wipes (i.e., KimWipes®)

5.9 vacuum pump with hose

6. SOLVENTS - Only pesticide grade or better solvents shall be used

6.1 methylene chloride (CH_2Cl_2), Burdick & Jackson #299-4 or equivalent

6.2 acetone

7. REAGENTS - Only reagent grade or better chemicals shall be used

7.1 sodium sulfate (Na_2SO_4), anhydrous, granular, EMD #SX0760E-5 or equivalent: purify by heating at approximately 400°C (i.e., kilning) for a minimum of four hours in a shallow tray.

7.2 Ottawa sand, EMD #SX0075-3 or equivalent

8. STANDARDS

8.1 All standards are maintained per PAR SOP 300 and are documented in Paragon's Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials, documents the concentration of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis for each standard are maintained by the applicable laboratory Department.

8.2 corn oil reference standard, Mazola® or equivalent: dilute in acetone to appropriate concentration, typically 0.1g/mL.

9. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 Samples should be collected according to an approved sampling plan.

9.2 Tissue samples should be collected in wide mouth glass jars, aluminum foil or resealable (Ziploc®) plastic bags and frozen as soon as possible after collection.

9.3 No holding time has been established for this test. Paragon follows a holding time for tissue samples of 28 days from collection to extraction.

10. PROCEDURE

10.1 For each field sample, add a few boiling chips to a uniquely identified, kilned flask. Use a dry, lint-free wipe to remove any dust or particulate matter present on the outside of the flask. Place flask in the dessicator and weigh to constant weight. Record weight on the benchsheet (Form 603).

10.2 For each field sample, weigh an appropriate mass of tissue (2-5g) into a suitably sized beaker. Add an equal or greater amount of granular sodium sulfate and stir until completely dry. Addition of more sodium sulfate may be needed. If enough sample material is present, then prepare one sample from each batch in duplicate (for duplicate analysis).

10.3 For each batch of 20 or fewer samples, prepare a method blank and a laboratory control sample (LCS) (see Section 11). If no sample duplicate will be prepared, prepare the LCS in duplicate (LCSD).

10.4 Transfer each prepared field and quality control (QC) sample to a Soxhlet thimble. Rinse the beaker into the thimble with methylene chloride to effect a full quantitative transfer. Spike the LCS/D with corn oil solution, typically 1mL of 0.1g/mL solution.

10.5 Assemble the Soxhlet apparatus and apply heat to the round bottom flask. Reflux for 18±2 hours.

10.6 Transfer the flask to the S-Evap and evaporate the extract to dryness. Evacuate

remaining solvent vapors using a vacuum pump with hose.

10.7 Place each flask in the desiccator and allow to sit – this process can take anywhere from several hours to several days.

10.8 Remove each flask from the desiccator. Weigh each flask on the analytical balance and record the weight on the laboratory benchsheet. Return each flask to the desiccator and allow to sit – again for a period of time from several hours to several days. Repeat this Step until a constant weight is achieved (note that if the flask hasn't achieved constant weight, it may still contain residual solvent vapors or moisture).

10.9 Calculate the lipid content as shown below:

$$lipids\ (mg/kg) = \frac{gain\ in\ weight\ of\ \ flask\ (mg)}{weight\ of\ \ tissue\ extracted\ (kg)}$$

11. QUALITY CONTROL

11.1 DEFINITION OF A BATCH

A batch is defined as a group of $\leq$20 field samples of like matrix that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS) and duplicate (Sample DUP or LCSD). All QC samples must be carried through all stages of the sample preparation and measurement steps.

11.2 METHOD BLANK

The method blank is an aliquot of clean matrix (i.e., Ottawa sand) that has been prepared and analyzed in the same manner as the associated field samples. To be acceptable, concentrations of lipids in the MB must be below the analyte reporting limit, or as otherwise specified in the LIMS program specification. If this criterion is not met, analyses should be halted and the source of the contamination found and corrected. See QC Table for further details.

11.3 LABORATORY CONTROL SAMPLE

The laboratory control sample is an aliquot of clean matrix (i.e., Ottawa sand) that has been "spiked" with a known concentration of target analyte, and is analyzed to demonstrate the accuracy of the analytical test. The recovery of target analyte (calculation shown below) should be within 80-120% of the expected (known) concentration of lipids:

$$\text{Percent Recovery (\%R)} = \frac{\text{Concentration}_{\text{Found}}}{\text{Concentration}_{\text{Expected}}} \times 100$$

See QC Table for further details.

11.4 LABORATORY DUPLICATE

A laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. To accomplish this, either a field sample or the laboratory control sample (LCS) is performed in duplicate. Precision is evaluated in terms of Relative Percent Difference (RPD):

$$RPD\ (\%) = \frac{|\ Result_x - Result_{Dup}\ |}{\frac{(Result_x + Result_{Dup})}{2}} \times 100$$

The RPD should be <20%. See QC Table for further details.

11.5 A METHOD DETECTION LIMIT (MDL) STUDY is performed as needed, at a minimum, annually, following the guidance of SOP 329. The MDL study shall consist of the analysis of a minimum of seven replicate analyses for a target analyte at a concentration level near to the capabilities of the method. The MDL generated by such a study must be less than the reporting limit (RL) of the method. See QC Table for further details.

12. DEVIATIONS FROM METHOD

This SOP is based on SW-846 Method 9071B. This is a confidential, proprietary procedure developed by Paragon.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Solid sample remnants shall be disposed of in the Contaminated Soils and Solids satellite collection vessel. Radioactive solids require special disposal, as do mixed wastes.

11.2.2 All empty solvent bottles are disposed of according to the appropriate procedures. All labels and markings must be defaced prior to disposal.

14. REFERENCES

US EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 3rd Edition, Final Update III, Method 9071B, Revision 2, April 1998.

DOCUMENT REVISION HISTORY

1/11/07: Added DOCUMENT REVISION HISTORY. Added Form.

8/16/07: Added SOLVENTS and STANDARDS Sections. PROCEDURES augmented and clarified. Added catalog #'s of consumables.

Analytical Method: Extraction & Gravimetric Determination of Lipids in Tissues	**Parameter:** Lipids		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria *	Corrective Action
* NOTE: Superceding criteria specified by the client and prescribed in the LIMS program specification may apply.			
Method Blank (MB)	One per each batch of ≤20 field samples; one each time a reagent is changed	MB must not yield a recovery greater than the reporting limit.	Check all calculations. If no computation errors are found, prepare a fresh MB and analyze, associated samples must also be re-extracted and re-analyzed (if possible).
Laboratory Control Sample (LCS)	One per batch of ≤20 field samples	Results obtained should be within 80-120% of expected (known) concentration of lipids	Check calculations and preparation for documentable errors. If no errors are found, reanalyze LCS; associated samples must also be re-extracted and re-analyzed (if possible). If samples cannot be re-extracted, discuss with Department/Project/QA Managers.
Laboratory Duplicate Sample	One per batch of ≤20 field samples	RPD should be <20%	For RPDs outside of QC limits, check all calculations for errors. If no errors are found, discuss with Department/ Project/ QA Managers.
Method Detection Limit (MDL) Study	As needed; at a minimum annually	Must yield a positive result < the analyte reporting limit (RL)	Determine the reason for failure and fix problem with the analytical system. Repeat the MDL study. Consult with the Department/QA Managers (the Managers may determine that an adjustment to the RL is needed).

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Page _____ of _____

OIL & GREASE -- PREPARATION / ANALYSIS / CLEANUP – BENCHSHEET

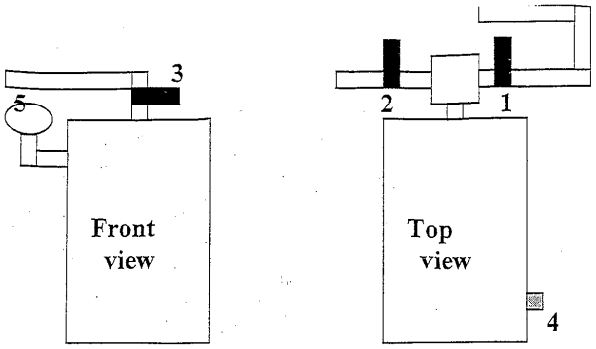
Form 603r11.doc (4/25/2007)

WO _____ AQ Solid _____ **Batch ID** _____ **M Spike Code** _____ **Analysis Code:** 9070A 9071 1664 Lipids **Balance ID** ____ **SOP** _____ **Rev** ___

Ex. Date/Time _____ (start) **Date/Time** _____ (stop) **Initials** _____ **Cleanup Code:** (3630C) Silica Gel **Cleanup Date/Time** _____ **SOP 644/Rev** __ **Initials** ____

SAMPLE					EXTRACT					COMMENTS
Sample No.	Amount (g / mL)	Matrix Spike (mL)	Matrix Spike Witnessed	Acidified? If so, amount used? (mL)	Date Evaporated to Final	Silica Gel (g)	Beaker Initial (g)	Beaker Final (g)	Difference (g)	Balance #5 2 mg wt. **#45458** **#35069** (circle) check between 0.0019 – 0.0021 g ? **Y / N**

Reagent Lots: HCl _____ H_2SO_4 _____ Silica Gel _____ Hexane _____ $NaSO_4$ _____ DCM _____ **Reviewed by / Date** _____



1. Water inlet valve
2. Steam blowout valve
3. Steam valve
4. Boiler switch knob
5. Steam pressure gauge

Steam Generator Start up

1. Check to see if steam blowout valve[2] is closed. (perpendicular to pipe) If not close it.
2. Open water inlet valve[1]. (parallel to pipe)
3. Turn boiler switch knob[4] on to 250. If boiler switch light does not come on re-check in five minutes. Light should be on. If light is not coming on contact supervisor.
4. After approximately 30 minutes Steam pressure gauge[5] should read between 20-60 psi. If not, wait until desired pressure is reached.
5. Open steam valve[3]. (parallel to pipe)

Steam Generator Shutdown

Caution: Pipes and Generator will be hot!

1. Turn boiler switch knob[4] to OFF
2. Close water inlet valve[1]. (perpendicular to pipe)
3. Close steam valve[3]. (perpendicular to pipe)
4. **SLOWLY*** open steam blowout valve[2]. (parallel to pipe)

****Caution: Do not open blowout valve fully until a majority of the steam is released. The tubing carrying the steam outside may come out of the wall.***

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 673 REVISION 2

TITLE: **EXTRACTION OF POLYCHLORINATED BIPHENYLS FROM WIPES USING ULTRASONIC BATH AGITATION**

FORMS: **616** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8.17.07
QUALITY ASSURANCE MANAGER _____ DATE 8/16/07
LABORATORY MANAGER _____ DATE 8-20-07

HISTORY: Rev0, 6/10/03; Rev1,7/26/05; Rev2, 8/16/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes Paragon's in-house procedure used to extract polychlorinated biphenyls (PCBs, Arochlors) from wipes. The procedure described is modified from SW-846 Method 3550 and is intended to extract removable PCBs from wipes used in assessing surface contamination on buildings and equipment.

2. SUMMARY

Environmental and laboratory quality control (QC) wipe samples are extracted with hexane for two hours using an ultrasonically agitated water bath after addition of surrogates or other standards. Extracts are then concentrated by nitrogen blowdown (SOP 637). Sulfuric acid cleanup (SOP 651) is then performed. The extracts are then ready for analysis by Method SW8082 (SOP 409).

3. RESPONSIBILITIES

3.1 It is the responsibility of the individual performing this procedure to prepare the samples according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of a proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the benchsheet indicates that this review for precision,

accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Corrective action must be taken and documented for any discrepancies noted.

4. INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences upon analysis. Only scrupulously cleaned glassware (SOP 334), reagent grade (or better) chemicals and pesticide grade (or better) solvents may be used. These materials and the analytical system are demonstrated to be free from interferences by the preparation and analysis of method blanks.

5. APPARATUS AND MATERIALS

5.1 sample vials with screw-tops, 40mL, glass, disposable, or equivalent

5.2 ultrasonic agitator water bath, Branson 8210 or equivalent

5.3 solvent dispensers, pump-style or equivalent

5.4 metal spatula

5.5 pipets, transfer, 10mL

5.6 Pasteur pipets, glass, disposable

5.7 extract vials with screw-tops, glass, or equivalent

5.8 gastight syringes, 1mL, or as needed

5.9 cotton gauze pads; Accolade 2”x2” Gauze Pads #908112 or equivalent

6. REAGENTS - Only pesticide residue grade (or better) solvents shall be used

Hexane (C_6H_{14}), Burdick & Jackson #216-4 or equivalent

7. STANDARDS

7.1 All standards are maintained per PAR SOP 300 and are documented in Paragon’s Standards and Solutions database. The information recorded in the database facilitates reordering, provides documentation of purity or concentration of purchased materials, documents the concentration of each intermediate dilution (as well as the analyst who prepared the dilution), and ensures traceability to the manufacturer. Additionally, Certificates of Analysis for each standard are maintained by the applicable laboratory Department.

7.2 The surrogate and spiking solutions are prepared by the Organics - Pesticides Group. The components and concentrations depicted below are provided as examples. Other surrogate compounds may be used or other Arochlors spiked per client project specifications. Refer to the applicable LIMS program specification, LIMS test code, or the Standards and Solutions database for specific information. *Allow all spiking solutions to come to room temperature before use.*

7.2.1 surrogate solution - tetrachloro-m-xylene (TCM) and decachlorobiphenyl (DCB), 500ng/mL

7.2.2 Arochlor spiking solution - Arochlors 1016 and 1260, 5000ng/mL

8. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 All samples should be collected using an appropriate sampling plan.

8.2 The wipes are frequently provided to the client by the laboratory. The wipes must be placed in glass containers with Teflon-lined lids after sampling. The wipes should be moist with the solvent used in the extraction process (hexane).

8.3 The wipe samples should be extracted within 14 days of collection. The extraction process can be thought of as being initiated at the time of sampling since the wipes are typically in hexane from that time until the extraction is completed.

9. PROCEDURE

9.1 Note all abnormal conditions on the extraction benchsheet (Form 616). Examples of notable items include: absence of a wipe in the jar, completely dry wipe, very oily wipe.

9.2 The wipes are generally extracted in the vials in which they were submitted to the laboratory. If a wipe must be transferred to a different vial for extraction, then any particles or liquid in the original vial must also be carefully transferred to the new vial. Complete the transfer by rinsing the original vial with several small aliquots of hexane and adding the rinsate to the new vial.

9.3 One method blank (MB) must be prepared for each batch of twenty (or less) environmental samples processed. Place an unused wipe into a labeled 40mL glass vial with a screw-top cap for use as the method blank.

9.4 One laboratory control sample/laboratory control sample duplicate (LCS/LCSD) must be prepared for each batch of twenty (or fewer) wipe samples processed. Place one wipe into each of two 40mL glass vials with screw-top caps for use as the LCS/LCSD pair.

9.5 Add the appropriate amount of surrogate solution (typically 1.0mL) to each

prepared vial of environmental or QC sample.

9.6 Add the appropriate amount of Arochlor spiking solution (typically 1.0mL) to both the LCS and LCSD.

9.7 Add enough hexane to each vial to completely cover the wipe being extracted. Addition of 10-20mL of hexane is generally sufficient to cover each wipe completely. Generally, the vials already contain a small volume of hexane that was used for sampling. This hexane should always be included in the total volume of hexane used, as the extraction is considered to have been started at the time of sampling. A spatula may be used to compress and submerge the wipe into the hexane – *make sure to rinse the spatula with hexane (into the vial) after this is done.*

9.8 Close the seal tightly on each vial after addition of the solvent. Place the vials in racks in the ultrasonic agitator bath. If necessary, add water to the bath so that the level of water is at or slightly above the solvent level in the vials.

9.9 Turn on the cold water tap that circulates cooling water to the bath.

9.10 Turn on the ultrasonic agitation power. After 2 hours have elapsed (±15min.), turn the power off and remove the vials from the agitator bath.

9.11 Transfer each extract to a concentrator tube or 40mL VOA vial prior to blowdown. A Pasteur pipet can be used to gently compress the wipe as the extract is pipetted into the concentrator tube. Rinse the vial (and again use the Pasteur pipet to compress the wipe) a minimum of three times to achieve an effective transfer, adding each rinsate to the concentrator tube.

9.12 Bring the extracts to final volume (10mL) per SOP 637.

9.13 Follow the instructions in SOP 651 (sulfuric acid cleanup) to clean up the extracts for analysis.

9.14 Observing proper internal chain-of-custody (SOP 318), deliver the extracts to the designated refrigerator for analysis by the Pesticides Group.

10. QUALITY CONTROL

10.1 DEFINITION OF A BATCH

For this method, a preparation batch is defined as a group of twenty (20) or fewer field samples that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS) and laboratory control sample duplicate (LCSD). An LCSD is always performed as each sample is extracted in its entirety as no

matrix spike or matrix spike duplicate can be performed. All quality control samples must be carried through all stages of the sample preparation and measurement steps.

10.2 METHOD BLANK

A method blank (MB) is analyzed to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. For this procedure, the blank consists of one wipe. For the method blank to be acceptable, the concentration of target compounds must be less than the reporting limit, or as otherwise specified in the applicable LIMS program specification.

10.3 LABORATORY CONTROL SAMPLE AND LABORATORY CONTROL SAMPLE DUPLICATE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method; the LCSD is analyzed (as a laboratory duplicate) to measure precision. A known amount of target analyte is added to a blank laboratory wipe, which is then prepared and analyzed. For this procedure, one wipe is used for the LCS and one for the LCSD. Results obtained are compared to results expected. To be acceptable, LCS/LCSD recoveries must be within the acceptance limits established by the applicable LIMS program specification or test code.

11. DEVIATIONS FROM THE METHOD

The extraction procedures documented in this SOP have been developed in-house. This procedure is modified from Method SW3550 as no documented procedures are known to be available for extraction of removable Arochlor contamination from wipes.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

12.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

12.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). Hexane TLV = 50ppm.

12.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with

compound name, NFPA Health, Flammability and Reactivity ratings, and date.

12.2 WASTE DISPOSAL

12.2.1 Hexane may be disposed of in the Acetonitrile/Non-halogenated Waste.

12.2.2 Extract vials and associated extracts are disposed by the analytical group into the appropriate extract and vial waste container.

12.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Note that all labels and markings must be defaced prior to disposal.

13. REFERENCE

USEPA SW846, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods", 3rd Edition, Final Update III, Method 3550B revision 2, December 1996.

DOCUMENT REVISION HISTORY

7/26/05: Added LIMS program specification language to Section 3.

8/16/07: Minor clarifications throughout. Added REAGENTS, STANDARDS and DOCUMENT REVISION HISTORY Sections. Added Form.

_____ A

PESTICIDES / PCBs -- EXTRACTION WORKSHEET

Paragon Analytics

WO #s _____ **Batch ID** _____ **Surr Code** _____ **Matrix Spike Code** _____

Ex Date/Time _____ (start) _____ (stop) **Matrix** Aq Solid Other _____ **Balance ID** _____ **Ex SOP** ____ **Rev**___ **Initials** ____

Ex Method: (3520C) CLE (3550B) SONC (3540C) SOX (3510) SEP (3580) Wdilute (SOP 673) Wipes **EX Code:** 8081B (pest) 8082 (PCB) 608 (pest) 8081B (TCLP pest)

Sample No.	Amount (g / mL)	pH	Surr. Spike Amt. (mL)	Matrix Spike Amt. (mL)	Spike Analyst / Witness	Date KD / Analyst	Final Solvent	Final Vol. (mL)	Cleanup Req. (y / n)	Comments
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Lots: $MeCl_2$ _____ Hexane _____ Na_2SO_4 _____

Form 616r13.xls (3/29/05)

_____ B

PESTICIDES / PCBs -- CLEANUP WORKSHEET

Paragon Analytics

WO #s _____ **Batch ID** _____ **Cleanup SOP** _____ **Rev**____ **Initials** _____

Cleanup Method: (3620B) Florisil (3665A) Sulfuric (3640A) GPC (See additional forms) Other _____

FLORISIL: Has lot check been done? y/n _____ **GPC** (Note: half the extract is lost during cleanup) **SULFURIC ACID**

Sample No.	Amount Extract (mL)/ Solvent	Date Cleanup / Analyst	Final volume (mL) / Solvent	Date Vialed / Analyst	Extract (mL) / Solvent	Date Cleanup / Analyst	Date KD / Analyst	Final volume (mL) / Solvent	Amount Extract (mL) / Solvent	Date Cleanup / Analyst	Comments

Lots: $MeCl_2$ _____ Hexane _____ Acetone _____ Florisil _____ Sulfuric acid _____ Na_2SO_4_____ **Reviewed by / date** _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 700 REVISION 10

TITLE: **PREPARATION OF ENVIRONMENTAL AND DRINKING WATER SAMPLES FOR TRITIUM ANALYSIS -- EPA METHOD 906.0**

FORMS: **302, 631, 1306** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 5/1/07

QUALITY ASSURANCE MANAGER _____ DATE 4/25/07

LABORATORY MANAGER _____ DATE 4-30-07

HISTORY: Rev0, 9/18/92; Rev1, 12/26/92; Rev2, PCN #145, 2/28/94; Rev3, PCN #333, 1/19/95; Rev4, 4/10/98; Rev5, 3/24/00; Rev6, 6/29/01; Rev7, 3/13/02; Rev8, 4/4/03; Rev9, 9/22/03 and 2/9/05 (no revisions); Rev10, 4/26/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the preparation of environmental and drinking waters for the quantitative measurement of tritium. This SOP is compliant with EPA Drinking Water Method 906.0.

2. SUMMARY

Environmental and drinking water samples are distilled in order to separate the water from any positive interferences and from dissolved or suspended materials which would cause "quenching" in the liquid scintillation process. Radioiodine and radiocarbon interferences are eliminated by distillation in an alkaline medium in the presence of potassium permanganate. Distillate aliquots are transferred to scintillation vials and mixed with liquid scintillation cocktail. The resulting emulsion is analyzed in a liquid scintillation counter calibrated against NIST-traceable tritiated water in the same geometry and cocktail as the samples.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the preparation or analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Remember that the target nuclide is an isotope of hydrogen (^3H) labeled on water molecules. Addition of water, acid or any other materials containing significant quantities of hydrogen can significantly alter the hydrogen concentration in the sample and could potentially compromise sample integrity.

4.2 Samples must be made basic (pH ~10) to prevent co-distillation of other radioactive analytes, such as carbon and iodine.

4.3 The sample is distilled in an oxidizing environment to break down organic sample constituents, which may cause quenching interference.

4.4 All glassware must be cleaned according to the glassware washing SOP 720, and thoroughly dried prior to use. The condenser columns are rinsed with DI water and dried with a small amount of anhydrous acetone between distillations. Distillation flasks should be thoroughly cleaned with aqua regia, as needed, to remove buildup of visible residues in the flasks.

4.5 Approximately every month, or as needed, the anhydrous $CaSO_4$ desiccant should be renewed. Remove the drying tube located on the top of the condenser and replace the spent $CaSO_4$, with fresh anhydrous $CaSO_4$.

NOTE: It may be necessary to use DI water to dislodge the $CaSO_4$ from the drying tube. Gently fill the drying tube with DI water; the $CaSO_4$ will dissolve. Be sure to allow the drying tube to dry fully before repacking.

4.6 The scintillation vial is an optical surface. Any markings or material on the

outside of the scintillation vial will interfere with the detection of scintillation. These marks should be removed prior to analysis by wiping the vial with a lint-free lab wipe and alcohol. All labeling must be done on the cap of the vial.

4.7 The presence of visible coloration in the distillate will act as an 'inner filter'. This effect, known as 'color quenching' is an interference to the detection of the scintillation. The quench indicating parameter (QIP, usually H-number or SQP(E)), should be monitored and variations in quench that could correspond to greater than 10% (or +/-15 number) relative bias in the efficiency should be addressed by using standard additions to determine a sample-specific efficiency.

4.8 The presence of particulate contaminant in the final water distillate may interfere with the detection of the scintillation. This effect is known as 'physical quenching'. The quench indicating parameter (QIP, usually H-number or SQP(E)), should be monitored and variations in quench which could correspond to greater than 10% relative bias in the efficiency should be addressed by using standard additions to determine a sample-specific efficiency.

4.9 The presence of chemical contaminants in the final water distillate may inhibit scintillation. This effect is known as 'chemical quenching'. The quench indicating parameter (QIP, usually H-number or SQP(E)) should be monitored and variations in quench which could correspond to greater than 10% relative bias in the efficiency should be addressed by using standard additions to determine a sample-specific efficiency.

4.10 The presence of volatile beta- (or alpha-) emitting materials (low boiling organics, etc.) that could co-distill with water is a positive interference to this method. The initial fraction of distillate is therefore discarded to remove the lightest potential interferences. The sample spectrum is subsequently monitored (window 2) for evidence of higher energy species in the distillate (especially ^{14}C) and corrective action taken when significant interference is observed.

4.11 The distillation apparatus (flask and still) used for each sample and the order of distillation are recorded to enable checking for potential cross-contamination in the case of a sample with significantly elevated activity. Experience indicates that using cleaning procedures defined in this procedure will achieve satisfactory decontamination of the apparatus to assure at least 100-fold differential between successive distillations. Successive samples showing activity differences greater than two orders of magnitude should be examined to ensure that results are not compromised by carry-over in the distillation apparatus. Evidence of contamination or carry-over will lead to re-preparation of the affected sample(s).

5. APPARATUS AND MATERIALS

5.1 Scintillation vials, low-potassium borosilicate glass, Wheaton™ or equivalent, 20mL

5.2 Condenser, Pyrex™ or equivalent, 400mm length, 24/40 ground glass joints

5.3 Receiver, Barrett type, graduated, Pyrex™ or equivalent, 20mL, 24/40 ground glass joints

5.4 Flask, round-bottom, Pyrex™ or equivalent, 500mL, 24/40 ground glass neck

5.5 Drying tube, polyethylene: Place a small amount of glass wool in the cap of the column. Fill the tube with Drierite™. Place the cap on the tube and place bottom of the tube into the stopper.

5.6 Heating mantle assembly to fit 500mL flasks

5.7 Spatula, stainless steel

5.8 Bottle-top dispenser, 10mL or adjustable repeat pippettor, 1-20mL, with disposable tips

5.9 Graduated cylinder, 50mL

5.10 Nalgene™ tubing for cooling water, attached to condenser inlet and outlet

5.11 One-hole stopper, for drying tube

5.12 Glass wool, for drying tube

5.13 Wide range indicating pH paper

5.14 Boiling beads, glass

5.15 Lubricant, silicon-based, used to seal ground glass joints

6. REAGENTS - only reagent grade or better chemicals may be used

NOTE: TLV and other hazard information may be given here. As stated in Section 13.6 below, any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not mean that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Anhydrous calcium sulfate ($CaSO_4$), or indicating Drierite™

6.2 Hydrochloric acid (HCl), concentrated, 12N. TLV = 5ppm (ceiling)

6.3 Nitric acid (HNO_3), concentrated, 16N. TLV = 2ppm (TWA); irritant, corrosive

6.4 Liquid scintillation cocktail, Ultima-Gold LLT™ or equivalent brand (Packard)

6.5 Potassium permanganate ($KMnO_4$), crystals. No TLV; Caution: strong oxidizer

6.6 Sodium hydroxide (NaOH), pellets. TLV = $2mg/m^3$ = 1.2ppm (ceiling); irritant

6.7 Tritium-free water: Water from a deep well, distilled or deionized, or other reagent water (e.g., deionized water) that shows activity indistinguishable from the method background. Historical data indicate that Paragon laboratory water is consistently free of contamination and may be used as tritium-free water. Activity levels measured for the reagent blank are tracked, and results deviating from historical values are identified with appropriate actions taken to remediate results or re-prepare samples.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Environmental and drinking water samples for tritium analysis should be collected in glass containers. *Tritium samples should not be preserved.*

7.2 Keep all sample containers tightly closed. If samples are to be stored for an extended period of time, refrigeration is recommended to prevent biological growth in the sample.

7.3 At the current time, there is no regulatory holding time for tritium. Many sampling and analysis plans, however, apply a default holding time of 180 days for this analysis. If samples are analyzed more than 180 days after collection, this fact should be noted in the data package case narrative.

8. PROCEDURE

8.1 WATER SAMPLE DISTILLATION

8.1.1 Verify and record the pH of the sample on a liquid sample condition form (Form 631) according to SOP 733.

8.1.2 Label (on the top of the lid) a glass scintillation vial for each sample to be distilled.

8.1.3 Remove all necessary glassware (round-bottom flask, Barrett receiver, and stopcock) from the oven and allow to cool for several minutes. Do not add samples to hot glassware, as tritium may be lost from the sample due to evaporation.

8.1.4 Use a clean and dry graduated cylinder to measure approximately 50mL of each water sample. Record the actual volume to the nearest graduation on the benchsheet.

8.1.5 Transfer the aliquot of each water sample into a labeled round bottom flask.

8.1.6 Prepare the appropriate batch quality (QC) samples as required in Section 9.2 of this SOP or as required to meet project-specific requirements. Note that the spikes are to be added after the samples have been transferred to a round bottom flask.

8.1.7 Make the sample basic as follows (see also comments in Sections 4.1 and 4.2):

8.1.7.1 Add approximately 0.1g (1 pellet) of sodium hydroxide to the round bottom flask.

8.1.7.2 If there is no unpreserved sample available for the tritium analysis, then an acid preserved sample may be used. However, enough NaOH pellets must be added to make the sample basic.

Samples with pH 1 will require roughly 0.2g NaOH (2 or 3 pellets), and those at pH 0 will require approximately 2g NaOH to be added.

Measure the pH of the preserved sample with pH paper and slowly add NaOH pellets accordingly. Verify that the pH of the sample after base addition is approximately 10. Record base addition and final pH on the sample condition form (Form 631). Also, submit a Quality Assurance Summary Sheet (QASS, Form 302) noting the use of a preserved sample.

8.1.8 Add ~0.01-0.05g of potassium permanganate to the round bottom flask. This can be accomplished by using a pair of forceps or a lab spatula.

8.1.9 Add 2 glass boiling beads to the flask. Swirl to dissolve the sodium hydroxide and potassium permanganate.

8.1.10 Lubricate all glass joints and stopcock with silicone-based lubricant as needed.

8.1.11 Place the flask into a heating mantle.

8.1.12 Attach the Barrett receiver (graduated) to the flask.

8.1.13 Attach the condenser to the top of the receiver.

8.1.14 Ensure that the drying tube is in place on the top of the condenser and that the desiccant does not need to be replaced.

NOTE: The desiccant appears caked, rather than having a bead-type appearance, when in need of replacement. Indicating type desiccant will turn pink when expended. Replace when the entire tube has turned pink.

8.1.15 Make sure the stopcock on the receiver is closed.

8.1.16 Record the appropriate information concerning the distillation apparatus used for each sample in the tritium run log (Form 1306).

8.1.17 Turn on the water to cool the condensers.

8.1.18 Turn on the mantle assembly to about 7. The water should come to a slow boil.

8.1.19 Allow the sample to start distilling.

NOTE: Some samples may become foamy or reactive while distilling. If this occurs, turn down the heat on the mantle to ensure that the sample does not boil over or contaminate the collected distillate.

8.1.20 Discard the first 5mL of distillate that has collected.

NOTE: It is important that the first 5mL of sample distillate be discarded to avoid low boiling contaminants from being included in the distillate taken for analysis.

8.1.21 Collect the next 20mL of distillate in the receiver.

8.1.22 Drain the distillate from the receiver into a labeled scintillation vial.

8.1.23 Cap the vial with the properly labeled lid until ready to aliquot.

8.1.24 After collecting 20mL from each sample distillation, turn off the mantle assembly.

8.1.25 Allow the flasks to cool.

8.1.26 Remove the flask from the mantle and clean.

8.2 LIQUID SCINTILLATION VIAL PREPARATION

8.2.1 Label (on each lid) a scintillation vial for each sample in the batch. Label one vial per batch for the reagent blank. Label with the batch ID and "CBX" (where CB is an identifier for calibration blanks and X denotes a sequential designation which will provide for a unique ID for this blank).

8.2.2 Pipet a 10.0mL (or an appropriate volume to match calibration geometry) aliquot of the sample distillate into the scintillation vial using a previously calibrated pipette with a fresh tip. Save the

remainder of the sample distillate for reserve.

8.2.3 Add 10.0mL (or an appropriate volume to match calibration geometry) of liquid scintillation cocktail to the sample vial with the bottle-top dispenser. Record the type of cocktail used, as well as the lot number, and dispenser ID on the benchsheet. If inadequate volume of distillate is available to match the calibration geometry, add the available volume and dilute to 10mL (or the appropriate calibration geometry volume) with tritium-free water.

8.2.4 Record the actual volume of distillate (mL or grams) added to each vial on the benchsheet as the analytical aliquot. In cases where volume is not measured using a calibrated 10mL pipettor, the aliquot volume may be measured gravimetrically assuming a density of 1 g/mL.

8.2.5 Cap the sample vial with its corresponding labeled lid and shake the sample thoroughly.

8.2.6 Clean the outside of scintillation vial using a lint-free lab wipe and alcohol to remove dust, smudges, and fingerprints.

8.2.7 Place the scintillation vials in racks.

8.2.8 Deliver the samples to the Counting Lab with the necessary documents. Place the racks in the liquid scintillation counter and allow at least 3 hours for the samples to "dark adapt" prior to counting. The Counting Lab will analyze and ultimately dispose of the scintillation vials in the manner described in SOP 704.

9. QUALITY CONTROL

9.1 CALIBRATION

9.1.1 Bottle-top dispenser calibration. The bottle-top dispenser is checked monthly, by dispensing a 10mL aliquot of scintillation cocktail into an appropriate volumetric measurement apparatus, typically a 10mL Class A volumetric flask. The volume dispensed should be 10mL +/- 0.1mL; if not, adjust the dispenser and re-check. Record the calibration check in the pipet calibration logbook.

9.1.2 Efficiency calibration source preparation. A one-point calibration source is prepared as follows: Prepare three 50mL aliquots of deionized water containing approximately 5000dpm of NIST-traceable tritium standard. This solution is then distilled and prepared for counting as described in Sections 8.1 and 8.2.

A one-point efficiency is highly accurate and will be used for the calculation of all results showing QIP results corresponding to the

average observed for the calibration standard (within +/- 10 % relative efficiency or lacking this calibrated range, +/- 15 of mean H-numbers). Any sample falling outside this range will be calibrated by sample-specific addition of a minimum known volume (< 200 µL) of NIST-traceable tritiated water. The efficiency from sample-specific standard additions is calculated as defined in Section 10.7.

9.1.3 Background calibration (calibration blank). An aliquot of tritium-free water equivalent to the calibration geometry is transferred to a scintillation vial, independent of the preparation process and cocktail added, such that the calibration geometry is reproduced. One calibration blank is submitted for each preparation batch and counted for a time period equal to or longer than the longest sample count. For samples counted in the default calibration geometry (10mL water + 10mL cocktail), cpm results (as well as blank ID, batch, and QIP result) of the calibration blank count are entered into a spreadsheet (H3_RB.xls) which tracks the running mean of the last seven calibration blanks, and compares each blank to historical control limits established from the first 20 data points in the population (+/- 3 sigma). The current running mean of the calibration blank cpm is used as the background in the calculation of associated results for the associated prep batch.

9.2 BATCH QC SAMPLE PREPARATION

Quality control samples are processed and results calculated in the same manner as the associated field samples, with the exception that Laboratory Control Samples (LCS) and matrix spikes are spiked after being transferred to the round bottom flask.

9.2.1 Blanks Process a method blank at a frequency of one per batch of 20 samples or 5%, whichever is greater. 50mL of 'tritium-free' water is transferred into a flask.

9.2.2 Laboratory Control Samples (LCS) Process an LCS at a frequency of one per batch of 20 samples or 5%, whichever is greater. Appropriate spiking levels are 5-50 times the requested minimum detectable concentration (MDC).

NOTE: Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the lab's internally derived acceptance criteria.

9.2.3 Sample Duplicates Process a sample duplicate at a minimum frequency of two per batch of 20 samples or 10%, whichever is greater.

If sample volumes are limited, an LCS duplicate may be substituted for duplicate sample analysis. The discrepancy should be noted in a QASS (Form 302) and in the data package narrative.

9.2.4 Matrix Spikes Process a matrix spike sample at a frequency of one per batch of 20 or 5%, whichever is greater. Appropriate spiking levels are five to ten times the native sample activity. If sample volumes are limited, an LCS duplicate may be substituted for matrix spike analysis. The discrepancy should be noted in a QASS (Form 302) and in the data package narrative.

10. CALCULATIONS

10.1 The sample activity is calculated as follows:

$$\text{Activity} = \frac{(\text{SmplGrCPM}) - (\text{BkgCPM})}{\text{Denom}}$$

10.2 The activity calculation denominator is calculated as follows:

$$\text{Denom} = \text{FinAli} * \text{Dec} * \text{ActCnv} * \text{DetEff}$$

10.3 As defined in SOP 743, the following uncertainty factors (1σ) are applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU):

10.3.1 Calculate the one-sigma counting uncertainty (CU) as follows:

$$\text{CU} = \frac{\sqrt{(\text{SmplGrCPM}/\text{SmplTime}) + (\text{BkgCPM}/\text{BkgTime})}}{\text{Denom}}$$

10.3.2 The one-sigma preparation uncertainty (PU) is 5.1%. This is based on one gross aliquotting, one volumetric measurement, one pipetting, and one reagent addition.

10.3.3 The one-sigma instrument uncertainty (IU) is 5.6%, based on the in-house preparation of calibration standards.

10.3.4 Calculate the one-sigma total propagated uncertainty (TPU) as follows:

$$\text{TPU}(\text{pCi/unit}) = \sqrt{\text{CU}^2 + (\text{Activity} * \text{PU})^2 + (\text{Activity} * \text{IU})^2}$$

10.4 The Minimum Detectable Concentration (MDC) is calculated as follows:

$$MDC = \frac{4.65 * \sqrt{BkgCPM * SmplTime} + 2.71}{SmplTime * Denom}$$

10.5 The Decision Level (DL) activity is calculated as follows:

$$DL = \frac{2.33 * \sqrt{(BkgCPM * SmplTime)}}{SmplTime * Denom}$$

10.6 The efficiency used for calculation of sample results is calculated as shown in the equation below:

$$DetEff = \frac{Net\,Cpm}{SpkDPM}$$

NOTE: Multiple standards are prepared and the measured values averaged for use in sample calculations.

10.7 The sample-specific efficiency is measured following addition of a known quantity of tritiated water (< 0.20mL) as follows:

$$Deteff = \frac{((SSGrCPM - BkgCPM) - (SmplGrCPM - BkgCPM))}{SpkDpm}$$

where:

Activity = Tritium activity corrected for decay to date of collection (default units pCi/L)

SmplGrCPM = Analyte gross count rate (cpm)

SmplTime = sample count time (min)

BkgCPM = Background count rate (cpm)

BkgTime = Background count time (min)

Denom = Activity calculation denominator

DetEff = sample detection efficiency for sample geometry / quench level

Counting Unc. = Counting Uncertainty (pCi/L)

FinAli = Final dilution/preparation adjusted aliquot (Note: dilution factor is included in this number to reflect the quantity of original sample taken for analysis (L)

ActCnv = Activity conversion factor from DPM to desired units (2.22 for pCi, 60 for Bq)

Dec = decay factor $e^{(-\lambda t)}$ (fractional)

$\lambda = \ln 2 / t_{1/2}$

$t_{1/2}$ = half-life for tritium in same units as decay time

t = decay time in same units as half-life

SSGrCPM = Spiked Sample Gross CPM

SpkDPM = Spike addition DPM decay corrected to count date

11. DEVIATIONS FROM METHOD

11.1 This procedure is compliant with EPA Drinking Water Method 906.0. There are no known deviations from the method.

11.2 This procedure is compliant with Eastern Environmental Radiation Facility (EERF) Procedures Manual Method H-02.

11.3 This procedure is compliant with Standard Methods for the Examination of Water and Wastewater, 18th Edition.

12. SAFETY HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

12.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

12.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

12.1.5 Care should be taken when working with the heating mantles and boiling water to prevent thermal burns. Occasionally, pressure will build up in the condenser and pop the drying tube off the top.

12.2 WASTE DISPOSAL

12.2.1 All empty radionuclide standard solutions are disposed of by rinsing the standard container with tap water a minimum of three times. The container must be surveyed prior to release. Please note that all labels and markings must be defaced or removed prior to disposal.

12.2.2 The tritium analytical process effluent has been determined to not be hazardous in any other way than corrosivity. This material may be

discharged into Paragon's wastewater treatment facility. Here the solution will be neutralized prior to discharge, and the radionuclide concentration will be monitored to ensure compliance with Colorado Rules and Regulations pertaining to Radiation Control, Part 4, regarding discharges to sanitary sewers.

12.2.3 Consult with waste management staff for the disposal of scintillation cocktail.

12.2.4 Vials of sample/cocktail mixture may be accumulated (intact) in a container provided by waste management staff.

13. REFERENCES

13.1 Handbook of Radiochemical Analytical Methods, Frederick B. Johns, EPA-680/4-75-001, February 1975.

13.2 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Herman L. Krieger and Earl L. Wittaker, EPA-600/4-80-0, Method 906.0, August 1980.

13.3 Standard Methods For The Examination of Water and Wastewater, 18th edition, Method 7500-3H, 1992.

13.4 Eastern Environmental Radiation Facility (EERF) Manual, Method H-02.

13.5 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.6 Paragon SOP 743 "Estimating Total Propagated Uncertainties for Radiometric Analyses", current revision.

DOCUMENT REVISION HISTORY

4/27/07: Revision 10. Added LIMS program specification language, 3.2. Added DOCUMENT REVISION HISTORY. Corrected Sample Condition form reference to Form 631. Added tritium run log (Form 1306) references. Attached Forms.

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics

TRITIUM RUN LOG

_____ Logbook/Page No. **SOP 700 Rev** ___ Form 1306r1.doc (3/30/2003)

Date	Workorder/ Sample Number	Column ID	Flask ID	Run No.	Comments	Technician's Initials

Reviewed by / Date _____

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PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 702 REVISION 19

TITLE: PREPARATION OF GROSS ALPHA AND GROSS BETA IN ENVIRONMENTAL MATRICES -- EPA METHOD 900.0 AND SW9310

FORMS: 631, 302 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/2/07

LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 9/21/92; Rev1, 12/15/92; Rev2, 2/25/93; Rev3, 6/17/93; Rev4, PCN #8, 9/20/93; Rev5, PCN #18, 11/4/93; Rev6, PCN #156, 3/7/94; Rev7, PCN #234, 6/7/94; Rev8, PCN #399, 2/25/95; Rev9, PCN #500, 6/20/95; Rev10, 3/27/96; Rev11, 7/19/97; Rev12, 12/29/98; Rev13, 3/23/00; Rev14, 9/20/01; Rev15, 3/14/02; Rev16, 4/03/03; Rev17, 3/15/05; Rev18, 2/27/07; Rev19, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references, EPA 900.0 and SW-846 Method 9310, describe the procedure used to determine non-volatile gross alpha and beta activity of waters, liquids, soils, non-soil solids, air filters and air filter composites, and certain non-aqueous liquids. The solids procedure is amenable to the preparation of suspended solids that have been removed by filtration from waters or other liquid matrices.

The gross alpha and gross beta activity are determined simultaneously in the same sample preparation by counting on the beta plateau. The raw count results are corrected for detector background, efficiency (referenced to ^{241}Am for alpha -or ^{230}Th to meet National Primary Drinking Water Standards using Method EPA 900.0- and ^{90}Sr/Y for beta), mass attenuation (sample self-absorption), and alpha and beta cross-talk. Default reporting units are picoCuries per liter (pCi/L) on an unfiltered basis, (waters), or per gram (pCi/g) on a dry weight basis (solids), or per filter or composite as appropriate to meet the client's data quality objectives.

This procedure is substantially compliant with methods EPA 900.0, SW-846 Method 9310, and Standard Methods (SM) Method 7110B for aqueous matrices.

2. SUMMARY

2.1 WATERS

Waters samples are routinely analyzed on a "filtered" or "unfiltered" basis. Samples containing visible sediment are routinely filtered prior to preparation according to SOP 721 unless EPA drinking water protocols are requested by the client. In this case, the sample must not be filtered so that the actual consumer

dose can be accurately measured. The aliquot size is determined for each sample by gravimetric measurement of the total solids. This aliquot is then evaporated to near dryness and a small volume (i.e., <5mL) is quantitatively transferred into a tared stainless steel planchet. The contents of the planchet are evaporated on a hot plate and cooled in a desiccator. After cooling, the planchet is weighed to determine the residual mass of nitrated sample solids. If the mass of solids is greater than 100 milligrams for alpha-only and simultaneous alpha/beta measurements, or greater than 200 milligrams for beta-only measurements, the sample is re-prepared using a proportionately smaller aliquot. Planchets containing solids in the acceptable range are sent to the Radiochemistry Instrument Group for analysis per SOP 724.

2.2 LEACHATES OR DIGESTATES

Following preparation, sample leachates or digestates are determined as described in Section 2.1 above for waters. The total solids spot check may be omitted at the analyst's discretion. The sample aliquot is adjusted to reflect the equivalent sample concentration (grams or mL sample per gram or mL leachate).

2.3 NON-AQUEOUS OR MIXED PHASE LIQUIDS

Non-aqueous liquids are analyzed and reported on an "as received" basis. They may be treated as waters as long as the physical or chemical characteristics of the sample are amenable to safe evaporation with the eventual addition of nitric acid. Questionable cases should be addressed to the Senior Scientist, Technical Manager, Project Manager, or Health and Safety Officer prior to initiation of analysis.

2.4 SOILS AND NON-SOIL SOLIDS (hereafter referred to as "solids")

Solids are analyzed on a "dry weight" basis. Routinely, a 3g aliquot (or other appropriate quantity) of the solid is digested in a known volume (usually 30mL) of 8N nitric acid in a 50mL centrifuge tube. The sample is then centrifuged. A volume aliquot which yields <100mg of nitrated solid residue is determined gravimetrically. This aliquot is then evaporated onto a tared stainless steel planchet, dried, flamed, and weighed. The planchet is then sent to the Radiochemistry Instrumentation Group for analysis. Results are reported on a default basis of pCi/g dried solids.

2.5 AIR FILTERS

Air Filters are processed in a manner similar to solids except they need not be weighed and the units are reported on a default basis as "per filter".

2.6 SUSPENDED SOLIDS

Solids suspended in aqueous solutions are filtered from a known quantity of sample onto tared glass fiber filters. The filters are dried and weighed to determine the mass of the suspended fraction. The entire filtered suspended solid

sample, up to 5 grams, is then treated as a solids sample. Results are reported on a default basis as pCi/g dried solids.

2.7 SWIPES
Swipes and some filters that are counted directly, or on an "as received" basis, are placed onto a clean stainless steel planchet and relinquished to the Radiochemistry Instrument Group for counting. Results are typically reported on a per sample basis, but may also be reported as pCi/air volume for filters at the client's request.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. The demonstration may come in the form of supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off on the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and brought to the attention of a Senior Scientist or Manager. Corrective actions taken must be approved, and promptly and thoroughly documented.

4. INTERFERENCES

4.1 Radionuclides that are volatile during evaporation in nitric acid or flaming of

planchets will not be dependably measured. This method is not applicable to the determination of Tritium (^{3}H) or Carbon 14 (^{14}C). Other problematic nuclides include Technetium 99 (^{99}Tc) and radioisotopes of iodine, cesium, and polonium.

4.2 If the radionuclides are not separated from the solids of the sample, the solids concentration is a primary limiting factor in the sensitivity of the method for any given water sample. Also, for samples with very low concentrations of radioactivity, it is essential to analyze as large a sample aliquot as possible to allow reasonable counting times.

4.3 The largest sample aliquot that should be counted for gross alpha activity is that size aliquot which gives a solids density thickness of $5mg/cm^2$ in the counting planchet. For a 2in diameter counting planchet, an aliquot containing 100mg of nitrated (sample evaporated with nitric acid present) dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted for gross alpha activity.

4.4 The largest sample aliquot that should be counted for gross beta activity is that size aliquot which gives a solids density thickness of $10mg/cm^2$ in the counting planchet. For a 2in diameter counting planchet, an aliquot containing 200mg of nitrated dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted for gross beta activity.

4.5 In some areas of the country, the nitrated water solids will not remain at a constant mass after being brought to dryness. Those types of water samples need to be heated to a dull red heat for a few minutes to convert the salts to oxides. Sample masses are then usually sufficiently stable to give consistent counting rates, and a correct counting efficiency can then be assigned. Some radioactive species, such as the cesium radioisotopes, may be lost when samples are heated to a dull red color. Such losses are limitations of the method.

4.6 This method is applicable to the measurement of alpha emitters having energies above 3.9MeV and beta emitters having maximum energies above 0.1MeV. Lower detection efficiency for emitters such as ^{99}Tc or ^{63}Ni will lead to an underestimation of the actual isotopic concentration for these species, if present in the sample.

4.7 Non-uniform distribution of the sample residue in the counting planchet interferes with the accuracy and precision of the method.

4.8 Moisture absorbed by the sample residue may interfere because it may change the sample residue mass affecting self-absorption characteristics. While the presence of hydrated solids is non-problematic to counting, residue mass should be stable enough to allow application of self-absorption corrections which meet the precision and accuracy requirements of the work being performed.

4.9 The minimum detectable concentration (MDC), applicable to this method, depends on sample size, counting system characteristics, background, and counting time. The formula for calculating an MDC is derived from ANSI N42.23 (rev. February 10, 1995). Due to industry-wide practice, and the need to demonstrate compliance with regulatory requirements, the "sample specific MDC" is routinely calculated and often reported in conjunction with sample activity and total propagated uncertainty values. The sample specific MDC makes a priori assumptions regarding the variance in the background count rate, but also reflects the actual conditions employed for the analysis, including aliquot, detection efficiency, solids residue, and count time. The routine solids digestion procedure will not completely remove radioactive elements from silica or absorbed radioactive materials. More aggressive digestion procedures may be necessary if determination of matrix constituents is required (see SOP 721).

4.10 Non-aqueous liquid, non-soil solids, and samples with high organic content may not be amenable to this procedure.

4.11 The presence of significant quantities of chloride salts in aqueous samples may lead to corrosion of the stainless steel planchet if the solution is not fully converted to a nitrate system prior to transfer. Repeated additions of concentrated nitric acid followed by evaporation are usually sufficient to address the problem.

4.12 Sample solution should be slowly evaporated to near dryness (≤5mL). Avoid evaporating the sample to complete or hard dryness that could lead to analyte loss resulting from poorly soluble residues in the beaker.

5. APPARATUS AND MATERIALS

5.1 2in stainless steel ringed planchets. Prior to use, the planchets are placed in a beaker and muffled at approximately 550°C for a minimum of 2 hours. This is done as a cleaning procedure.

5.2 pipettors, Eppendorf™ or equivalent

5.3 centrifuge tubes with caps, plastic, 50mL

5.4 polypropylene beakers, 250mL

5.5 balance, top loading, 0.1g sensitivity

5.6 balance, analytical, 0.1mg sensitivity

5.7 pleated filter paper

5.8 plastic funnels

5.9 hot plate

5.10 wash bottles

5.11 drying oven

5.12 graduated cylinders

5.13 desiccator

5.14 Meeker burner

5.15 tongs

5.16 glass rods

5.17 rubber policeman

5.18 disposable transfer pipettes, plastic, ~3mL and disposable pipette tips

5.19 filtering apparatus and 47mm glass fiber filters

6. REAGENTS - TLV and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Deionized (DI) water, ASTM Type II, minimum

6.2 Nitric acid, concentrated, 16N, ACS grade
TLV = 2 ppm (TWA) Irritant, corrosive

6.3 Nitric acid, 8N: Cautiously add 500mL of reagent grade concentrated HNO_3 to approximately 400mL of DI water and dilute to 1.0L.

6.4 Nitric acid, 1N: Cautiously add 62.5mL of reagent grade concentrated HNO_3 to approximately 500mL of DI water and dilute to 1.0L.

6.5 ^{90}Sr spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.6 ^{241}Am spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.7 ^{230}Th spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.8 Modified USGS Simulated River Water Reagent (salt solution): Dissolve 3.72g $MgSO_4$, 3.10g NaCl, and 3.24g $CaCl_2$ in 200mL 1N HNO_3.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Although the client is responsible for conducting the sampling process, it is emphasized that water samples be collected in a manner that addresses the considerations discussed in EPA 900.0 Section Three or Chapter Nine of EPA SW-846, as appropriate. Also, it is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15mL of 1N HNO_3 per liter of sample is usually sufficient). If water samples are collected without preservation, they should be brought to the laboratory within 5 days, and then be preserved and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.2 The container should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.3 SW-846 specifies the holding time for Method 9310 as 180 days.

8. PROCEDURE

8.1 PREPARATION OF CALIBRATION STANDARDS

8.1.1 EFFICIENCY CALIBRATIONS

8.1.1.1 Gross Alpha Efficiency Planchets: Spike five ringed stainless steel planchets directly with ~8,000 to 15,000 dpm each of NIST-traceable ^{241}Am. Submit to the Radiochemistry Instrument Group with appropriate documentation.

8.1.1.2 Gross Alpha Efficiency Planchets for Drinking Water Protocols: Spike five ringed stainless steel planchets directly with ~8,000 to 15,000 dpm each of NIST-traceable ^{230}Th. Submit to the Radiochemistry Instrument Group with appropriate documentation.

8.1.1.3 Gross Beta Efficiency Planchets: Spike five ringed stainless steel planchets directly with ~8,000 to 15,000 dpm each of NIST-traceable ^{90}Sr. Submit to the Radiochemistry Instrument Group with appropriate documentation.

NOTE: If the standard matrix is HCl, convert to the nitrate system before planchetting to avoid corroding the planchet.

8.1.2 MASS ATTENUATION CALIBRATION

8.1.2.1 Supply the Radiochemistry Instrument Group with a series of planchets containing a range of mass from ~10mg to ~145mg, including a duplicate for each mass. The

approximate target masses in mg are: 10, 25, 40, 55, 70, 85, 100, 115, 130, and 145.

NOTE: A separate set of planchets must be prepared for gross alpha, gross alpha for drinking water protocol, and for gross beta calibrations

8.1.2.2 Label and tare weigh 10 stainless steel ringed planchets. Label a plastic disposable cup for each sample.

8.1.2.3 Add the appropriate amount of Simulated River Water Reagent to give the target mass to each cup (1mL of reagent typically gives 35-40mg dried mass on the planchet).

8.1.2.4 Spike each sample cup with ~8,000 to ~15,000dpm of the appropriate NIST-traceable radionuclide (routinely ^{241}Am for gross alpha and ^{90}Sr for gross beta).

8.1.2.5 Add ~5mL of concentrated nitric acid to each to convert chloride salts to nitrate salts.

8.1.2.6 Take to near dryness on a steam bath.

8.1.2.7 Transfer with at least three rinses of 1N nitric acid to a tared stainless steel planchet.

8.1.2.8 Dry on a hot plate set at 3.

8.1.2.9 Once dry, continue heating for 20-30 minutes with the hot plate set at 10.

8.1.2.10 Cool in a desiccator.

8.1.2.11 Weigh on an analytical balance and record the data on a benchsheet

8.1.2.12 Submit to the Radiochemistry Instrument Group with the appropriate documentation, where the planchets will be analyzed per SOP 724.

8.2 CALIBRATION PROCEDURES

8.2.1 Efficiency and Attenuation Calibration: Analysis systems will be calibrated at least annually or as indicated by routine instrument response check results.

8.2.2 Gross Alpha measurements are routinely referenced to ^{241}Am.

8.2.3 Gross Beta measurements are routinely referenced to ^{90}Sr/Y.

8.2.4 EPA drinking water compliance testing for gross alpha requires that the gross alpha measurement be referenced to ^{230}Th instead of ^{241}Am. (EPA 816-D-00-002, December 2000).

8.2.5 All standards used to develop efficiency and attenuation curves shall be traceable to the National Institute for Standards and Technology (NIST).

8.2.6 Detectors must be calibrated to obtain the ratio of net count rate to disintegration rate. ^{241}Am has higher alpha particle energy (5.49MeV) than those emitted by the naturally occurring uranium and ^{226}Ra radionuclides, but is close to the energy of the alpha particles emitted by naturally occurring ^{228}Th and ^{224}Ra.

8.2.7 ^{90}Sr/Y and ^{137}Cs have both been used quite extensively as standards for gross beta activity. Cesium, however, may become volatile at elevated temperatures (above 450ºC) and may volatilize at temperatures observed while flaming a sample containing hygroscopic salts.

8.2.8 Each instrument used for the analysis of gross alpha and beta shall be calibrated to correct for alpha and beta sample self-absorption (residue mass vs. zero mass normalized efficiency). Mass attenuation curves will be prepared for this purpose. The mass stable standards should be alpha or beta counted (as appropriate) until 10,000 counts have been accumulated. A single set of standards for each nuclide (^{241}Am, ^{230}Th, and ^{90}Sr/Yis suitable for calibration of instruments and re-verification of curves, whenever needed.

8.2.9 Data acquisition is conducted according to instrument manufacturer instructions.

8.2.10 Calculations for attenuation and crosstalk are defined in Section 9. Meticulously document steps taken to produce calibration data.

8.3 PROCEDURE FOR WATERS

8.3.1 Verify with pH paper that the sample has been properly preserved to a pH <2. Record the pH on the sample condition form (Form 631).

8.3.1.1 If the pH is > 2, notify the appropriate Project Manger to determine if further analysis will be acceptable to the client and whether the sample should be (re-)preserved prior to

continuing with analysis. If the Project Manager determines that the situation is acceptable to the client's DQOs, acidify to pH<2 with conc. HNO_3. Wait for two (2) minutes and retest pH. Record the acid addition and the final pH on a Quality Assurance Summary Sheet (QASS) or NCR form (Form 313), as appropriate. The date and time of acidification must be noted.

8.3.1.2 Return the sample to storage for at least 24 hours before proceeding. Record the beginning date and time on a Sample Condition Form. If twenty-four (24) hours causes a scheduling difficulty, notify the Project Manager to determine if a deviation from this requirement is acceptable. Document any deviations thoroughly on a QASS that accompanies the project file.

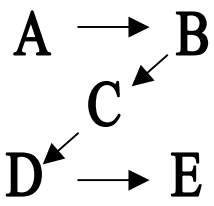
8.3.1.3 When resuming the analysis, record the date/time of resumption on the Sample Condition form. Also, calculate and record the number of elapsed hours since acidification.

8.3.2 To determine the mass of solids in 10mL of the sample, proceed as follows:

8.3.2.1 Place all planchets to be used onto a steel desiccator tray. Each space on the tray is numbered and that number corresponds with the sample ID on the mass benchsheet.

8.3.2.2 Label and tare a planchet on an analytical balance to nearest 0.1mg. Record the mass in the appropriate column on the mass benchsheet.

8.3.2.3 Place the planchets in the following order on the hotplate:



Where 'A' corresponds to the first planchet, 'B' to the second, and so on.

8.3.2.4 Shake the sample well and pipet 10.0mL of sample into the labeled, tared planchet using a calibrated pipettor. Place on

hotplate set at 3.

8.3.2.5 When dry, turn the hotplate setting to 10 and maintain at this heat for 20-30 minutes.

8.3.2.6 Transfer the planchets to the steel tray, making sure that each sample is returned to its proper numbered space, and place the tray directly in the desiccator to cool. Be sure to note which numbered space in the pan corresponds to which sample on the benchsheet.

8.3.2.7 When the planchets are cool, weigh each one to the nearest ±0.1mg. Record the mass in the appropriate column on the mass benchsheet.

8.3.2.8 The solid mass and volume aliquot will be calculated using Equation 1 (shown below), and the results will be shown in the respective cells in the "Init Mass" and "Sugg. Alq" columns in the Mass section of the electronic benchsheet. The "Sugg. Alq" column shows the calculated aliquot plus the 10mL used for aliquot determination as final aliquot used. (V is the volume of the spot check used, in mL and W is the mass calculated in the "Init Mass" column, in g.)

$$V(g) = \frac{0.75}{W(g)}$$

EQUATION 1

8.3.2.9 If the planchet mass is unstable, flame the 10mL planchet and recalculate. If that is done, the resultant sample planchet needs to be flamed also.

8.3.2.10 The default maximum aliquot size for water samples is 200mL. If the calculated aliquot volume is greater than 200mL, use the default aliquot size unless DQOs demand a higher aliquot to achieve required detection limits.

8.3.2.11 If the predicted final residue mass for a sample is estimated to be below 20 milligrams (1.0mg residue for 10mL spot check), simulated river water reagent is added, in Step 8.3.4 below, to provide between 20 and 100 milligrams equivalent of final residue.

8.3.2.12 1mL of simulated river water reagent is added to provide

between 20 and 100 milligrams equivalent of final residue for each of the batch QC samples (Method Blank and LCS).

8.3.3 Measure the calculated sample aliquot from a well-shaken sample container into a labeled disposable poly beaker. If DQOs demand the use of a larger sample size, a glass beaker may be used and taken to near dryness on a hotplate.

NOTE: The same planchet will be used for the sample as was used for the determination of the residue. Thus only 190 additional mL would be necessary to make up the final volume to 200mL.

8.3.4 Add the appropriate spike and amount of spike per Section 10. Add simulated river water reagent to the blank, LCS, and any samples that require it (see Section 8.3.2.11). Typically, 1mL of simulated river water reagent is added for waters analysis to produce 35-40mg of nitrated solids on the planchet.

8.3.5 Add concentrated HNO_3 in the ratio of 1/10th the sample volume. (e.g., 19mL acid per 190mL of sample). The samples may be diluted to a single volume (e.g., to the largest volume of any sample in the batch).

8.3.6 Slowly evaporate the sample solution to near dryness (≤5mL). Avoid evaporating the sample to complete or hard dryness that could lead to analyte loss resulting from poorly soluble residues in the beaker.

8.3.7 If significant concentrations of chlorides are suspected to be present, a second 5mL portion of concentrated nitric acid may be added to complete conversion of the sample to a nitrate system. The sample is once again evaporated to near dryness.

8.3.8 Using a disposable plastic transfer pipet, quantitatively transfer the solution to the labeled stainless steel planchet used for the 10mL aliquot determination. If solid residues are present, it may be necessary to use a rubber policeman to effect the transfer.

NOTE: Any rubber policeman that shows signs of deterioration should not be used.

8.3.9 Rinse the beaker with three successive 2mL portions of 1N HNO_3 transferring each of the rinses to the appropriate planchet on a hotplate in a fume hood. If the planchet cannot hold all rinses, add them as planchet volume is evaporated in the next Step.

8.3.10 Take the solution to dryness as in Step 8.3.6. Avoid excess heating that can cause spattering or boiling during drying. Turn the hotplate setting to highest and maintain at this heat for 20-30 minutes.

8.3.11 Flame the planchet if the 10mL planchet was flamed.

NOTE: Be sure the sample is well distributed on the planchet. This will assure proper counting efficiency.

8.3.12 When all the planchets are dry, remove and cool in a desiccator for at least 30 minutes. Note the time and date of the desiccation in the Notes section on the benchsheet.

8.3.13 Remove the samples from the desiccator and weigh them on an analytical balance. Record the mass to the nearest 0.1mg in the designated cell mass benchsheet. If the planchet mass is unstable on the balance and noticeably gains weight proceed with Step 8.3.15.

8.3.14 Let planchet stand outside of the desiccator for 15 minutes. If the samples are not noticeably hygroscopic, they are ready for counting; (if they are hygroscopic, proceed with Step 8.3.15.

8.3.15 If the samples demonstrate hygroscopicity, cautiously flame planchet to dull redness over a Meeker burner. Avoid popping and spattering. Maintain heat for at least one minute. Cool in a desiccator. Reweigh to nearest 0.1mg and reenter the new mass in the electronic benchsheet. Submit the planchets and any necessary documentation to the Radiochemistry Instrument Group. The Radiochemistry Instrument Group will analyze and ultimately dispose of the planchets in a manner described in SOP 724.

8.3.16 Store the samples in a desiccator for at least 72 hours before counting. Where EPA methodologies are not required, such as for non-water matrices, etc., the samples should be desiccated overnight or until they are ready for counting.

8.4 PROCEDURE FOR SOLIDS

8.4.1 Analysis is routinely reported on a dry weight basis. The use of oven dried solid samples allow direct calculation of aliquot mass without the need to correct for sample moisture content. Rocky, coarse or non-homogeneous solids should be milled or ground to pass a No. 4 sieve before taking an aliquot for analysis. See SOP 721 for soil preparation procedure.

8.4.2 Weigh 3g of solid sample to the nearest 0.1g into a labeled 50mL centrifuge tube.

8.4.3 Add the appropriate spike and amount of spike per Section 10. Add 2mL of simulated river water reagent to the blank and LCS.

NOTE: It is important protocol to always add QC spikes *before* any chemical treatments applied during sample processing.

8.4.4 Slowly add 8N HNO_3 to give a total volume of 30mL. Be sure to account for the volume of salt solution and spiking solutions. (i.e., the LCS would receive only 26mL of nitric acid if it already contains 2mL of salt solution and 2mL of spiking solution). Some samples may react vigorously with the acid, so it may be necessary to add the acid in small increments.

8.4.5 Mix to break up clumps.

8.4.6 Heat on a steam bath with caps on loosely for (1) one hour. Allow samples to cool and mix by vortexing.

8.4.7 Centrifuge for 10 minutes and filter the supernatant using VWR Grade 313 pleated paper, or equivalent, into a new, labeled centrifuge tube.

8.4.8 Determine the mass of solids as in Section 8.3.3, except use 5mL instead of 10mL. **The planchet should be flamed for all solid samples unless otherwise indicated by applicable DQO's or the client.** Calculate and record the required aliquot volume of solution using Equation 2 shown below:

$$V(mL) = \frac{0.375}{W(g)}$$

EQUATION 2

8.4.8.1 If the calculated aliquot exceeds 20mL, use a 20mL aliquot. Aliquots should be in increments of 5 up to 20mL. Directly transfer the additional aliquot to the planchet used for the 5mL aliquot. Proceed with Step 8.4.9.

8.4.8.2 If the mass of the residue from the 5mL aliquot is more than 100mg, calculate the required amount less than 5mL. Aliquots should be calculated in increments of 1mL (unless an aliquot smaller than 1mL is appropriate). Directly transfer the calculated aliquot to a clean, labeled, and tared

planchet.

8.4.9 Dry the sample on a hot plate set to 3. Once the sample is dry, turn the hot plate up to 10 for 20-30 minutes. After the sample has been heated for 20-30 minutes, cautiously flame the planchet to a dull redness over a Meeker burner. Avoid popping and spattering. Maintain heat for at least one minute.

8.4.10 When all planchets are dry, remove and cool in a desiccator for at least 30 minutes. Note the date and time of the desiccation in the Notes section on the benchsheet. Also, in the Notes section, note that all samples were flamed.

8.4.11 Remove the samples from the desiccator and weigh the planchets on an analytical balance. Record the mass to the nearest 0.1mg in the designated cell of the mass benchsheet.

8.4.12 Submit the planchets and any necessary documentation to the Radiochemistry Instrument Group. The Radiochemistry Instrument Group will analyze and ultimately dispose of the planchets in a manner described in SOP 724. Store the planchets in a desiccator at least overnight or until they are ready for counting. Be sure to note the date and time the samples were placed in the desiccator on the benchsheet.

8.5 PROCEDURE FOR SUSPENDED SOLIDS

8.5.1 Label a 2in stainless steel planchet for each sample. Tare each planchet with a 47mm glass fiber filter. Record the tare weights on a QASS.

8.5.2 Filter a known volume of aqueous sample through the tared glass fiber filter. Record the volume of sample filtered on the benchsheet. Return the filter to the labeled planchet.

8.5.3 Reweigh the planchet/filter and record on the QASS.

NOTE: If the samples that have been submitted are already filtered on a glass fiber filter, the analyst may omit Section 8.5.2 and 8.5.3 and enter the procedure at this point.

8.5.4 Subtract the tare weight in Section 8.5.1 from the gross weight in Section 8.5.3 to determine the mass of suspended solids. If results are requested on a dry weight basis, the filters must be dried overnight prior to re-weighing in Section 8.5.3. Samples yielding over 5 grams of suspended material should be scraped down gently with a spatula until the mass is approximately 5 grams. Record the final mass of suspended solids in the sample weight column of the soils benchsheet.

8.5.5 The sample preparation now proceeds as a solid in Section 8.4. The entire sample on the filter, including the filter, is transferred to the centrifuge tube in Section 8.4.1. Submit the QASS with the benchsheet and note on the benchsheet that the analysis is for suspended solids rather than solids.

9. CALCULATIONS

9.1 Calculate the mass of solid deposited by subtracting the tare weight (g) from the gross weight (g). This gives the solids deposit weight in grams. To convert to mg, multiply the grams by 1000.

9.2 Calculate the alpha and beta activity, counting uncertainty, TPU, MDC and crosstalk factors in activity units per aliquot unit following SOP 708.

9.2.1 TPU FACTORS. As defined in SOP 708, the following one-sigma preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU):

Water samples require a preparation uncertainty factor of 0.0565. This is based on one gross aliquoting (sample homogeneity), one quantitative transfer, one pipetting, two mass measurements and one volumetric measurement. See the following equation:

$$0.0565 = \sqrt{0.05^2 + 0.025^2 + 0.004^2 + 0.003^2 + 0.003^2 + 0.006^2}$$

Solid samples require a preparation uncertainty factor of 0.0567. This is based on one gross aliquoting (sample homogeneity), one quantitative transfer, two pipetting, two mass measurements, and one reagent addition. See the following equation:

$$0.0567 = \sqrt{0.05^2 + 0.025^2 + 0.004^2 + 0.004^2 + 0.003^2 + 0.003^2 + 0.006^2}$$

In practice, these two TPU factors are statistically equivalent. To simplify the data reporting procedure, the greater of the two (0.0567) may be used for both matrices.

9.2.2 Calculate the alpha and beta activity according to SOP 708, except for solids, the final sample aliquot is calculated as:

$$\text{Final Sample Aliquot} = \frac{\text{SampMass} * \%\text{Sol} * \text{AnalAliqVol}}{\text{DigTotVol}}$$

where:

SampMass = Initial Sample mass taken for digestion

%**Sol** = percent solids for sample

AnalAliqVol = Volume of digestate taken for analysis

DigTotVol = Total Volume of Digestate

10. QUALITY CONTROL

10.1 Method blanks will be run at a frequency of five-percent (i.e., one per 20 field samples) with a minimum of one per batch. Method blanks for water consist of deionized (DI) water and match the largest sample volume used. Nitric acid is added to the method blank, as it is to the samples, prior to evaporation. Method blanks for solids are 2mL of salt solution brought up to 30mL with 8N nitric acid.

10.2 Laboratory Control Samples (LCS) will be run at a frequency of five-percent with a minimum of one per batch. Known quantities of NIST-traceable alpha (e.g., ^{230}Th for Drinking Water Compliance using Method EPA 900.0 and ^{241}Am for any others) and beta (^{90}Sr/Y) emitters are spiked into DI water at the start of the procedures. The spiking levels are determined according to specific data quality objectives for the work being performed, but will generally be 5-50 times the required minimum detectable concentration for the respective analyte or at an activity level roughly equivalent to levels expected to be observed in the samples. The volume for the LCS is as large as the largest sample volume. The LCS consists of deionized water at the correct volume and the appropriate spike and spike volume. The LCS for solids consists of 2mL of salt, the appropriate spikes and spike volume, brought up to 30mL with 8N nitric acid.

10.3 Duplicate samples will be run at a frequency of ten percent with a minimum of one per batch. Client requested duplicate analyses shall be run as required and may count as the QC replicates for that batch.

10.4 Matrix Spike (MS) will be run at a frequency of five-percent with a minimum of one per batch. Known quantities of NIST-traceable alpha (i.e., ^{230}Th for Drinking Water Compliance using Method EPA 900.0 or ^{241}Am for any others) and beta (^{90}Sr/Y) emitters are spiked into a representative sample at the start of the procedures. The spiking levels are generally 5-50 times the analyte activity level expected to be observed in the samples.

10.5 The LIMS Standards Database should be consulted for the identification of the proper ^{241}Am or ^{230}Th, and ^{90}Sr working standards and spike activities.

10.6 Method blanks for air filter and suspended solids samples may be prepared to reflect the proper background contribution of the filter medium used for analysis. Method blanks for suspended solids consist of clean glass fiber filter medium

from the same batch used for capturing the solids. Air filter blanks, if supplied by the client, may be used as a "reagent" blank. Otherwise, a blank planchet is usually the best representation of the sampling medium background.

10.7 LCS for filter-mounted samples consists of a planchet containing a known amount of standard ^{241}Am and ^{90}Sr.

11. DEVIATIONS FROM METHOD

This SOP is substantially compliant with SW-846 Method 9310 and EPA Method 900.0. The following information states deviations from and distinctions between the two reference methods as well as other regulatory issues that should be considered.

11.1 In this procedure, alpha and beta activities are determined simultaneously on the beta plateau. Crosstalk calibration of the proportional counter allows for correction of the contribution of "crosstalk" into respective opposing channels (beta-to-alpha and alpha-to-beta). Methods 9310 and 900.0 instruct the counting of alpha and beta at their respective plateaus. By setting the alpha/beta discriminators such that there is negligible contribution of beta events to the alpha energy region, there is no advantage for counting on the respective voltage plateaus. However, there are significant disadvantages to counting on the two plateaus independently: (1) The count time required immediately doubles and (2) the alpha efficiency is lower at the alpha plateau such that analysis time may need to be increased more to reach the same required detection limit.

11.2 This procedure has been modified to accommodate matrices other than drinking waters. The procedure treats solubilized radioactive constituents in digestate or leachate solutions as a water sample.

11.3 Implementation Guidance for Radionuclides (December 2000) indicates that ^{230}Th is to be used for purposes of demonstrating compliance with the standard. Unless otherwise specified, all other results are completed using ^{241}Am as the reference nuclide for gross alpha.

11.4 SW-846 defines sampling and preservation protocols that may diverge from the requirements of Method 900.0. The sampling process is completed prior to receipt and processing of water samples by the laboratory and does not directly affect laboratory operations. SW-846 does specify a holding time of 180 days. The SOP references both protocols that are to be used to ensure compliance with applicable regulation.

11.5 A second deviation between the two methods is the Method 900.0 requirement that a minimum 10,000cts/detector and standard be accumulated during the absorption curve calibration. This SOP requires that 10,000 counts be accumulated, satisfying both methods.

11.6 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the laboratory's internally derived acceptance criteria.

11.7 Methods 9310 and 900.0 are otherwise substantially identical. This SOP meets or exceeds the requirements of the methods for the analysis of water samples.

12. SAFETY HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Safety glasses, lab coats and gloves should be worn in the laboratory at all times.

12.1.2 Use care when handling strong acids (e.g., HNO_3, HCl, etc.). Work only in a fume hood with adequate ventilation and wear appropriate eye, face, and body protection.

12.2 WASTE DISPOSAL

12.2.1 The Gross Alpha/Beta analytical process liquid effluent, from the solid procedure, has been determined to not be hazardous other than corrosivity. This material may discharged into the Paragon wastewater treatment facility. Here the solution will be neutralized prior to discharge and the activity will be monitored to ensure compliance with Colorado Rules and Regulations pertaining to Radiation Control Part 4 regarding discharges to sanitary discharges to sanitary sewers.

12.2.2 Solids and filtered residues should be accumulated in a 2 liter wide-mouth container. The accumulated solids may be disposed of in the proper solids waste stream when it is determined that the pH is between 5 and 12 units. If the pH of the accumulated solids is determined to be <pH 5, the pH should be adjusted to between 5-12 units using NaOH solution. All free liquids must be drained prior to transfer to the appropriate waste accumulation container. Consult with the Heath and Safety Coordinator or with the lab Supervisor for proper procedures for testing and disposing of solid wastes.

13. REFERENCES

13.1 Method 9310, EPA SW-846, Gross Alpha and Gross Beta, Revision 0, September 1986.

13.2 Method 900.0, Prescribed Procedures for Measurement of Radioactivity in Drinking Waters, EPA-600 4-80-032, August 1980.

13.3 Method 7110B, Standard Methods for the Examination of Water and Waste Water, 18th Edition, APHA, 1992.

13.4 EPA 816-D-00-002, Implementation Guidance for Radionuclides, December 2000.

13.5 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

2/27/07: Slight title change for rev18 (SW-846 METHOD 9310 to SW9310). Added DOCUMENT REVISION HISTORY Section and Forms.

8/31/07: Added LIMS program specification language (RESPONSIBILITIES). Clarified use of second independent source for spiking (SECTION 6). Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Sections 7.1 and 8.3.1.2. Added note, 8.4.3, that it is important protocol to add spikes before any chemical processing. Removed activity calculations from SECTION 9 and referenced SOP 708 instead.

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 703 REVISION 8

TITLE: SAMPLE PRESCREENING

FORMS: 214, 796 **use current iteration**

APPROVED BY:

TECHNICAL MANAGER Renee Hallegos DATE 7/21/08
QUALITY ASSURANCE MANAGER Deb Schert DATE 7/20/08
LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: Rev0, 9/18/92; Rev1, PCN #40, 12/13/93; Rev2, PCN #338, 1/24/95; Rev3, 10/08/99; Rev4, 3/17/00; Rev5, 4/26/02; Rev6, 10/3/03 and 2/9/05 (no revisions); Rev7, 8/18/06; Rev8, 7/17/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the semi-quantitative determination (i.e., prescreening) of non-volatile gross alpha and beta activity in samples. Prescreen results enable the Radiation Safety Officer (RSO) to determine what precautions are necessary in order to process the samples in the laboratory safely.

2. SUMMARY

2.1 The RSO develops protocols for deciding which samples need to be prescreened. Where sufficient prior knowledge regarding a client's samples exists, a determination of "always prescreen" or "prescreening not required" may be made in advance. Where previous knowledge about a client's samples is insufficient, the RSO uses prescreen results to determine what precautions are necessary for processing the samples in a manner that is safe to laboratory personnel.

If it is known in advance that incoming samples require prescreening, the Project Manager (PM) can use an Incoming Project Notice Form (Form 214, or equivalent) to inform Sample Control and other laboratory staff before the samples arrive. Samples that need to be prescreened may also be determined as a result of the sample login survey performed by Sample Control staff upon sample receipt (SOP 202).

Regardless of which mechanism triggers the prescreen test, Sample Control staff are responsible for notifying the RSO or designee when prescreening is required.

2.2 Liquid samples are prepared for prescreening by drying an aliquot of liquid on a planchet. The mass of solid residue is determined, and the planchet is counted in a proportional counter. Solid samples are prepared for prescreening by transferring a known mass (approximately 100mg) to a stainless steel planchet, adding nitric acid, then evaporating the planchet's contents to dryness on a hotplate. If a high degree of sample inhomogeneity is expected (consult RSO or

Radiochemistry Supervisor), the samples may alternately be leached with nitric acid, and after the suspended solids are allowed to settle, an aliquot of the resulting leachate may be tested as previously described for liquids. The prescreening of other sample matrices, such as non-aqueous liquids, must be handled on a case-by-case basis.

2.3 Gross alpha prescreen measurements are referenced to ^{241}Am; gross beta prescreen measurements are referenced to ^{90}Sr/Y.

3. RESPONSIBILITIES

3.1 This procedure is to be performed only by personnel who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review or the successful completion of precision and accuracy tests performed.

3.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. All personnel who work with samples involving this method are responsible for noting any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Emitters that are volatile in hot acidic solution are not amenable to measurement by this method.

5. APPARATUS

5.1 Low-level gas flow proportional counter

5.2 Stainless steel planchets, two inch, ringed bottom

5.3 Beaker, 50 or 100 mL, Pyrex™

5.4 Pipettors, Eppendorf™ or equivalent, 1 and 5 mL, with disposable tips

5.5 Transfer pipets, disposable

5.6 Balance, analytical, 0.0001g sensitivity

5.7 Petri dishes

5.8 Hot plate and steam bath

5.9 Infrared lamp

5.10 Tweezers

5.11 Tongue depressors

5.12 Centrifuge tube, 50mL

5.13 Rubber policeman

5.14 Centrifuge

6. REAGENTS

6.1 Deionized (DI) water, obtainable from the laboratory's deionized water system

6.2 Nitric acid (HNO_3), concentrated. TLV = 2ppm (TWA); irritant, corrosive

6.3 Nitric acid, 8N: Cautiously add 500mL conc. HNO_3 to approximately 400mL DI water, dilute to 1 L. TLV = 2ppm (TWA); irritant, corrosive

6.4 Nitric acid, 3N: Cautiously add 190mL conc. HNO_3 to approximately 700mL DI water, dilute to 1 L. TLV = 2ppm (TWA); irritant, corrosive

6.5 ^{241}Am spiking solution, NIST-traceable, independent second source

6.6 ^{90}Sr spiking solution, NIST-traceable, independent second source

Note: All spiking solutions are from a source that is different than that used for calibration.

6.7 Modified USGS Simulated River Water Reagent (salt solution): Dissolve 3.72g $MgSO_4$, 3.10g NaCl, and 3.24g $CaCl_2$ in 200mL 1N HNO_3.

6.8 Anhydrous calcium chloride ($CaCO_4$) or indicating Drierite™, for desiccator

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Store samples to be prescreened in the Sample Control walk-in cooler RU #20. Sample containers may be taken to the Prescreen Lab for aliquotting, but must be returned to the walk-in cooler as soon as the aliquots are obtained.

NOTE: Samples designated for prescreening are NOT to be prepared in normal sample preparation areas without specific permission from a Radiochemistry Supervisor.

8. PROCEDURE

8.1 GROSS SCREEN PREPARATION WORKSHEET

Initiate a Gross Screen Preparation Worksheet (Form 796) for each group of samples to be prescreened. Use the information on the chain of custody (COC) or workorder to fill out the Sample ID. Locate one of the containers for each sample and transfer them to the Prescreen Lab. Return these samples to the cooler as soon as the aliquots have been obtained.

8.2 PREPARATION OF LIQUIDS FOR PRESCREENING

8.2.1 Label and tare a clean, dry planchet for each sample to be prescreened. Record the weight on the worksheet (Form 796) to the nearest 0.0001g. Prepare quality control (QC) samples per Section 9.

8.2.2 Use a calibrated pipettor (SOP 321) with a clean pipet tip to acquire a 10mL aliquot of sample from the container.

NOTE: A reduced aliquot may be taken for samples with expected activities above 5000cpm. The RSO will determine when a reduced aliquot is used. Also, aliquot sizes should be decreased for samples with significant quantities of suspended solids.

8.2.3 If the sample is unpreserved, or preserved with anything other than HCl, proceed to Step 8.2.5.

8.2.4 If the sample has been preserved with HCl, it will corrode the planchet. Convert to a nitrate system as follows:

8.2.4.1 Place the aliquot (Step 8.2.2 above), in a labeled 50mL beaker and add 5mL conc. HNO_3.

8.2.4.2 Slowly evaporate to near dryness on a hot plate, avoiding spattering.

8.2.4.3 Add 1mL of conc. HNO_3 to the residue and repeat evaporation.

8.2.4.4 Dissolve the residue in 1-2mL of 3N HNO_3, slurry any undissolved solids.

8.2.4.5 Quantitatively transfer the beaker's contents to a labeled, tared planchet using 3N HNO_3. Rinse the beaker 3 times with small portions (≈1mL) of 3N HNO_3. Transfer all rinses to the planchet. Use a rubber policeman to help transfer solids.

8.2.5 Add the sample to the planchet and dry the planchet on a hot plate.

8.2.6 Remove the planchet and allow to cool for about 15 minutes.

8.2.7 Weigh the planchet and record the weight on the worksheet. This weight will later be used in determining the solids present during counting.

NOTE: The amount of solids should be within the range of the instrument calibration, so as to reduce self-absorption losses in activity measurements. If the solids are greater than the range of the instrument calibration, a proportionately smaller aliquot will have to be processed as above per Steps 8.2.1.

The proportionate amount of reduced aliquot to use may be estimated using the following equation:

$$V\ (mL) = \frac{0.95}{W\ (g)}$$

where:

V (mL) = volume of reduced aliquot
W (g) = mass of solids present in the original 10mL aliquot

Note that if a 1mL aliquot was originally used, divide the V(mL) in the equation above by ten to get the correct new aliquot.

8.2.8 Transfer the planchets to a clean petri dish.

8.2.9 Proceed to Section 8.5.

NOTE: Prepare oils as described in section 8.3 for solids. Be aware to avoid spattering. Due to the nature of the matrix (oil), extra drying time may be required. Consult Supervisor with any questions.

8.3 PREPARATION OF SOLIDS FOR PRESCREENING (DIRECT DEPOSITION)

8.3.1 Label and tare a clean, dry planchet for each sample to be prescreened. Record the weight on the worksheet (Form 796) to the nearest 0.0001g. Prepare QC samples per Section 9.

8.3.2 Transfer approximately 100mg of sample directly to the tared planchet. Record the mass to the nearest 0.0001g on the benchsheet.

NOTE: Some samples may contain standing water at the top of the container. Homogenize these samples thoroughly (i.e., mix-in the water) before obtaining an aliquot.

8.3.3 Place the planchet on a hotplate. Set the heat to low-medium. Carefully add 5mL conc. HNO_3.

8.3.4 Slowly evaporate to dryness, avoiding spattering.

8.3.5 Remove the planchet from the hotplate and allow to cool for about 15 minutes.

8.3.6 Weigh the planchet and record the weight on the worksheet. This weight will later be used in determining the solids present during counting. **See NOTE, Step 8.2.7 above.**

8.3.7 Transfer the planchets to a clean petri dish.

8.3.8 Proceed to Section 8.5.

8.4 PREPARATION OF SOLIDS FOR PRESCREENING (LEACHING) - **Consult with a Radiochemistry Supervisor before preparing samples in this manner!**

8.4.1 Weigh 2 grams or 0.5 grams (see note below) of solid, on an analytical balance whose calibration has been previously verified (SOP 305), into a 50mL centrifuge tube. Record the weight on the worksheet (Form 796).

NOTE: Two (2) grams of sample should be aliquoted for samples with expected activities less than 5000cpm. An aliquot of 0.5 grams or less, may be used for samples with higher expected activities.

8.4.2 Add 8mL concentrated nitric acid to the centrifuge tube.

8.4.3 Leach the sample fifteen minutes on a steam bath.

8.4.4 Remove the sample from the steam bath and allow to cool.

8.4.5 Add 17mL of 8N HNO_3 to bring the digest volume to 25mL. Swirl sample to mix completely.

8.4.6 Centrifuge the samples at 3500rpm for 15 minutes.

8.4.7 Prepare QC samples per Section 9.

8.4.8 Take a 2mL aliquot of the leachate and deposit this onto a labeled, tared planchet.

NOTE: The proportionate amount of solid aliquot used may be calculated using the following equation:

$$W_{aliquot}\,(g) = \frac{W_{total}\,(g) \times V_{aliquot}\,(mL)}{V_{total}\,(mL)}$$

where:

Valiquot (mL) = volume of aliquot used

Vtotal (mL) = total volume of leachate

Waliquot (g) = mass of solids present in the original 2 mL aliquot

Wtotal (g) = mass of sample recorded from step 8.4.1.

8.4.9 Follow Steps 8.2.1 to 8.2.7, as for liquids.

8.5 COUNTING OF PRESCREEN SAMPLES

8.5.1 Determine the mass of solids (i.e., residue), in mg, per Section 8.6 below.

8.5.2 Samples are counted in the Prescreen Lab per SOP 724.

8.5.3 Verify that all information has been recorded on the Gross Screen Preparation Worksheet where needed, and is legible. Sign your initials in the space at the top of the form provided for "Analyst".

8.5.4 Give a copy of the prescreen results, including the blank and LCS, to the appropriate PM or the RSO.

8.6 CALCULATIONS

Amount of solids (mg) = [Gross wt of planchet (g) - tare wt of planchet (g)] x 1000 mg/g

NOTE: Activity, uncertainty, and minimum detectable concentration (MDC) calculation formulae may be found in SOP 708.

9. QUALITY ASSURANCE/QUALITY CONTROL

9.1 One blank is to be prepared and analyzed each day prescreen samples are processed. This one blank will be used for all matrices prepared that day. Prepare the blank by pipetting 5.0mL of concentrated nitric acid onto a labeled planchet; add 1mL of salt solution and dry on a hotplate. This blank is subject to the same acceptance criteria specified in the Gross α/β procedure (SOP 724).

9.2 One laboratory control sample (LCS) is to be prepared and analyzed each day prescreen samples are processed. This one LCS will be used for all matrices prepared that day. The LCS consists of approximately 100dpm of ^{90}Sr and 100dpm of ^{241}Am spiked onto a tared planchet, containing approximately 5mL of conc. nitric acid. ***If the spike solution was made in HCl, the solution must be converted to a nitrate system prior to planchetting in order to prevent corrosion of the stainless steel planchet.*** One (1) mL of salt solution is added to the planchet prior to drying. The LCS is acceptable if the value yielded is +/-30 % of the expected value. If this criterion is not met, notify a Radiochemistry Supervisor immediately for possible corrective actions.

10. DEVIATIONS FROM METHOD

This is a proprietary method, developed by Paragon. Therefore, there are no deviations from promulgated methods.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Safety glasses should be worn when working with nitric acid.

11.1.2 When working with large amounts of acid, a plastic apron should be worn and use of a face shield is highly recommended.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 12.2 below.

11.2 WASTE DISPOSAL

11.2.1 The prescreen liquid analytical process effluent has been determined to not be hazardous in any other way than corrosivity. This material may, therefore, be discharged to the Paragon wastewater treatment facility. Here the solution will be neutralized and the radionuclide concentration will be monitored to ensure compliance with Colorado Rules and Regulations.

11.2.2 Disposal of solids should be in an appropriate waste carboy and stored for further evaluation under the direction of the RSO.

12. REFERENCES

12.1 Eastern Environmental Radiation Facility Radiochemistry Procedure Manual, EPA 520/5-84-006, 00-01.

12.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

8/18/06: Clerical corrections. Updated Form references and added Form attachments. Added missing items to equipment list. Included NOTE regarding oils. Added DOCUMENT REVISION HISTORY section.

7/17/08: Added 6.6 note that all spiking solutions are from a source that is different than that used for calibration. Changed volume used from 5mL to 10mL under Note in Section 8.2.7. Added note and calculation in Step 8.4.3.

Kit: Y / N **Rush?** Y / N **Prescreen?** Y / N ***Paragon Analytics***

INCOMING PROJECT NOTICE

Date: _____ **Copy to:** Sample Control

Initiator: _____ _____

Date(s) expected: _____ _____

Client: _____ Assigned PM: _____

Address: _____ Client Contact: _____

_____ Phone: _____

Report to: _____ Fax: _____

Proj. Name/Number: _____

# Samp	Matrix	Analysis/Method	Price	Sub Lab	# x Cont. Type	Preserv.	Tot. Bottles
					X		
					X		
					X		
					X		
					X		
					X		
					X		
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QC Level: _____ Disposal or handling? $5 / $10 / $15 / $_____ / RTC

Report Level: _____ TAT (working days): 20 / 15 / 10 / 5 / 3 / 2 / 24hr /____

EDD: N / Y Format: Report: Wet Weight / Dry Weight / As Received

Kit to:

Date kit needed: _____ **am / pm**

Attention: _____

Company: _____

Address: _____

_____

Phone: _____

Potential Radioactivity:

Do the samples contain radioactive materials?	Y / N
Are any samples potentially mixed hazardous materials?	Y / N
Are any samples from a known RAM site?	Y / N

Additional Special Handling:

Include: COC(s) Bubble Wrap Labels Seals Blue Ice Temp. Blks

Comments: Rush Special Test Special Analyte Special Charge Detection Limits (see attached)

Kit Prepared by: _____ Date: _____ Picked up by: _____ Date: _____

i:\oprtns\misc\forms\IPN_Form214r5.xls (10/29/03)

SOP 703 Rev ____ LB5100A *Paragon Analytics*

Date	Sample ID	Group	Carrier	Filename	Count Duration (minutes)	Start Time	Analyt's Initials	Position Check Initials	Comments

Reviewed by / Date _____

Form 796r5.xls (12/15/2003)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 704 REVISION 9

TITLE: ANALYSIS OF TRITIUM AND OTHER BETA-EMITTING NUCLIDES BY LIQUID SCINTILLATION COUNTING -- METHOD EPA 906.0

FORMS: 700_Quantulusr1.xls (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/4/07

LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 9/18/92; Rev1, 3/8/93; Rev2, 5/10/93; Rev3, 7/27/93; Rev4, PCN #148, 3/2/94; Rev5, 10/8/99; Reviewed and distributed without revision, 3/14/02; Rev6, 4/7/03; Rev7, 12/13/04; Rev8, 9/1/06; Rev9, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform analysis of samples of various media using Paragon's one Wallac Quantulus 1220 and two Beckman LS6000 and LS6500 liquid scintillation counters (LSCs). Samples will normally be liquids in a 20mL scintillation vial, which may represent the sample directly (water samples) or indirectly (extracts from soil samples, silica gels, etc.).

This procedure provides the analysis portions of EPA Method 906.0. This procedure is applicable to the determination of tritium (^{3}H), as well as ^{14}C, ^{63}Ni, ^{99}Tc, ^{241}Pu, ^{210}Pb, ^{147}Pm, and other radionuclides.

2. SUMMARY

Beta emissions are detected by a fluor (i.e., a fluorescing molecule) mixed with the sample in a 20mL liquid scintillation vial, which in turn emits light in direct proportion to the beta emission energy and intensity. This light pulse is converted to an electronic pulse and recorded as a beta emission event on the instrument's multi-channel analyzer (MCA). The data collected by the MCA are subsequently interpreted by a software program, generating results in units of radioactivity per unit sample volume.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.2 It is the responsibility of the instrument operator to perform the analyses within

the specified hold time for the method to ensure timely analysis of samples with short-lived radionuclides or other time-sensitive concerns. The instrument analyst must ensure optimum instrument capacity through the timely performance and documentation of calibrations, daily performance checks, routine maintenance, etc., as described in Table 1.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the workorder file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples utilizing this method to note any anomalous or out-of-control events associated with the preparation and analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 The scintillation vial is an optical surface. Any markings or material on the outside of the scintillation vial will interfere with the detection of scintillation. These should be removed prior to analysis by wiping the vial with a lint-free lab wipe and alcohol. All labeling must be done on the cap of the vial.

4.2 The quench indicating parameter (QIP, usually H-number or SQP(E)) must be within the established calibration range for the specific analysis. Refer to Table 1 for evaluation of QIPs. Nitromethane, or other suitable quenching agent, is added to samples that are not sufficiently quenched to bring them within the calibrated range. Consult with the Radiochemistry Manager for guidance if quenching is necessary.

4.3 The QIP should be monitored and variations in quench that could correspond to greater than 10% (or +15 H or SQP(E) numbers) relative bias in the efficiency, should be addressed by using standard additions to determine a sample-specific efficiency.

4.4 The presence of visible coloration in the distillate will act as an 'inner filter'. This

effect, known as 'color quenching' is an interference to the detection of the scintillation.

4.5 The presence of particulate contaminant in the final water distillate may interfere with the detection of the scintillation. This effect is known as 'physical quenching'.

4.6 The presence of chemical contaminants in the final water distillate may inhibit scintillation. This effect is known as 'chemical quenching'.

4.7 The scintillation cocktail contains a fluorescing molecule that is subject to excitation in the presence of light. Samples must be "dark adapted" for at least 3 hours prior to counting to minimize this effect. For instruments that do not allow an accurate luminescence correction (i.e., the LS6500 and Quantulus), the sample luminescence should be monitored and appropriate corrective action taken as described in Table 1.

4.8 Sample luminescence (LUMEX) interferes with the analysis of low-energy beta activity, and is monitored by the instruments. Sample LUMEX should be less than 5% for routine analyses on instruments that do not perform an automatic LUMEX correction. In instruments that perform an automatic LUMEX correction to the data, the sample LUMEX should be less than 10% in routine analyses. LUMEX values above 10% may be acceptable, with approval from the Department Manager.

4.9 The Window 2 count rate is monitored for high-energy beta contamination. Control limits are calculated as the mean of the Window 2 count rates for the sources in the efficiency calibration ± three standard deviations of those count rates. Counts outside of the derived control limits should be evaluated and appropriate corrective action taken. Corrective action may include the re-preparation of the sample, reanalysis, or the qualification of the data based on the analyst's judgment of the impact on the sample data quality.

5. APPARATUS AND MATERIALS

This procedure is conducted with the use of installed beta detection and analysis equipment, consisting of a liquid scintillation counter (LSC), analysis software, and associated nuclear electronics and cabling. In the case of the LS6000, the data may be transferred directly to a floppy disk using a PC with the appropriate interface hardware and software. The LS6500 has these features built-in and can write to a floppy disk with an internal disk drive.

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) or Permissible Exposure Limit (PEL) below 50ppm must be worked with in a laboratory fume hood. The absence of this

information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Nitromethane, reagent grade
TLV = 20 ppm (TWA). Extremely hazardous, highly reactive, highly flammable, flashback hazard, carcinogen.

6.2 Methanol, reagent grade
TLV = 200 ppm (TWA).

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Chemical preparation steps performed for this analysis are detailed in the appropriate Paragon preparation SOPs. Samples to be analyzed by this procedure will have been prepared by radiochemical procedures that include distillation of liquids, or azeotropic distillation of soils/solids.

7.2 The prepared scintillation vials for Total Activity are prone to building up pressure and rupturing in storage. It is the responsibility of the instrument analyst to dispose of the scintillation vials as soon as is practical after review and verification of the data, preferably within 60 days after preparation.

7.3 Certain analyses are prone to interference from either short-lived radionuclides (e.g. ^{99m}Tc, ^{222}Rn) or rapidly ingrowing progeny (e.g. ^{210}Bi). Time-sensitive counting constraints are specified in the individual preparation SOPs.

7.4 Certain analyses are prone to rapid quenching after preparation (e.g. ^{63}Ni). These samples must be counted as soon as possible after preparation, before the QIP drifts outside the calibration range.

8. PROCEDURE

8.1 OPERATING CONDITIONS

The LSC shall be operated according to the instructions provided by the manufacturer. All instrument settings shall be determined during instrument installation and/or calibration. The operating conditions shall be verified daily by performance of the daily quality control (QC) checks (discussed subsequently in this SOP). *Be sure the samples have been allowed to dark-adapt for a period of at least 3 hours prior to analysis.*

8.2 SAMPLE LOADING FOR BECKMAN INSTRUMENTS

8.2.1 Normally, the samples will be placed in the rack in the order they are listed on the benchsheet. Place the rack(s) in the counter with the front (i.e., side with rack number and/or user number) facing *away* from the operator.

The first rack to be counted must have a user number (see below) installed in the left (looking at the front of the rack) card slot.

Subsequent racks will not have a user number card unless a different analysis is required for that rack.

Ensure that the counting position of each sample is correctly recorded on the benchsheet and that the user number has the correct settings.

8.2.2 USER NUMBERS

User numbers provide the count and data output parameters. User number programs can be set by pressing the "Main Menu" button, then using the cursor arrows to highlight "Review and Edit User Programs". Using the cursor arrows, highlight the user number to be edited, then highlight the parameter to be set, and follow any prompts given at the bottom of the screen. For more details on setting the user number parameters, see the instrument's operating manual.

Default settings for all of the user numbers are:

- Count Blank: NO
- Two Phase: NO
- Scintillator: LIQUID
- Low Level: YES
- H#: YES
- IC#: NO
- LUMEX: YES (This option is available only on the LS6000. The LS6500 doesn't correct for luminescence.)
- Half Life Correction Date: NONE
- Sample Repeats: 1
- Cycle Repeats: 1
- Cycle Repeats: 1
- Low Sample Reject: 0
- Printer: STD
- RS232: STD

Other parameters may vary for each user number. These are:

8.2.2.1 MANUAL WINDOW SETTINGS

In order to determine the manual window settings, a source (count long enough to achieve approximately 10,000 counts) and blank (count for approximately 90 minutes or as long as the longest count time typically observed for the method of interest) are counted on the instrument.

The user number is set with Window 1 at WIDE, and the raw data output is set for Spectral Data, to give a channel-by-channel output. Once the data are collected, a Figure of Merit (FOM) is calculated to optimize the window settings in order to minimize the MDC (minimum detectable concentration). Windows are set for each analysis type (i.e., ^{3}H, ^{14}C, etc.). For analyses with multiple counting geometries (i.e., 10mL or 5mL) a single, optimized window setting is preferred.

A FOM determination should be performed following replacement of any major instrument hardware or bi-annually, whichever comes first.

$$FOM = \frac{(\text{Source Counts})^2}{\text{Background Counts}}$$

The FOM should be maximized by changing the window settings to determine the greatest efficiency and the lowest background.

8.2.2.2 COUNT TIME

The count time should be determined taking into consideration the required MDC and sample volume. Samples should not be counted for longer than 2-3x the normal count time for a standard aliquot size unless contractual requirements are in place. For most analyses, the standard count time is approximately 60 minutes.

8.2.2.3 COUNTING PRECISION

The instrument can be set to stop counting once a required numbers of counts have been accumulated. For the analyte of interest window, the precision is generally set to 1.75% to 2.5%.

8.3 SAMPLE LOADING FOR QUANTULUS INSTRUMENT

8.3.1 The Quantulus contains three “racks” each having four rows of five positions. The first rack contains positions 1 through 20, the second rack positions 21 through 40 and the third rack 41-60. Positions 57 through 60 are reserved for daily check vials. Position numbers are arranged as shown below:

1	2	3	4	5
6	7	8	9	10
11	12	13	14	15
16	17	18	19	20

Ensure that the counting position is correctly recorded on the benchsheet.

8.3.2 PROTOCOL SELECTION

8.3.2.1 From the Windows Program Manager, select the "WinQ" icon. There will be two buttons at the top of the screen.

8.3.2.2 Select the button marked "Users." Three columns will appear on the screen: "Users," "Protocols," and "Queue."

8.3.2.3 Highlight the nuclide of interest (e.g., H3-5mL for tritium analysis in a 5mL geometry) in the "Users" column.

8.3.2.4 Protocols for the nuclide of interest will appear in the "Protocols" column. There are three screens within each Protocol.

- In the first screen "General Parameters," enter the folder name and save path. For example, one would enter "C:\H3-5ML\H-0406" for a tritium analysis in a 5mL geometry that was the first of such analyses loaded on the sixth of April.

  For the second of such analyses loaded on the same day, the folder name and save path would be:"C:\H3-5ML\H-0406a".

- On the "Sample Parameters" screen within the protocol, enter the identification of the samples to be counted, the sample position, the count time and the specifications as listed below:

  COUNTS: No Lim
  CUCNTS: No Lim
  MCW: 1
  REP: 1

ST: Y
STMS: 1/1
STIME: 00:30

- On the "MCA & Window Settings" screen within the protocol, specifications are made for each analysis as described below:

DAILY PERFORMANCE CHECKS

Configuration: 3H
Send Spectra: 11, 12
Coincidence Bias: Low
PAC: n/a
PSA: n/a

TRITIUM (and other low-energy beta emitters)

Configuration: 3H
Send Spectra: 11, 12
Coincidence Bias: Low
PAC: 1
PSA: n/a

CARBON-14

Configuration: 14C
Send Spectra: 12
Coincidence Bias: High
PAC: 1
PSA: n/a

ALPHA/BETA DISCRIMINATION

Configuration: Alpha/Beta
Send Spectra: 11, 12
Coincidence Bias: Low
PAC: 1
PSA: The default setting is 100, the optimum PSA value should be determined experimentally as it depends on the quench of the sample and the nuclides being analyzed.

8.3.3 PROTOCOL DELETION

CAUTION: Protocols should only be deleted with the approval of the Department Manager.

8.3.3.1 From the "Users" screen (accessed by clicking the "Users" button at the top left of the screen at any time), entire protocols may be deleted by highlighting the protocol in the center of the screen and clicking the "Delete" button.

8.3.3.2 A protocol may be removed from the queue (i.e., be removed from the counting line-up but not actually deleted) by highlighting the protocol in the "Queue" column at the right of the screen and pressing the DELETE key on the keyboard.

8.4 DATA COLLECTION

8.4.1 THE FOLLOWING PROCEDURE IS FOR THE LS6000 *ONLY*
To use this option, the user number used to count the samples must have the STD RS232 Format selected.

8.4.1.1 From the Main Menu of the support computer for the LS6000, choose "Tritium Data Capture" and press <Enter>. When the Data Capture software starts, choose "1. LS6000" <Enter>, then "1. RECEIVE data from instrument" <Enter>.

The program will provide a table with the header "Drive and Subdirectory"; press <Enter>. Send the data to the b:\ drive (be sure that a disk is inserted into the b drive). The upper left corner of the display will read "Awaiting Response".

8.4.1.2 Press the "Main Menu" key on the front panel of the counter. Use the cursor arrows to highlight "Automatic Counting", then press "Start" to begin counting.

The counter will analyze each sample and generate results in CPM for each vial counted. The Data Capture software will have a message in the upper left corner which reads: "Status: Receiving Record XXXX", where XXXX is the number of the data record which will increase as samples are analyzed.

The Data Capture software will now also display the filename in which the data is stored in the center of the screen. This file is named "\TRITIUM\UNXX-YYY.BSF", where XX is the user number, YYY is the next sequential number for files created with that user number, and .BSF is the default extension for Beckman Standard Format files. *Note this file name in the filename section of the benchsheet.*

8.4.1.3 When the count is complete (i.e., LS6000 Main Menu has returned to the display), complete the liquid scintillation run log.

To process the data, press <Esc> on the LS6000 support computer. The Status message in the upper left corner of the display, will read "Capture Completed". Press <Esc> twice to return to the Data Capture software main menu. Remove the disk from the b:\ drive and take the disk to the tritium reporting PC.

Copy the correct file to the c:\ drive of the reporting PC. Open the “dc” program on the c:\ drive by typing “dc” then <Enter>. Use the cursor arrows to move the highlight bar to "DATA CAPTURE SUPPORT", press <Enter> to choose this option, then choose "3. Convert BSF to dBASE File", then press <Enter>. Press 1 (Convert); the software will then prompt for "Input Filename (.BSF)" and "Output Filename (.DBF)". Type the name of the file recorded on the benchsheet, without an extension (for example, "UN01-001"), and press <Enter> for each prompt. The software will then present a default format titled "Tritium"; press <Enter> to accept this format.

A message at the bottom of the screen will read "Use actual dBase file structure (Y/N) [Y]"; press <Enter> to accept the default "Y". Then data will then be converted and displayed on the screen, with the message "Conversion Completed !".

Press <Esc> 4 times to return to the PC's Main Menu. Copy the new file to the r:\tritium directory. The data may now be accessed from any PC that is a part of the Paragon network.

8.4.2 THE FOLLOWING PROCEDURE IS FOR THE LS6500 *ONLY*

8.4.2.1 To start the sample count, press the "Main Menu" key on the front panel of the counter. Use the cursor arrows to highlight "Automatic Counting", then press "Start" to begin counting. The counter will analyze each sample and generate results in CPM for each vial counted.

8.4.2.2 When the count is complete (LS6500 Main Menu has returned to the display), complete the liquid scintillation run log.

8.4.2.3 To create a disk to transfer run information from the LSC to the tritium reporting PC, select “Data Management” from the

main menu on the LS6500. Next, select "Access Data Buffer/Disk", then select "Move Files to Disk". Enter the user number for the files that you want to move.

8.4.3 THE FOLLOWING PROCEDURE IS FOR THE QUANTULUS *ONLY*

8.4.3.1 After the protocol has been modified for the specific desired analysis, click the "OK" button on the left of the screen. Highlight the protocol in the center of the screen and click on the "Queue" button to add the protocol to the queue to be counted. If the instrument is currently running, the protocol will automatically count after all protocols listed before it in the queue have counted. If the instrument is not currently running, it is necessary to click on the "Counters" button at the top left of the screen. When the "Counters" screen appears, press the "play" (►) at the bottom center of the screen.

8.4.3.2 QUANTULUS LOGBOOK
Samples are recorded in the logbook (Form 700_ Quantulusr1.xls) at the start of analysis. The "Count Time (minutes)" and "Position Check" will be completed after the samples have been counted.

8.4.3.3 When the data collection is complete, the protocol will disappear from the queue. The sample data may be accessed by one of two ways -- through the registry, or through the software analysis program EASY view.

- REGISTRY SAMPLE DATA
  This is the data stored as a text file. To access the registry, use Windows Explorer to access the folder chosen as described in Section 8.3.2. Double-click the file named REGISTRY.TXT within that folder and the file may be printed.

- EASY VIEW SOFTWARE ANALYSIS
  From the main menu of the support computer for the Quantulus, select Programs→Wallac→ EasyView. At the top left of the screen, right-click the word "spectra" and select the option "New".

  Navigate to the folder of interest and choose the desired files. Note: the files are named "QXXYYZZ", where Q refers to the instrument designation, XX is the count order, YY is the

sample position, and ZZ is the repetition (usually 01).

Next, at the top left of the screen, right-click the word "Setup" and select the option "Properties". The "Window Settings" window will appear. Select the channels of interest for the given nuclide. For ^{14}Carbon, spectrum 12 only need be chosen. For all other analyses, both spectra 11 and 12 need to be chosen for each window. After selecting the desired windows, click "Close".

To print the data, choose File→Print and click the printer icon at the top of the page.

8.5 SAMPLE ANALYSIS

Data from all instruments may be entered manually into LIMS. Alternately, data from the LS6000 and LS6500 may be automatically uploaded, as described below:

8.5.1 On the LS6000 or LS6500, move the desired .ASC file into "I:\Operations\LSC\LIMS Data." When the file is moved, add the letter "Y" in front of the file name to denote that the file is from instrument LS6500 or add the letter "X" in front of the file name to denote that the file is from instrument LS6000. The text file should be reviewed to ensure that the correct file has been chosen.

8.5.2 Instructions for processing and reporting radioanalytical data are found in the Paragon LIMS Manual, which is available as a reference on the network.

9. CALIBRATION

9.1 EFFICIENCY CALIBRATION

Standards for calibration shall be traceable to the National Institute for Standards and Technology (NIST). Standards for tritium counting will normally be prepared from commercially available NIST-traceable stock solutions. The analysis system shall be calibrated at least annually. Instructions for the preparation of calibration sources are provided in the individual preparation SOPs.

9.1.1 In cases where a quench curve calibration is performed, a review of the data and the fitted curves may indicate one or more outlying data points that prevent an adequate fit of the data. At the analyst's discretion, one or more data points may be removed as outliers, provided that the number of remaining data points is at least twice the order of the polynomial used to fit the curve. The fitted curve should be re-

generated after the removal of outlying data points. In all cases the effective range of the quench curve will be bounded by the upper and lower data points used to fit the curve.

9.1.2 In cases where a single-point efficiency calibration is performed (i.e. the method of constant quench), the QIP for sample analyses will correspond to the average observed for the calibration standard (within ±10 % relative efficiency or, lacking this calibrated range, ±15 of mean H-numbers).

9.1.3 Any sample falling outside this range will be calibrated by sample specific addition of a minimum known volume (<200µL) of NIST-traceable standard. The efficiency from sample specific standard additions is calculated as defined below:

$$\text{Deteff} = \frac{(\text{SSGrCPM} - \text{SmplGrCPM})}{\text{SpkDpm}}$$

In cases where the method of standard addition is employed, a calibration blank must be deliberately quenched to approximately the quench factor of the sample, so that an appropriate background determination can be made.

9.2 BATCH-SPECIFIC BACKGROUND CALIBRATIONS (REAGENT BLANKS)

9.2.1 Instructions for the preparation and analysis of background determinations are provided in the individual preparation SOPs.

9.2.2 For methods that require the preparation and analysis of batch-specific background determinations, three reagent blanks will be prepared for analysis with the sample batch. The blanks will preferentially be distributed among the beginning, middle, and end of the count batch and should be counted as long as the longest sample count duration in the batch.

9.2.3 For single-point calibrations (method of constant quench) the average count rate of the three reagent blanks will be used directly as the method background determination.

Interim acceptance criteria for the reagent blanks will be derived initially from the blanks used in the efficiency calibration and verification. Interim limits background calibrations will be +/- (3 times the Poisson uncertainty of the initial measurements). After sufficient batches are analyzed to produce reliable statistical control limits from the population of previously analyzed reagent blanks, those interim

control limits will be replaced with limits that are ±3 standard deviations about the mean value.

9.2.4 For methods utilizing a quench curve, three reagent blanks will be analyzed, as described above. The reagent blanks will, ideally, have quench factors approximately at the middle part of the curve, though unquenched reagent blanks are acceptable as long as the quench factors lie within the calibration curve.

The average difference between the individual observed values and the expected values from the quench curve coefficients will be used to adjust the existing quench curve along the dependent axis (i.e. adjust the curve up or down by adding the average difference value to the curve equation).

Interim acceptance criteria for the reagent blanks may be derived initially from either the expected uncertainty in the initial calibration, or from the three reagent blanks used in the analysis of the first sample batch. After sufficient batches are analyzed to produce reliable statistical control limits from the population of previously analyzed reagent blanks, those interim control limits will be replaced with limits that are ± 3 standard deviations about the mean value.

9.2.5 Historical reagent blank results are maintained in the following spreadsheets:

- R:\INST\LSC\ has one subdirectory for each instrument; \LS6500\ , \LS6000\ , \QUANTULUS\
- Each instrument directory has a \CBs_BKG_WIND2_CHKS\ directory with the following files, where appropriate:

RB_C14.XLS
RB_FE55.XLS
RB_H3_5ML.XLS
RB_H3_10ML.XLS
RB_NI63.XLS
RB_TC99.XLS
RB_TOTA.XLS
RB_P241.XLS
and RB_C14_NaOH.XLS

9.3 GAIN CALIBRATIONS

For liquid scintillation counters in which the gain adjustment needs to be calibrated manually, the gain calibration will be performed at least monthly by

placing a sealed, unquenched C-14 source into a rack and initiating the manufacturer's AUTOCAL program.

10. QUALITY CONTROL

10.1 GENERAL

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike (MS) recovery acceptance criteria shall be ±20%, irrespective of the laboratory's internally derived acceptance criteria.

10.2 DAILY QA CHECKS ON THE BECKMAN INSTRUMENTS

Standards for Daily QA Checks consist of unquenched ^{3}H and ^{14}C standards (NIST-traceable), a flame-sealed, vendor-supplied background, and an in-house prepared blank sample.

10.2.1 Place the unquenched ^{3}H calibration standard in position 1, the unquenched ^{14}C calibration standard in position 2, the blank in position 3, and the vendor-supplied background in position 4 of the sample rack labeled "User No. 1".

10.2.2 Place the rack in the right front position in the counter. Place the "HALT" (red) rack immediately after the "User No. 1" rack.

10.2.3 Start the Daily checks by pressing "Main Menu", selecting "Automatic Counting" from the menu with the cursor arrows, then pressing "Start" to begin the counting sequence. The QA Check process will initiate a 10 minute count of the ^{3}H standard, the ^{14}C calibration standard, the blank, and the vendor-supplied background. At least 100,000 counts should be acquired for the ^{3}H and ^{14}C check sources.

10.2.4 When the count is complete, enter the count results for the standards and blank in the LSQA spreadsheet (located at R:\inst\ls6000\daily QC\ lsqa6000.xls or R:\inst\ls6500\daily QC\lsqa6500.xls) using a network computer.

Count results from Window 1 are used for the ^{3}H standard, count results from Window 2 are used for the ^{14}C standard, and count results from Window 1 are used for the blank and vendor-supplied background.

The spreadsheet compares each count result to historical control limits established from the first 60 data points in the population. Sixty data point are used for these systems due to the potential for long-period variance in the instrument response. Control limits are set at ± 3 standard deviations (above and below) the means for the standards and blank.

In the absence of a sufficient number of data point to generate reliable historical control limits, interim limits may be used. Interim limits for daily check sources will be +/- 5% of the initial measurements for H-3, C-14 and H#. Interim limits for quenched background checks will be +/-(3 times the poisson uncertainty of the initial measurements).

If any of the Daily QC results fall outside the defined control limits, re-analyze the samples. If the current data points are still outside of control limits, do not operate the instrument until notifying the Supervisor and resolving the problem. *Note that Paragon does not control on the results of the flame sealed vendor-supplied background sample.*

10.3 DAILY QA CHECKS ON THE WALLAC INSTRUMENT

10.3.1 Place the unquenched ^{3}H calibration standard, the unquenched ^{14}C calibration standard, the blank, and the vendor-supplied background in the sample rack and note the positions.

10.3.2 Count the daily check samples, as described in Section 8.3.2, selecting the Daily QC user option.

10.3.3 In the "General Parameters" tab, enter the folder name and save path as "C:\DAILYQC\QC-*mmdda*", where *mm* is the month, *dd* is the day, and *a* is a sequential identifier, if needed, when multiple counts are performed in a single day.

10.3.4 In the "Sample Parameters" tab, enter the sample IDs as "3H", "14C", "Reagent Blank", and "BKG STD".

10.3.5 For each vial, specify the sample position, enter the count time as 10 minutes, and verify that the other settings are set as described in Section 8.3.2.

10.3.6 Click the "OK" icon to save.

10.3.7 Make sure the current protocol is highlighted. Click on the "Queue" icon, select the "Counters" icon, then press "Play" (►) to start the counts.

10.3.8 When the count is complete, enter the count results for the standards and blank in the LSQA spreadsheet (located at R:\inst\quantulus\daily QC\dqaquantulus.xls using a network computer.

The spreadsheet compares each count result to historical control limits established from the first 30 data points in the population. Control limits are set at +3 standard deviations (above and below) the means for

the standards and blank.

If any of the current data points fall outside the default control limits of ±10% of the mean, re-analyze the QC samples. If the current data points are still outside of control limits, do not operate the instrument until notifying the Supervisor and resolving the problem. *Note that Paragon does not control on the results of the flame sealed vendor-supplied background sample.*

10.4 SCINTILLATION COCKTAIL VERIFICATION BY LOT NUMBER

10.4.1 Scintillation cocktail performance for each manufacturing lot must be verified prior to use. The background count rate, counting efficiency, luminescence, and quench factor must be demonstrated to be equivalent to the previous lot of cocktail used for each analytical method.

10.4.2 Three efficiency calibration standards and three background calibration samples should be prepared using both the new lot of cocktail and the old lot. These should be prepared according to the appropriate preparation SOP. The final sample set will, therefore, consist of four sets of three samples each; one spiked set with the old cocktail, one with the new, one blank set with the old cocktail, and another with the new.

10.4.3 In the review of the final counting results, each set of three samples will be reviewed to ensure that the gross count rate for no one sample deviates from the average gross count rate of the three by more than the average 2σ counting uncertainty for that set. Counting uncertainty is described in SOP 708. Subsequent evaluations, described below, will use the combined count rates for the three samples in each set. Luminescence and quench factors will be evaluated for each individual vial in the set.

10.4.3.1 COUNTING EFFICIENCY
The spiked samples should be counted long enough to achieve a 2σ counting uncertainty of 2% or less. This equates to a minimum 10,000 net counts per vial.

10.4.3.2 DER
The Duplicate Error Ratio, described in SOP 715, between the two spiked sample sets will be less than 1.0.

10.4.3.3 RPD
The Relative Percent Difference, described in SOP 715, between the two spiked sample sets will be less than 5.0%.

10.4.3.4 BACKGROUND COUNT RATE
The unspiked samples will counted long enough to achieve a Minimum Detectable Activity, described in SOP 708, that is at least as low as the lowest anticipated client-requested MDA for that analysis. The Duplicate Error Ratio between the blank sets will be less than 1.0.

10.4.3.5 LUMINESCENCE
The luminescence for each blank sample will either be less than 0.5% or within two standard deviations (Excel® formula STDEV()) of the average of the blank luminescence values in the OLD cocktail.

10.4.3.6 QUENCH FACTOR
The quench factor for each sample will be within a margin that is equivalent to a counting efficiency change of less than 5% in the OLD cocktail. If this value is not determined, a margin of ±5 quench factor units may be used.

10.4.3.7 ACCEPTANCE OF RESULTS
Cocktail lot verifications that meet the above criteria may be approved for use by the group supervisor or department manager. Excursions from the above acceptance criteria may be approved by the Department Manager, with appropriate technical justification.

11. CALCULATIONS

Data calculations are found in the preparation SOPs, as well as in SOPs 708 and 715.

12. DEVIATIONS FROM METHOD

This procedure contains no known deviations from the analytical portion of EPA 906.0.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 SAFETY AND HAZARDS

13.1.1 Normal laboratory safety procedures must be complied with during the conduct of this procedure. No special safety requirements are mandated by this procedure.

13.1.2 High voltage in the range of 1000 volts DC is applied to the photomultiplier tubes in these instruments. This can result in electric shock if the instrument is disassembled with power applied. To minimize the possibility of electric shock, turn off the power and unplug the instrument prior to any disassembly.

13.2 WASTE DISPOSAL

Liquid scintillators contain a solvent and an emulsifying agent to promote mixing with aqueous samples. The solvents used by Paragon are biodegradable, but may not be suitable for sewer disposal. Additionally, the samples may contain concentrations of radioactivity above sewer disposal limits. Contact the Waste Disposal Coordinator and/or Radiological Safety Officer (RSO) for disposal instructions.

14. REFERENCES

14.1 Beckman LS6000 Series Liquid Scintillation System Operators Manual, June 1991.

14.2 Beckman LS6500 Series Liquid Scintillation System Operators Manual.

14.3 Lloyd A. Currie, "Limits for Qualitative Detection and Quantitative Determination", Analytical Chemistry, Volume 40, pages 586-593, March 1968.

14.4 National Council on Radiation Protection and Measurements (NCRP), Report No. 58, page 309, September 1984.

14.5 EPA 520/1-80-012, "Upgrading Environmental Radiation Data", Health Physics Society Committee Report HPSR-1, pages 6-26, August 1980.

DOCUMENT REVISION HISTORY

9/1/06: Wallac LSC procedures incorporated. Various interferences discussed. DOCUMENT REVISION HISTORY section added.

8/31/07: Updated Title. In Section 9, added allowance for interim control limits for Daily QC until sufficient historical data is generated. Added provision to remove outlying data points in a quench calibration curve (Section 9.1.1). Added requirements for monthly gain calibrations, where appropriate (Section 9.3). Updated Table 1 contents.

TABLE 1

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency, Background and Quench Factor Checks	Daily	Within derived control limits, as defined in network spreadsheet.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Efficiency Calibration	Yearly	For single point efficiency calibrations, the value will be within 5% of the previous calibration value. For quench curves, the fitted values shall be within 5% of the observed value for each point on the curve. Post-calibration method spikes (LSCs) will meet normal LCS acceptance criteria. *	Tag method off-line. Determine and correct problem; verify source activity; recount and/or recalibrate or document why condition is acceptable.
Background Calibration	Continuous	Control limits set from initial calibration run, per details given in SOP Section 9.2.3.	Tag method off-line. Determine and correct problem, re-establish limits; or document why condition is acceptable
Chemical Yield	Each sample, where method allows.	Each sample meets current control limits for analysis. *	Re-prep; or Qualify or narrate why condition is acceptable
Spectral Interferences	Evaluate each result for spectral interferences.	WIND2 count rate within current control limits (SOP Section 4.9) or interfering activity does not compromise quantitation	Re-prep/ recount affected samples; Consult with supervisor or department manager; Determine and correct problem; or qualify or narrate why condition is acceptable

NOTE: This SOP and SOP 715 contain acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

* as established in the applicable LIMS nickname (e.g., Paragon Standard or as created for a specific client).

Paragon Analytics

LSC Run Log

Instrument ID: ***Quantulus 1220***

	Load Date	Sample ID	CountTime (min.)	Position	Protocol	File Name	Batch ID	Position Check	Initials	Comments
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
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Reviewed by / Date _____

FORM 700_Quantulusr0.xls (7/11/2004)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 707 REVISION 10

TITLE: **RADIOSTRONTIUM IN WATER, SOIL, FILTERS, VEGETATION AND HAZARDOUS WASTE SAMPLES**

FORMS: **631, 302** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07
QUALITY ASSURANCE MANAGER _____ DATE 9/2/07
LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 2/10/93; Rev1, 4/7/93; Rev2, PCN #387, 2/21/95; Rev3, 5/3/1996; Rev4, 1/12/00; Rev5, 10/2/00; Rev6, 4/24/02; Rev7, 4/7/03; Rev8, 9/23/04; Rev9, 9/11/06; Rev10, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the method to be followed for the determination of radiostrontium (Total Radiostrontium or ^{89}Sr or ^{90}Sr) in environmental, drinking and wastewaters, organic liquids, soils, sediments and solids, air filters, wipes, and vegetation.

2. SUMMARY

2.1 SAMPLE PREPARATION (MINERALIZATION/ CONCENTRATION/ DISSOLUTION)

2.1.1 **Aqueous Samples:** Strontium carrier solution is equilibrated with an aliquot of the sample. A portion of the sample is removed for inductively coupled plasma (ICP) atomic emission spectrometry determination of the pre-separation concentration of strontium in the sample. Aqueous samples are concentrated using cation exchange. The column eluate is taken to dryness and redissolved in 8N nitric acid. Strontium is separated from the concentrated sample as described in Section 2.2 below.

2.1.2 **Soils, Sediments, Vegetation, and Non-organic Solids:** A representative subsample of the sample is dried and ground. The sample may be muffled if significant organic material (e.g., humic soils or oily solids) is present. Strontium carrier solution is equilibrated in 1g of the ground sample. The sample is digested on a steam table in 8N nitric acid. A portion of the sample is removed for ICP determination of the pre-separation concentration of strontium in the sample. The sample is taken to dryness and redissolved in 8N nitric acid. Strontium is separated from the digestate as described in Section 2.2 below.

2.1.3 **Organic Liquids and Hazardous Waste:** Many different challenges may present themselves in this category. In general, the strontium must be liberated from the organic matrix and made soluble in nitric acid. Most frequently, this involves a combination of evaporation and/or ashing followed by digestion steps. Hazardous waste samples are to be run through a cation exchange column. Strontium carrier solution is equilibrated as early in the procedure as practicable, but always prior to the strontium separation step. A portion of the sample is removed for ICP determination of the pre-separation concentration of strontium in the sample. Strontium is separated from the digestate as described in Section 2.2 below. Often other techniques are necessary to ensure thorough solubilization of strontium. These steps should be carried out under direction of the Supervisor or Senior Chemist, and should be carefully documented on a Quality Assurance Summary Sheet (QASS, Form 302) and in the data package case narrative.

2.1.4 **Air Filters:** The preparation of air filters depends upon whether a single filter or a composite is being analyzed and upon how many tests are to be performed on the sample. The digestion of air filters is routinely performed according to SOP 773. The digestate is converted to the nitrate system by evaporation, followed by the addition of nitric acid. Strontium carrier is added to the digestate aliquoted for analysis. A portion of the sample is removed for ICP determination of the pre-separation concentration of strontium in the sample. Strontium is separated from the digestate as described in Section 2.2 below.

2.1.5 **Sample Pretreatment:** Additional preparation steps not defined in this SOP are considered sample pretreatment. These steps should be carried out under direction of the Supervisor or Senior Chemist. All non-routine pretreatment should be carefully documented on a Quality Assurance Summary Sheet (QASS, Form 302) and in the data package case narrative.

2.2 SEPARATION, PURIFICATION, AND MOUNTING

Strontium is separated from the nitric acid digestate/concentrate generated above using Eichrom Sr-Resin. A second aliquot of sample is removed from the eluate following separation for ICP determination of the post-separation concentration of strontium in the sample. The remaining eluate is quantitatively transferred to a stainless steel planchet.

2.3 COUNTING, CALCULATION, AND REPORTING

2.3.1 The planchet is submitted for beta counting on a low background gas flow proportional counter (GFPC), as described in SOP 724. Total Radiostrontium may be determined from one count of the separated Strontium. For the isotopic determination of ^{89}Sr and ^{90}Sr, the planchet should be counted immediately following separation to minimize ingrowth of Yttrium-90. The planchet is then stored and recounted approximately 3-7 half-lives (usually ~14 days) following ^{90}Y ingrowth.

2.3.2 The counting result, immediately ascertained, represents the Total Radiostrontium activity (^{89}Sr + ^{90}Sr plus the fraction of ^{90}Y that has grown in from the separated ^{90}Sr). For samples where only ^{90}Sr is requested and one may safely assume the absence of the short-lived species ^{89}Sr, Total Radiostrontium is routinely reported as ^{90}Sr. This assumption is noted in the narrative.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 The presence of elemental lead, in the sample aliquot in milligram quantities is an interference to this method. The ICP results should be monitored for elevated lead concentrations. The presence of elevated lead concentration in samples necessitates use of reduced aliquots. Initial results for samples showing low chemical yield will be accepted and appropriately qualified in the case narrative, when elevated levels of lead interfere with strontium recovery and re-preparation of the sample is not expected to generate improved results.

4.2 Samples with very elevated native, non-radioactive strontium concentrations will overwhelm the capacity of the Sr-Resin and lead to low chemical yield in the sample. The same is true for elevated levels of native calcium, magnesium, lead and sodium. ICP results should be consulted in cases of anomalously low (or high) chemical yield to determine the possible cause of the occurrence. In such cases, the Supervisor and the Project Manager should be notified as soon as the situation is recognized. The client should be notified of the presence of the matrix interference and be involved in deciding what appropriate course of action should be taken. Generally, re-preparation of such samples will not improve results since the sample quantity that may be processed by the method has effectively been maximized. The sample may be reprocessed with a smaller aliquot, and a matrix spike may be utilized to provide feedback on the quality of data produced in the presence of the matrix interference. Generally, the client would be responsible for the additional cost of ameliorating the effects of the matrix inference in the sample.

4.3 Samples with very elevated dissolved solids interfere with the pre-separation ICP measurement of Sr and will lead to overestimation of the chemical recovery of strontium in the sample. This will result in a low bias in final yield corrected sample activity. The situation is recognized as follows: a) the pre-separation measurement is less than the concentration as calculated from the known quantity of carrier added (Action: narrate interference in pre-separation measurement, low bias in reported result); or b) the pre-separation measurement exceeds the concentration of strontium from the carrier but is less than the post-separation concentration of strontium in the sample (Action: narrate native strontium present in sample, low bias in reported result).

4.4 Elevated levels of ^{85}Sr in the sample may lead to a high bias in the reported sample activity.

4.5 Sr-Resin, with an 8N nitric acid load solution is used to effectively remove Barium-140 and Potassium-40 isotopes as well as other matrix interferences. Tetravalent plutonium, neptunium, cerium and ruthenium, however, are not removed using nitric acid. These isotopes can be effectively removed by including an additional rinse of approximately 5mL of 3N nitric acid-0.05M oxalic acid.

4.6 Solid samples are prepared via nitric acid leaching. Certain forms of Sr, including those bound into the geologic matrix of some soils or rock, may not be effectively addressed by this method. As this method has proven to be sufficient for most forms of surficial contamination, the majority of solid samples analyzed are not likely to be affected by this limitation.

4.7 If the alpha count rate is greater than 10 times background level, there is a potential interference in the analytical method. Consult your Supervisor if this situation occurs.

5. APPARATUS AND MATERIALS

5.1 Disposable ion exchange columns: 15mL resin volume with attachable funnel to receive 2L bottle. Environmental Express #R1010 and #R1030 or equivalents

5.2 Sr-Resin column: Use a Bio-Rad #731-1553 column or equivalent, and transfer the Sr-Resin to the column as a slurry with laboratory water. Add resin up to the ~1.6mL mark on the column. The Sr-Resin is held in place in the column by a layer of clean silica sand on top.

5.3 planchet, flat, cupped, stainless steel, 2" diameter

Prior to use, the planchets are soaked in diluted Radiacwash™ for a minimum of three hours, drained, rinsed with deionized water, transferred to a metal pan, and placed in the drying oven to dry.

5.4 analytical balance, 0.0001g resolution, Mettler® AE 200, or equivalent

5.5 Re-pipettor, Eppendorf® Model 4780 or equivalent, and disposable pipet tips

5.6 filter paper, qualitative, VWR #313, or equivalent

5.7 transfer pipet, 7mL polyethylene, disposable

5.8 graduated cylinder, 1L

5.9 centrifuge, Beckman® GS-6, or equivalent

5.10 centrifuge tubes, polypropylene, 50mL

5.11 plastic bottles, disposable, 2L

5.12 test tubes, disposable, 15mL

5.13 Parafilm™

5.14 watch glass, Pyrex®

5.15 pH paper

5.16 Static Guard™ spray, or equivalent

5.17 specimen cups, polypropylene, 250mL or equivalent

5.18 Radiacwash®

6. REAGENTS

NOTE: TLV and other hazard information may also be given here. Refer to Section 12.1.3 regarding TLVs.

6.1 Deionized (DI) water, from the laboratory DI water system

6.2 Silica sand

6.3 Methanol, reagent grade
TLV = 200ppm

6.4 Strontium carrier, 2.0 mg $^{Sr}/_{mL}$: Dissolve 4.84g reagent grade $Sr(NO_3)_2$ in DI water and dilute to 1L. Record the preparation of this carrier in the Reagent Prep Logbook.

6.5 ^{90}Sr spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.6 ^{89}Sr spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.7 Nitric acid, concentrated, 16N, ACS grade.
TLV = 2ppm (TWA) Irritant, corrosive

6.8 Nitric acid, 8N: Cautiously add 500mL of conc. HNO_3 to approximately 400mL DI water and dilute to 1L.
See 6.7 for TLV

6.9 Nitric acid, 1N: Cautiously add 63mL of conc. HNO_3 to approximately 400mL DI water and dilute to 1 L.

See 6.7 for TLV

6.10 Nitric acid, 0.1N: Add 6.3mL conc. HNO_3 to approximately 900mL DI water and dilute to 1 L.
See 6.7 for TLV

6.11 Nitric acid, 0.05N: Add 3.1mL conc. HNO_3 to approximately 900mL DI water and dilute to 1 L.
See 6.7 for TLV

6.12 Nitric acid (3N)-Oxalic acid solution (0.05M): Add 191mL of concentrated nitric acid and add 6.3g of oxalic acid dihydride to 800mL of DI water and dilute to 1L with DI water.
See 6.7 for TLV for Nitric acid
TLV for Oxalic acid = 1 mg/m3 = 0.3ppm

6.13 Cation exchange resin, AG50x8 or AG50x4, Bio-Rad®, Eichrom® or equivalent

6.14 Sr-Resin extraction chromatography resin, particle size 50-100 µm

6.15 ICP Diluting Solution: Carefully add 10mL of conc. Nitric acid and 50mL of conc. Hydrochloric acid to 940mL of DI water.
TLV = 5ppm (ceiling) for HCL Irritant, corrosive
TLV = 2ppm (TWA) for Nitric Acid Irritant, corrosive

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 per liter of sample to bring the pH to 2 (15mL 1N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.2 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 WATER PREPARATION

8.1.1 Verify and record the pH of the sample on a liquid sample condition form (Form 631) according to SOP 733.

8.1.2 Measure the sample volume using an appropriate sized graduated cylinder. The sample is filtered through qualitative filter paper into the graduated cylinder to speed up passage through the column. Transfer the sample into a labeled 2L disposable plastic bottle. Record the volume V_i (in mL) on the benchsheet. Typical sample volume is 1L. If sample is not 1L, note the volume on the benchsheet and dilute to 1L with filtered DI water.

8.1.3 Prepare quality control (QC) samples per Section 10.

8.1.4 Add 0.5mL of Sr carrier. Record the carrier volume and reagent ID in the space provided on the benchsheet.

8.1.5 Mix the sample thoroughly by inverting the disposable bottle 15-20 times and remove a 10.0mL aliquot (or similar known volume using a calibrated pipettor, SOP 321) for ICP determination of Sr. Pipet the aliquot into a 15mL test tube, seal with Parafilm and label with sample ID and "initial-Sr".

8.1.6 In addition, a replicate 0.5mL aliquot (or similar known volume from a calibrated pipettor) of Sr carrier is diluted with 5mL conc. nitric acid and DI water to the default volume used for the water samples. After mixing thoroughly, a 10.0mL aliquot of this dilution is transferred to a test tube labeled ‘reference carrier’ and submitted with the initial samples to provide a reference concentration for the ICP calculations discussed subsequently.

8.1.7 Precondition a disposable ion exchange column with 1-2mL of methanol, just enough to pass filter (the frit at the orifice of the column is hydrophobic). Transfer AG50x8 or AG50x4 resin to the stem of the column as a slurry with DI water to at least the 7cm mark. Place a layer of sand with a spatula (~1cm) on top of the resin bed to hold the resin in place. Attach the funnel to the column (make certain that the column and funnel fit tightly), and precondition with 30mL of 1N HNO_3 to check for leaks.

8.1.8 Pass the sample through the column at a rate of about 1-2mL/min. This is accomplished by inverting the 2L bottle into the funnel that is attached to the top of the cation exchange column. Secure the bottle with a rubber band. The sample will feed automatically through the column.

8.1.9 After the sample has completely passed through the resin, rinse the column with 10mL of 0.1N HNO_3.

8.1.10 Discard the feed and rinse solutions into the Paragon wastewater treatment facility (down the laboratory sink followed by plenty of tap water).

8.1.11 Elute Sr and other cations with 100mL of 8N HNO_3. Collect the solution in a labeled 250mL disposable cup. Place the solution on a steam bath and evaporate to dryness.

8.1.12 The used resin from the column is collected in a wide mouth jar labeled "Used Cation Resin" for disposal. When the container is full, contact the Waste Management Officer for disposal instructions.

8.1.13 The columns are then soaked in Radiacwash®, rinsed with tap water, and disposed of in the sanitary trash.

8.1.14 Dissolve the salts in 5mL of 8N HNO_3 solution. Add the 8N HNO_3 to the specimen cup while the sample is on the steam bath to facilitate complete dissolution of the salt residue.

8.1.15 Proceed to Section 8.5 (isolation of strontium using Sr-resin).

8.2 SOIL PREPARATION

8.2.1 Verify and record the sample condition on a solids sample condition form (Form 631).

8.2.2 Solid samples used in this method should be dried and ground per SOP 721 prior to analysis. If the samples are not conducive to grinding, consult with your Supervisor prior to analysis of samples.

8.2.3 Weigh 1.0g of soil into a labeled 50mL centrifuge tube. Centrifuge tubes may be sprayed with static spray prior to aliquoting samples. Record this initial sample weight on the benchsheet.

8.2.4 Prepare QC samples per Section 10.

8.2.5 Add 0.5mL (or similar known volume using a calibrated pipettor, SOP 321) of carrier solution to the sample in the centrifuge tube.

8.2.6 In addition, a replicate 0.5mL aliquot of Sr carrier is diluted by adding 10mL of 8N nitric acid and bringing up to 50mL with DI water in a labeled centrifuge tube. After vortexing thoroughly, a 0.5mL aliquot of

this solution is transferred to a 15mL test tube labeled with the batch ID and "reference carrier" and diluted with 9.5mL of ICP diluting solution. This tube is submitted to the Metals Lab with the initial and final ICP tubes for analysis.

8.2.7 Add 10mL 8N HNO_3 to each tube from Step 8.2.5. **CAUTION: a vigorous reaction may occur.**

8.2.8 Place the centrifuge tubes on a pre-heated steam bath, with the lids on loosely, for one hour.

8.2.9 Remove from the steam bath and allow to cool.

8.2.10 Centrifuge for 10-15 minutes at 3500rpm. Decant the supernatant into a clean, labeled centrifuge tube.

8.2.11 Add 20mL of DI water to the original tubes containing the soil fraction and vortex thoroughly. Centrifuge and add the supernatant to the tubes from Step 8.2.10 above.

8.2.11.1 Dispose of the soil fraction into the waste container labeled "Contaminated Soils and Solids" (Either LLRW or Non-Rad, depending on the screening data).

8.2.11.2 Soak used centrifuge tubes in Radiacwash®, rinse with tap water, and discard in the sanitary trash.

8.2.12 Dilute the combined solutions from Steps 8.2.10 and 8.2.11 to a final volume of 50mL with DI water.

8.2.13 **Vortex to mix completely.** Using a calibrated pipettor, remove 0.5mL of the solution and transfer to a test tube containing 9.5mL of ICP diluting solution. Seal with parafilm and invert several times to mix thoroughly. Label tubes with sample ID and "initial" Sr.

8.2.14 Transfer the entire solution into a labeled 250mL specimen cup. Rinse the centrifuge tube into cup with DI water to ensure complete transfer. Place on a steam bath and evaporate to dryness.

Soak used centrifuge tubes in Radiacwash®, rinse with tap water, and discard in the sanitary trash.

8.2.15 Dissolve the salts in 5mL of 8N HNO_3 solution. Add the 8N HNO_3 to the specimen cup while the sample is on the steam bath to facilitate complete dissolution of the salt residue.

8.2.16 Proceed to Section 8.5 (isolation of strontium using Sr-resin).

8.3 FILTER PREPARATION

8.3.1 This preparation procedure may begin after a filter has been leached or digested as a common pretreatment step. Frequently, a sub-aliquot of the total volume of digestate is carried through the preparation process. The aliquot volume/total volume ratio represents the fraction of the total activity leached from the filter that is prepared for radiostrontium determination. This fraction, Fi, must be recorded on the benchsheet. If the filter needs to be leached, start at Step 8.3.2. If the filter has been leached and the aliquot size of the leachate is less than 200mL, but the solution is not 8N nitric acid: transfer an appropriate aliquot of digestate to a specimen cup, add carrier as described in Step 8.3.4, and convert to a nitrate system by taking to dryness and redissolving in nitric acid as described in Steps 8.3.9 and 8.3.10. If the aliquot size of the leachate is less than 200mL and the solution is in 8N nitric acid, transfer an appropriate aliquot of digestate to a specimen cup, add carrier as described in Step 8.3.4 and then begin with Step 8.3.9. However, if the aliquot size of the leachate is greater than 200mL, then proceed with Section 8.1 (concentration by cation exchange for waters).

8.3.2 Place the filter sample into a labeled 250mL specimen cup.

8.3.3 Prepare quality control (QC) samples per Section 10.

8.3.4 Add 0.5mL (or similar known volume using a calibrated pipettor, SOP 321) of carrier solution into the specimen cup.

8.3.5 In addition, a replicate 0.5mL aliquot (or similar known volume from a calibrated pipettor) of Sr carrier is diluted in 8N nitric acid to 5mL. A 0.1mL aliquot (or similar known volume from a calibrated pipettor) of this dilution is transferred to a test tube labeled ‘reference carrier’ and submitted with the initial samples to provide a reference concentration for the ICP calculations discussed subsequently.

8.3.6 Add 50mL of 8N HNO_3 to the specimen cup and heat on a steam bath (in a fume hood) for approximately 30 minutes.

8.3.7 Turn the filter over and allow to digest for an additional 30 minutes.

8.3.8 Remove the filter from the liquid and thoroughly rinse both sides into the cup with DI water.

8.3.9 Place the cup on a steam bath and evaporate the solution to dryness.

8.3.10 Dissolve the residue by adding 5mL of 8N HNO_3 to the beaker with a repeater pipette.

8.3.11 After dissolution is complete, pipet a 0.1mL aliquot (or similar known volume using a calibrated pipettor) of the solution into a 15mL test tube. Make certain that the solution is well mixed before pipetting.

8.3.12 Dilute the aliquot in Step 8.3.11 above by adding 9.9 or 10mL of ICP diluting solution. Be sure to record the final diluted volume. Cover the solution with Parafilm and mix thoroughly. This diluted solution will be analyzed by ICP to determine the initial Sr concentration (Ci). Label with the sample ID and "initial Sr".

8.3.13 Proceed to Section 8.5 (isolation of strontium using Sr-resin).

8.4 PREPARATION OF ORGANIC LIQUIDS AND HAZARDOUS WASTE SAMPLES

8.4.1 Organic liquids and hazardous waste samples require muffling in a 600°C (approximately) furnace prior to digestion. The Pyrex® brand glass beaker number (all labware to be used for muffling must have a permanent ID engraved on its surface) is written on the benchsheet in association with the corresponding sample number. For the blank and blank spike a beaker containing a piece of ashless filter paper will be muffled.

8.4.1.1 Weigh 2g up to 10g (to the nearest 0.01g) aliquot of the ground sample into the corresponding labeled Pyrex® beaker. Filters should be cut or folded such that they fit into the bottom of the beaker. Cover the dishes using watch glasses to protect the contents during the muffling.

8.4.1.2 Prepare quality control (QC) samples per Section 10.

8.4.1.3 Add 0.5mL (or similar known volume using a calibrated pipettor) of carrier solution into the specimen cup.

8.4.1.4 In addition, a replicate 0.5mL aliquot (or similar known volume from a calibrated pipettor) of Sr carrier is diluted in 8N nitric acid to 5mL. A 0.1mL aliquot (or similar known volume from a calibrated pipettor) of this dilution is transferred to a test tube, diluted to 10mL, labeled 'reference carrier', and submitted with the initial samples to provide a reference concentration for the ICP calculations discussed subsequently.

8.4.1.5 Place the beaker without the watch glass on a hot plate and take to dryness to prevent splattering in the muffle furnace.

8.4.1.6 Place the beaker with a watch glass in the muffle furnace and heat for at least 4 hours after the temperature reaches the 600ºC preset (approximate temperature). Highly organic materials (or oil matrices) should be muffled overnight.

8.4.1.7 Carefully remove the dishes from the muffle furnace using thick furnace gloves and long tongs. Allow the samples to cool. Alternately, the furnace may be turned off and the samples may cool in the furnace.

8.4.2 The ashed samples are dissolved in hot nitric acid prior to chemical separation.

8.4.2.1 Add 10mL conc. HNO_3 to each beaker and heat on a hot plate at medium setting for approximately one hour, or until a complete dissolution is achieved. If necessary, use a rubber policeman to remove residual material from the surface of the beaker.

8.4.2.2 To a one liter graduated cylinder, add 500mL DI water. Add the dissolved sample and HNO_3. ALWAYS ADD ACID TO WATER. DO NOT ADD WATER TO STRONG ACID.

8.4.2.3 Ensure a quantitative transfer of sample material by rinsing the beaker three times with DI water and adding the rinsate to the graduated cylinder. After transferring the sample digestate, add additional DI water to bring the volume up to one liter.

8.4.3 The diluted sample digestate is then taken through the standard water procedure, beginning at Step 8.1.2.

8.5 ISOLATION OF STRONTIUM USING SR-SPEC COLUMN

8.5.1 Prepare a Sr-Spec column by passing 2mL of 8N HNO_3 through the column. Let the solution drain by gravity flow.

8.5.2 Transfer the sample solution (feed solution) to the Sr-Spec column reservoir using a transfer pipet. Collect the eluate from the column in waste cups.

8.5.3 Rinse the sample cup with 2mL of 8N HNO_3. Add the rinsate to the column after the feed solution has passed through.

8.5.4 Repeat Step 8.5.3 after the first rinse solution has completely passed through.

8.5.5 Repeat Step 8.5.3 again after the second rinse solution has completely passed through.

NOTE: After this Step the column will have been rinsed a total of three times with 2mL volumes of 8N HNO_3. Allow each addition to pass completely through the column before adding the next.

8.5.6 Add 5mL of 3N nitric acid -0.05N oxalic acid into each column and allow to drain.

NOTE: The 3N nitric-0.05N oxalic acid removes Pu(IV), Np(IV) or Ce(IV), which are retained by Sr-resin.

8.5.7 Add 5mL of 8N nitric acid to each column and allow the rinse solution to drain through each column.

NOTE: This additional 8N nitric acid rinse removes any residual oxalic acid and ensures full removal of K^+ and Ba^{2+} that may be present.

8.5.8 Record the end time of the last rinse on the benchsheet, to the nearest 15 minutes. This is the start of ^{90}Y ingrowth. If Sr-89/90 are being determined, proceed through the following steps of this SOP without stopping to minimize the ^{90}Y ingrowth.

8.5.9 The rinse solution collected in the waste cups may be discarded into the laboratory wastewater treatment facility (down the laboratory sink

followed by plenty of cold tap water). The cups may be soaked in Radiacwash®, rinsed with tap water, and reused for waste collection.

8.5.10 Elute Sr from the column by pipetting 5mL of 0.05N HNO_3 into the column with a repeater pipette. Collect the eluate in a labeled 15mL disposable test tube. After this aliquot elutes through the column, pipet another 5mL of 0.05N HNO_3. The final volume in the test tube is 10mL.

8.5.11 After mixing the eluate thoroughly, transfer a 0.1mL (or similar known volume using a calibrated pipettor) aliquot of the solution to a second culture tube labeled with the sample ID and "final-Sr". Dilute to 10mL with ICP diluting solution. The dilution is accomplished by adding the 0.1mL aliquot to 10mL of ICP diluting solution in a 15mL test tube. Be sure to record the final diluted volume. Seal the tube with Parafilm™ and mix well.

8.5.12 Submit both the "initial-Sr" and the "final-Sr" to the Metals Lab for Sr analysis by ICP.

8.5.13 Upon the return of the ICP sample fractions to the lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the laboratory wastewater treatment facility (down the drain in the lab sinks with plenty of cold water). The test tubes may be rinsed with a Radiacwash® solution, followed with tap water and discarded into the sanitary trash.

8.5.14 Place a labeled planchet for each sample on a hot plate (in a hood). Transfer the remaining portion of the Sr eluate to the planchet. As evaporation proceeds, rinse the tube with about 1mL of DI water. Combine the rinsate with the solution in the planchet. Continue heating until the evaporation is complete.

8.5.15 Prepare petri dishes by spraying the inside with static guard, and labeling the cover with the batch ID and sample ID.

8.5.16 Submit planchets to the Instrumentation Group as soon as practical. The counting lab will analyze and ultimately dispose of the planchets in the manner described in SOP 724.

8.6 PREPARATION OF CALIBRATION STANDARDS

NOTE: Calibration standards for this method are prepared annually, or as requested by the Analyst of the Gas Flow Proportional Counter.

8.6.1 Label five flat 2" diameter stainless steel planchets.

8.6.2 Spike each planchet directly with ~500-1000dpm of NIST-traceable ^{90}Sr standard.

8.6.3 Add 0.5mL of Sr carrier.

8.6.4 Dry on a hot plate set at 2 or 3.

8.6.5 Submit to the Instrument Lab with the appropriate documentation.

9. CALCULATIONS

NOTE: Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

9.1 CHEMICAL YIELD CALCULATIONS FOR WATER SAMPLES

NOTE: The ICP data is generally imported directly into the LIMS benchsheet where the chemical yield recovery is automatically calculated. The chemical yield calculations outlined in this Section can also be conveniently and accurately carried out by using an Excel Spreadsheet. To do this, call up the Sr water template from the appropriate subdirectory on the network R:\ drive. The calculations provided by either program mentioned above should be verified periodically by manually calculating the yield.

9.1.1 The following parameters must be recorded on the benchsheet. These values are necessary to calculate chemical recovery and to provide the Instrumentation Group with the sample volume to be used in calculating the final results.

V_i = initial sample volume (mL)

A = volume of acid added to bring sample to 0.1N acidity (mL)

S = volume of carrier solution spiked into sample (mL)

R_i = volume of solution removed for "initial-Sr" ICP analysis (mL)

C_i = concentration of Sr determined in "initial-Sr" aliquot (µg/mL)

C_f = concentration of Sr determined in "final-Sr" solution (µg/mL)

V_f = final volume (mL) of Sr eluate. V_f = 10.0 mL or other calibrated volume as appropriate.

9.1.2 Calculate percent chemical recovery using the following equations:

9.1.2.1 Mi = initial mass of Sr (µg) = (Ci) (Vi + A + S - Ri)

NOTE: The initial mass of strontium added may be underestimated due to matrix interference in the ICP measurement of the pre-separation concentration of strontium. This is the case when the calculated initial Sr (µg) is less than the 'reference carrier' concentration measured parallel to the samples. (The calculation for the reference carrier is the same as the calculation for M_i.) In this case, the reference carrier concentration is substituted for Mi below. If the discrepancy between the measured pre-separation Sr and the carrier reference Sr is greater than 15%, a note about the matrix interference is made in the case narrative.

9.1.2.2 Mf = final mass of Sr (µg) recovered after separation and purification. = (Cf) (Vf) (100)

NOTE: The factor of 100x is due to the dilution made in Step 8.5.11. This may vary according to the actual calibration of the pipettor used to conduct the measurement.

9.1.2.3 % Chemical recovery = Mf/Mi * 100

Chemical recovery results must be submitted to the Instrumentation Lab and recorded on the benchsheet.

9.1.3 Corrected Sample Volume Calculation for Waters, Vc: The sample aliquot volume to be used in calculating the final results must be reduced slightly since two aliquots were removed to determine chemical recovery. If 1L of water is used for analysis, this correction is rather insignificant (approximately 2%). The correction becomes more significant for smaller initial sample volumes.

V_c = sample volume used in calculation of final results (mL):

$$= V_i * \frac{(V_i + A + S - R_i)}{(V_i + A + S)} * \frac{(V_f - 0.1)}{(V_f)}$$

V_c must be submitted to the Instrumentation Group in order to allow calculation of the final results. It is recorded on the benchsheet under the 'Fin Aliq'column in units of mL.

9.2 CHEMICAL YIELD CALCULATIONS FOR SOIL SAMPLES

NOTE: The ICP data is generally imported directly into the LIMS benchsheet where the chemical yield recovery is automatically calculated. The chemical yield calculations outlined in this Section can also be conveniently and accurately carried out by using an Excel Spreadsheet. To do this, call up the Sr soil template from the appropriate subdirectory on the network R: drive. The calculations provided by either program mentioned above should be verified periodically by manually calculating the yield.

9.2.1 The following parameters must be recorded on the benchsheet. These parameters are necessary to calculate chemical recovery and also to provide the instrumentation group with the sample volume to be used in calculating the final results.

W_i = initial mass (g) of sample weighed out in Step 8.2.3

Ci = concentration of Sr determined in "initial-Sr" aliquot (µg/mL)

NOTE: The initial mass of strontium added may be underestimated due to matrix interference in the ICP measurement of the pre-separation concentration of strontium. This is the case when the calculated initial Sr (µg) is less than the 'reference carrier' concentration measured parallel to the samples. In this case, the 'reference carrier' concentration is substituted for Sr_i below. (The calculation for the reference carrier is the same as the calculation for Sr_i.) If the discrepancy between the measured pre-separation Sr and the carrier reference Sr is greater than 15%, a note about the matrix interference is made in the case narrative.

C_e = concentration of Sr determined in "final-Sr" solution (µg/mL)

Sr_i = initial mss (µg) of Sr (after spiking with Sr carrier) in sample aliquot = (C_i) (50) (10)

where: the factor (50) is the leachate volume (in mL), and the factor (10) is the amount the solution was diluted prior to ICP analysis. (Note: dilution volumes may vary according to actual dilutions performed and calibrated volumes for the pipettors used).

Sr_e = mass of Sr in final eluate (µg) = (C_e) (10) (100)

where: the factor (10) is the volume of eluate (in mL) collected during Step 8.5.10, and the factor (100) is the amount the solution was diluted prior to ICP analysis. (Note: Dilution volumes may vary according to actual dilutions performed and calibrated volumes for pipettors used).

V_T = Total volume (in mL) of leachate in Step 8.2.8 (V_T = 50.0 mL)

NOTE: Dilution volumes may vary according to actual dilutions performed and calibrated volumes for pipettors used.

V_A = Aliquot volume (in mL) of leachate purified through Sr-Spec (V_A = 49.5 mL)

NOTE: Dilution volumes may vary according to actual dilutions performed and calibrated volumes for pipettors used).

9.2.2 Calculate the percent chemical recovery using the following equation:

$$\% \text{ Chemical recovery} = \frac{(Sr_e)}{(Sr_i)} \times \frac{(V_A)}{(V_T)} \times (100)$$

9.2.3 Corrected Sample Aliquot Calculation for Soils: The sample weight used in calculating the final results, W_c, should be adjusted according to the following equation:

$$W_c = (W_i) \times \frac{(V_A)}{(V_T)} \times (0.99)$$

W_i = initial sample weight from Step 8.2.3

The factor (V_A / V_T) is used because only a fraction of the total sample digestate solution is aliquotted in Step 8.2.13 for the purification process. The (0.99) factor is included because a 0.1mL aliquot is removed from the 10mL of final eluate in Step 8.5.11, hence the fraction of purified sample evaporated on the planchet = 0.99 (1.00 - 0.1/10 = 0.99).

$$(W_i) x \frac{(V_A)}{(V_T)} x (0.99)$$

9.3 CHEMICAL YIELD CALCULATIONS FOR FILTER SAMPLES
The calculations for filter samples are carried out similar to those for soils above. Aliquot, splits, spiking, and dilution volumes are reflected in the calculations.

9.4 TPU FACTORS (PREPARATION UNCERTAINTY, PU)

9.4.1 As defined in SOP 708, the following preparation uncertainty factors (1σ) should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty. The Prep uncertainty for water and solid samples are statistically equivalent and the greater value should be used in calculations.

9.4.2 Water samples require a preparation uncertainty factor of 0.1033. This is based on one gross aliquotting, two quantitative transfers, one volumetric measurement, and one ICP yield determination.

$$0.1033 = \sqrt{.05^2 + .025^2 + .025^2 + .006^2 + .083^2}$$

9.4.3 Solid samples require a preparation uncertainty factor of 0.1031. This is based on one gross aliquotting, two quantitative transfers, one mass measurement, and one ICP yield determination.

$$0.1031 = \sqrt{.05^2 + .025^2 + .025^2 + .003^2 + .083^2}$$

9.4.4 Filter samples require a preparation uncertainty factor of 0.1033. This is based on one gross aliquotting, two quantitative transfers, one volumetric measurement, and one ICP yield determination.

$$0.1033 = \sqrt{.05^2 + .025^2 + .025^2 + .006^2 + .083^2}$$

10. QUALITY CONTROL

10.1 Method Blank: One method blank is processed per batch of up to 20 samples

(minimum 5% frequency).

10.1.1 Use an appropriate volume of DI water for aqueous samples. Acidify to 0.1N with concentrated HNO_3.

10.1.2 Use an empty centrifuge tube for solid samples.

10.1.3 Use an unused filter (of the same type, if possible) for filter samples.

10.2 Sample Duplicate: One sample duplicate is processed per batch of 10 samples (minimum 10% frequency). A duplicate blank spike may be substituted if the sample size is limited.

10.3 LCS: One Laboratory Control Sample (LCS, blank spike) is processed for each batch of up to 20 samples (minimum 5% frequency). The LCS is prepared as in Section 10.1 and then spiked with ^{90}Sr and/or ^{89}Sr at 10-30 pCi/mL, before processing begins.

11. DEVIATIONS FROM METHOD

There are no known deviations from the referenced methods.

12. SAFETY, HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

12.1.2 Wear gloves, safety goggles, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

12.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). The absence of this information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

12.1.4 Care should be taken when diluting acids. Always add the acid *slowly* to the water, not water to acid. Remember acids have a high heat of solution in water and the solution may become hot.

12.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with

compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

12.2 WASTE DISPOSAL

12.2.1 Corrosive only wastes such as glacial acetic acid and sulfuric acid waste are disposed of by discharging into the laboratory wastewater treatment facility. These materials that are corrosive only (i.e., no hazardous components or characteristics other than corrosivity) may be neutralized in our water treatment facility.

12.2.2 All non-hydrofluoric acid wastes collected from samples loaded on an ion exchange column are collected in awaste tray or cup. The collected non-hydrofluoric acid wastes may be discharged into the laboratory wastewater system for neutralization.

12.2.3 All corrosive used resins (cation exchange and Sr-spec) are extruded from the column into an appropriately labeled carboy. The resin is neutralized with baking soda, allowed to dry, and disposed of as neutralized resin.

12.2.4 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

13. REFERENCES

13.1 Methods Sr-01/Sr-02, USDOE Environmental Measurements Laboratory (EML) HASL-300 Procedures Manual, 27th edition, 1990 (revised 1992).

13.2 Method Sr-04, EPA Eastern Environmental Radiation Facility, Radiochemistry Procedures Manual, EPA 520/5-84-006, December 1987.

13.3 ASTM Method D5811-00; ASTM. "Standard Test Method for Strontium-90 in Water". Annual Book of ASTM Standards. Designation: D 5811-95. ASTM, 1995).

13.4 DOE Method RP500: Goheen, S.C., et al. "Purification of Strontium in Water Before Strontium-89/ Strontium-90 Measurement." DOE Methods for Evaluating Environmental and Waste Management Samples. DOE/EM-0089T. Pacific Northwest Laboratory, Richland, WA. October, 1993.

13.5 Horwitz, E P et al. "A Novel Strontium-Selective Extraction Chromatographic Resin". Solvent Extraction and Ion Exchange. 10 (1992) 313. (HP292).

13.6 P. Horwitz, M.L. Dretz, and D.E. Fisher, "Separation and Preconcentration of Strontium from Biological, Environmental, and Nuclear Waste Samples by Extraction Chromatography Using a Crown Ether", Analytical Chemistry, 63:522-525 (1991).

13.7 Jump, Robert et al. "Simultaneous ICP in Conjunction With Sr-Spec as a Tool for Improving Sr-89/90 Determination in Environmental Samples". 40th Annual Conference on Bioassay Analytical and Environmental Radiochemistry. Cincinnati, Ohio. November 1994. (JR194).

13.8 Strontium 89/90 in Water, Environment, Safety and Health Division - Argonne National Laboratory; Spec News, Vol. 1, Issue 2 (1992). (A publication of Eichrom Industries, INC, Darien IL).

13.9 N. Vajda, A. Ghods-Esphahani, E. Cooper, P.R. Danesi, “Determination of Radiostrontium in Soil Samples using a Crown Ether, J”. Radioanalytical Nuclear Chemistry, 1993.

13.10 Subsampling for Soils and Sediments (workorder review\QAInfo\Guidance Documents), Paragon Analytics, 4/19/06.

13.11 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

9/7/06: No technical changes. Augmented LIMS program specification language. Added DOCUMENT REVISION HISTORY section. Other minor clerical corrections.

8/31/07: Clarified use of second independent source for spiking (SECTION 6), added comment, 10.3, to add spike before any chemical processing. Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Section 7.1. Removed activity calculations from SECTION 9, and referenced SOP 708 instead.

Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 708 REVISION 8

TITLE: CALCULATIONS FOR RADIOANALYTICAL RESULTS

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7/21/08

QUALITY ASSURANCE MANAGER _____ DATE 7/20/08

LABORATORY MANAGER _____ DATE 7/21/08

HISTORY: Rev0, 10/1/92; Rev1, PCN#11, 10/15/93; Rev2, 10/5/99; Rev3, 9/20/02; Rev4, 3/6/04; Rev5, 7/5/06; Rev6, 4/13/07; Rev7, combined with TPU SOP 743, 8/31/07; Rev8, 7/18/08.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) provides the basic calculations for Activity Concentration, Total Propagated Uncertainty (TPU), Decision Level (DL), and Minimum Detectable Concentration (MDC). The algorithms provided in this SOP accurately reflect the processes used in the Paragon LIMS system for performing the same calculations.

Deviations from these calculations are special cases, requiring the approval of the Department Manager. These deviations are documented in the individual method SOPs. In addition, method-specific descriptions of uncertainty coefficients and calculational "switches" are also found in the individual method SOPs.

Paragon standard (i.e., default) practices are discussed in this SOP. Client-specified calculations that deviate from Paragon standard practices are defined in the LIMS program specification applicable to the samples being processed.

Where uncertainty calculations are concerned, this SOP describes the principles and practices taken to estimate the TPU in radioanalytical procedures. This procedure incorporates recommendations from the NIST Technical Note 1297, "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results", which is equivalent to ISO "Guide to the Expression of Uncertainty in Measurements".

DL and MDC calculations provide analytical values that respectively describe the limits of statistical probability for blank sample analyses and for analyses that are distinguishable from a blank sample.

2. SUMMARY

This SOP first describes the calculation of the various correction factors that are applied to all Activity, TPU, DL and MDC calculations.

2.1 CORRECTION FACTORS

Most correction factors are combined and applied as the denominator in the final calculations. The specific correction factors include the following:

- Crosstalk
- External Background
- Base Counting Efficiency
- Efficiency Correction (e.g. Mass Attenuation)
- Progeny Ingrowth
- Progeny Efficiency
- Decay
- Chemical Yield
- Sample Volume
- Emission Abundance
- Units Conversion

After the correction factors have been determined, this SOP describes the appropriate calculations for Activity, TPU, DL and MDC.

Due to the complexity of radioanalytical calculations, Paragon has devised a system that employs a universal calculation format with a series of arithmetic "switches" that allow for the inclusion (or exclusion) of the various correction factors.

2.2 UNCERTAINTY

Radioanalytical data reporting convention includes the estimated analysis uncertainty. This procedure provides estimates of uncertainties throughout the radiochemical preparation and counting process, such that the reported uncertainty includes all known sources of potential error. Individual uncertainty estimates, determined at the one-sigma (1σ) level, are "summed in quadrature" to estimate the one-sigma Total Propagated Uncertainty. Total Propagated Uncertainties (TPU) may subsequently be reported at a multiplier of the sigma value (two- or three-sigma) or at a specific confidence interval (95%, 99%, etc.), as requested by a particular client or procedure. All uncertainties listed in this procedure are given as 1σ values.

Where possible, estimates of uncertainties in various significant steps of radioanalytical procedures are established, either by the collection of empirical data, or by reference to a reliable authority, such as the ANSI N42 standards. These include uncertainty estimates in volume and mass determinations, process reproducibility, instrument calibration and operation, and counting uncertainty.

Estimated uncertainties may be calculated either in activity units (e.g., pCi/g) or as a relative uncertainty (e.g., a percentage of the measured activity). By convention, any uncertainty calculated as a relative value must be multiplied by the sample activity, thereby converting the value to activity units, before using that uncertainty component in the final TPU calculation.

2.3 DLs and MDCs

On a practical basis, the MDC is the level of activity required to be present in a sample to be able to statistically distinguish that sample from one with no activity, at the 2σ confidence interval. More specifically, in a paired observation, in which sample results are background-corrected, the "Decision Level" (or "Critical Level") is the maximum expected result, at the 2σ confidence interval, for a sample with no activity. Therefore, in a sample with an activity concentration equal to the MDC, the minimum expected result at the 2σ confidence interval would be equal to the Decision Level.

Decision Level and MDC determinations are a priori calculations that are generally independent of the actual measured activity concentration in the sample. These calculations can be accurately performed prior to the analysis. Gamma spectroscopy is the exception to this statement, because spectral background is affected by sample activity in a gamma spectroscopy analysis.

As with Activity and TPU, DLs and MDCs for radioanalytical procedures are determined by mathematical formulae that take into account sample volume, chemical recovery, instrument detection efficiency and background, and sample counting duration. This calculation provides for analysis of actual samples to demonstrate the ability to meet desired or required detection limits. This calculation, or an alternative as specified by the client, shall be performed for each type of analysis as a verification of detection limit capabilities.

It is noted that the traditional formulae, described in Section 5.5.1 and 5.5.2 of this SOP, rely on the assumption that the sample count duration and the background calibration count duration are equal. In cases where this assumption does not hold, the refinement in the calculations shown in Section 5.5.3, is appropriate. It is also noted, however, that the use of the traditional formulae is well-entrenched among some clients, despite any differences in count times, and changing this formula may cause unacceptable discontinuity in historical monitoring programs and other scenarios. Consequently, Paragon continues to provide the traditional formulae by default, and offers the revised formula upon request.

The analyst should note that improved detection limits may be obtained through use of larger sample volumes, longer counting times, or improved sample analysis geometries if the *a priori* calculation reveals an inadequate detection limit.

3. RESPONSIBILITIES

3.1 Paragon's Project Managers (PM) serve as the primary interface with the client. To the extent possible, it is the PM's responsibility to understand the client's needs with regard to the manner in which radioanalytical results are calculated, and to inform the client of the option to request client-specified calculations, if necessary. The PM is responsible for creating/maintaining LIMS program specifications that satisfactorily address the clients needs, as applicable.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specifications supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 It is the Department Manager's responsibility to ensure that any material changes to this SOP, which may affect the calculations performed in LIMS, are reflected in the LIMS program. These changes may include correction factors, uncertainty component factors, etc. Updates in LIMS may require the assistance of the IS Department, to make changes to the LIMS program. In all cases, it is also the Department Manager's responsibility to ensure that the calculational changes made in the LIMS program are properly verified.

3.4 It is the analyst's responsibility to be familiar with both the preparation SOP and the analysis SOP for the method results being reported. These SOPs will include calculation coefficients, as well as provide guidance in the fundamental concepts behind the analytical method.

3.5 Analysts must demonstrate the capability to generate acceptable results using the procedures described herein. This demonstration typically comes in the form of supervisory training and review, as well as periodic documentation of the validation of the LIMS program that generally performs these calculations.

3.6 It is the responsibility of all personnel to perform the tasks as described in this SOP. Any anomalies or out-of-control events must be noted, and corrective action taken and documented. For the purpose of this SOP, out-of-control events are defined as those calculations that cannot be validated, by manual calculation, to within 3% of the reported LIMS result. This criteria is defined in SOP 709.

4. APPARATUS AND MATERIALS

There are no apparatus or materials, including reagents and standards, used in this SOP. It is noted, however, that calibration factors and other calculation coefficients may be defined in the individual preparation and analysis SOPs used for a particular method.

5. CALCULATIONS

5.1 GENERAL CORRECTION FACTORS

These general correction factors are applicable to all calculated results for a given sample analysis. The calculation of Activity Concentration, TPU, DL and MDC require identical correction factors, such as chemical yield, etc., to ensure that the final reporting units are comparable, thereby allowing for a valid comparison of results.

5.1.1 Instrument Background (CalBCPM)

The basic instrument background count rate, in counts per minute (cpm), is described in the individual instrument SOPs. This value is subtracted from the gross sample count rate (GCPM) to determine the net sample count rate for the analysis.

This is the background count rate that is subtracted in all analytical methods performed on a given instrument. Additional background correction factors, such as filter contributions or quench curve adjustments, that are applicable to a single method are described below as "External Background (ExtBCPM)".

5.1.2 External Background (ExtBCPM)

External background contributions, such as the additional contribution of paper filters to a beta analysis, which are not accounted for in the basic instrument background calibration, are described in the individual preparation and analysis SOPs.

Additional examples of external background contributions include the batch-specific adjustment of the background quench curve in liquid scintillation analyses, and the yield-dependent beta contribution from the Sm carrier in a Pm-147 analysis.

5.1.3 Crosstalk Count Rate (XTLK)

The Crosstalk Count Rate refers to the additional background contribution, in multi-channel analyses such as gross alpha/beta, in which the analyte results in a region of interest exhibit an interference from other analyte results in a different region of interest. The Crosstalk Count Rate is a function of the Crosstalk Calibration Ratio, which is determined during the base efficiency calibrations.

The primary region of interest is sometimes called the minor region (m) and the interfering region is sometimes called the major region (M). The presence of measurable activity in the major region contributes additional counts to the minor region of interest. These additional counts must be treated as additional background counts since they

interfere with the accurate quantification of activity in the minor region of interest.

For example, in gas-flow proportional counting there are alpha- and beta- regions of interest. The presence of measurable alpha activity primarily shows up in the alpha region. In addition, some alpha activity will also show up in the beta region. These counts are not attributable to beta activity and must be subtracted from the gross beta count rate in order to accurately quantify the true beta activity in the sample. See Figure 1 .

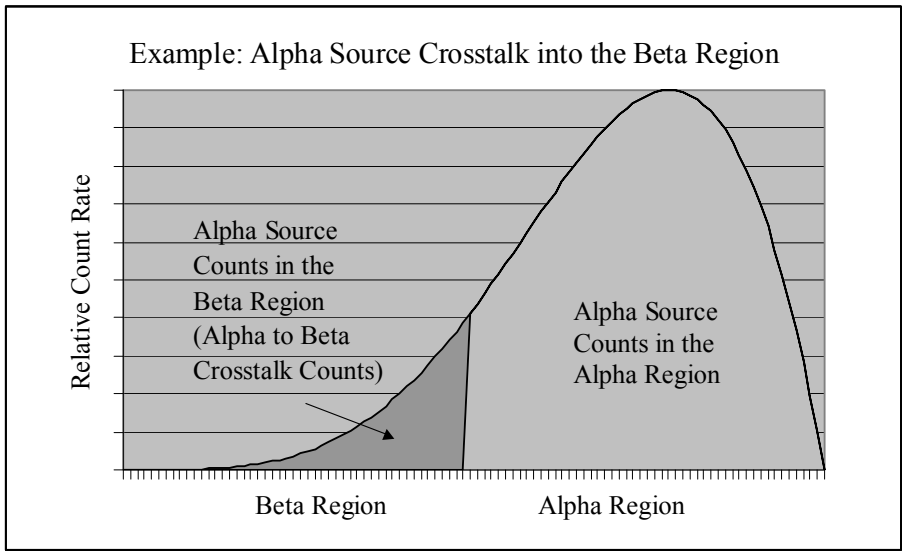

Figure 1

The Crosstalk Calibration Ratio is determined during the base efficiency calibration of the major region and is simply the ratio of net counts in the minor region to net counts in the major region;

$$XTLK_{M>m} = (NetEffCPM_m / NetEffCPM_M)$$

where:

$XTLK_{M>m}$ = Crosstalk Calibration Ratio

$NetEffCPM_m$ = Net count rate in the minor region of interest, during the efficiency calibration of the analyte primarily found in the major region.

$NetEffCPM_M$ = Net count rate in the major region of interest, during the efficiency calibration of the analyte primarily found in the major region.

In alpha/beta example given above, $XTLK_{M>m}$ would be the alpha to beta Crosstalk Calibration Ratio, determined during an alpha efficiency calibration. $NetEffCPM_m$ would be the net beta count rate observed during the alpha efficiency calibration process. $NetEffCPM_M$ would be the net alpha count rate observed during the same alpha efficiency calibration.

The Crosstalk Count Rate in a sample analysis is calculated as the additional count rate in the minor region and is a function of the net sample count rate in the major region;

$$XTLK = (XTLK_{M>m})(NetCPM_M)$$

where:

XTLK = Crosstalk Count Rate in the minor region during a sample analysis, to be treated as additional background.

$NetCPM_M$ = Net count rate in the major region, during a sample analysis.

In alpha/beta example given above, $NetCPM_M$ would be the net alpha count rate. XTLK would be the beta Crosstalk Count Rate, attributable to the sample alpha activity, to be subtracted from the gross beta count rate as additional background.

5.1.4 Base Counting Efficiency (BaseEFF)
The determination of the base counting efficiency is described in the individual preparation and instrument SOPs. The base counting efficiency factor gives the ideal instrument response, in the presence of a particular radionuclide. The units for counting efficiency are "counts per emission".

5.1.5 Efficiency Correction (BaseMassAtt)
The determination of the base efficiency correction factor is described in the individual preparation and instrument SOPs. The correction factor is a unit-less multiplicative correction factor, less than one, that accounts for physical interferences that reduce the sample counting efficiency, such as mass attenuation in a gross alpha/beta analysis or a quench correction in a liquid scintillation analysis.

5.1.6 Progeny Ingrowth (ING)
In cases where the analyte that is isolated in the preparation method decays into a radioactive progeny that is observable in the analysis, the resulting ingrowth of progeny is taken into consideration.

The progeny ingrowth factor describes the relative activity of the ingrown daughter product, as compared to the parent. This special form of the equation assumes that the half-life of the daughter is much shorter than the half-life of the parent;

$$ING = 1 - e^{\lambda * t4}$$

where:

e = the base of the natural logarithm

λ = the decay factor for the progeny;

= ln(0.5) / (progeny half-life)

t4 = the elapsed time the isolation of the parent nuclide to the beginning of the sample count.

Note that in this calculation, as in any decay or ingrowth calculation, the units of time in which the half-life is expressed (e.g. years, days, etc.) must be the same units in which the elapsed time is expressed.

For example, Sr-90 undergoes beta decay, with a half-life of 28.5 years into a radioactive daughter Y-90, which also undergoes beta decay with a half-life of 64 hours. Upon chemical isolation of the Sr-90, the ingrowth of Y-90 immediately resumes. If the sample is held for 72 hours before analysis, the degree of ingrowth of the Y-90 daughter is;

$$1-e^{((ln(0.5)/64h*72h)} = 0.5415$$

Consequently, for a given amount of Sr-90 activity present in the sample, 72 hours after chemical separation there will also be 54.15% of that amount, which will be present as Y-90 activity.

5.1.7 Progeny Efficiency (ProgEFF)

In some cases the progeny emissions are measured and the counting efficiency for the progeny emissions are sufficiently different from the counting efficiency of the parent emissions. In these cases, the counting efficiency of the progeny are determined separately, and are analogous to the base counting efficiency determination. As in any counting efficiency determination, the units are "counts per emission".

5.1.8 Progeny Efficiency Correction (ProgMassAtt)

As with the determination of the base efficiency correction factor, the progeny counting efficiency may need to be corrected for physical interferences, such as mass attenuation in a gross alpha/beta analysis or

a quench correction in a liquid scintillation. This progeny efficiency correction is also a unit-less factor, less than one.

5.1.9 Decay to the Sampling Date (D)

The decay factor is a unit-less correction factor that describes the amount of radioactive parent material remaining after a given period of decay time. By convention, radioanalytical results are generally decay-corrected to the sampling date unless otherwise specified;

$$D = e^{\lambda * t0}$$

where:

λ = the decay factor for the parent;

= ln(0.5) / (parent half-life)

t0 = in the GENERAL CASE, the elapsed time from the field sampling or reference date to the beginning of the sample count (as in H-3).

in the case where INGROWN PROGENY are counted, the elapsed time from the reference date to the isolation/separation of the parent nuclide (as in Sr-90).

5.1.10 Decay During the Count (L)

Since radioactive decay is measured by observation of the radiation emissions over a period of time (usually between 1 and 1,000 minutes), and since the rate of decay changes over time, the change in the decay rate over the duration of the count must be accounted for. This is especially important during the measurement of radionuclides for which the half-life is less than ten times the count duration.

The decay during the count (L) is calculated as follows;

$$L = \left(\left(1 - \exp^{\lambda * t3}\right)/\left(-\lambda * t3\right)\right)$$

where:

λ = the decay factor for the first radionuclide in the chain of radionuclides that are present during the sample count.;

= ln(0.5) / (half-life)

For example, in a Sr-90 analysis in which Sr-90 and its Y-90 daughter are both present, use the half-life of the Sr-90 parent. In a Ra-228 analysis in which the only nuclide present is the Ac-228 daughter, use the half-life of the Ac-228 daughter.

5.1.11 Chemical Yield (yield)

The determination of chemical yield is described in the individual preparation SOPs. Chemical yield is generally determined by pre-separation and post-separation measurement of stable carriers or radioactive tracers added to the sample, and is expressed in decimal format. *For example, a chemical yield of 95.13% is expressed as 0.9513.*

5.1.12 Sample Volume (vol)

The sample volume is the equivalent amount of sample material actually presented for analysis. Described in the individual preparation SOPs, the sample volume for analysis is equal to the original volume of sample aliquotted, less any amounts removed for yield determinations, splits, etc.

5.1.13 Emission Abundance (abund)

Emission abundance values (like half-lives) are derived from published reference tables. These values describe the frequency with which a given emission of radiation occurs for each decay of a parent atom.

For example, the decay of Ba-137m results in a 662 keV gamma photon emission 89.98% of the time. The emission abundance is 0.8998.

In some cases, the analysis of a particular radionuclide may require the measurement of one or more progeny. The creation of these progeny may only occur during a fraction of the parent atom disintegrations. The "branching ratio" for a particular decay scheme describes the frequency of the resulting progeny. As a practical consideration in the Paragon LIMS reporting software, the abundance values and branching ratios are multiplied into a single correction factor.

*For example, in the determination of Cs-137, 94.6% of decays result in the creation of Ba-137m. When measuring the resulting 662 keV gamma emissions, the rate of Cs-137 decay can be inferred by correcting the observation by both the gamma emission abundance and the branching ratio. See Figure 2. The effective correction factor is 0.8998 * 0.9460 = 0.8512.*

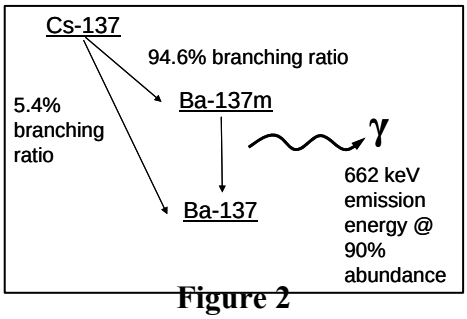

Figure 2

5.1.14 Units Conversion (actconv)
Results are converted into conventional activity reporting units through the application of an appropriate conversion factor. Paragon default reporting units of picoCuries (pCi) are achieved through the application of the conversion factor 2.22 dpm/pCi.

5.2 "SWITCHES" and the STANDARD DENOMINATOR (k)
The application of the various correction factors described above is achieved with a series of arithmetic "switches" that allow for the inclusion (or exclusion) of those factors.

A table of values for the various switches described below, as they are applied to individual methods, is provided in Appendix A. These values may be superseded by subsequent revision of the analytical methods. Consult the individual preparation and analysis SOPs for the latest revisions to the methods.

The combination of selected correction factors and their related arithmetic switches create a standard denominator (k), to be applied in the calculation of Activity, TPU, DL, and MDC;

$$k = (A + B) * C * K * L$$

where:

$$A = \left(BaseEFF * BaseMassAtt^{\mathbf{c}} \right) * \left(1 + \left(1 - \exp^{\lambda * t4} \right) * \mathbf{d} \right)$$

and where:

BaseEFF = Base calibration efficiency (cpm/dpm).

Base MassAtt = Mass attenuation factor for the base efficiency (no units).

switch c = 0, if there is no mass attenuation correction in this method.

1, if there is a mass attenuation correction in this method.

switch d = 0, if there is no ingrowing daughter product present during the count that has the same counting efficiency as the parent (as in gross α/β).

1, if there is an ingrowing daughter product present during the count, and it has the same counting efficiency as the parent (as in Sr/Y-90).

exp = the base e of the natural logarithm (2.718).

λ = the decay constant [ln(.5)/(half-life of the nuclide of interest)].

Similarly,

$$B = \left(ProgEFF * ProgMassAtt^{\mathbf{e}} \right) * \left(1 - \exp^{\lambda * t4}\right) * \mathbf{f}$$

where:

ProgEFF = Progeny calibration efficiency (cpm/dpm), if applicable. See switch f below.

ProgMassAtt = Mass attenuation factor for the progeny efficiency (no units).

switch e = 0, if there is no mass attenuation correction for the progeny in this method.

1, if there is a mass attenuation correction for the progeny in this method.

switch f = 0, if there is no ingrowing daughter products present during the count that have a different counting efficiency from the parent (as in Sr/Y-90 and gross α/β).

1, 2, 3, etc., based on the number of ingrowing progeny present during the count, with a different counting efficiency from the parent (as in Total Radium, where f=3).

$$C = \left(\exp^{\lambda * t2} * \left(1 - \exp^{\lambda * t1}\right)\right)^{\mathbf{g}}$$

where:

switch g = 1, if the analyte to be counted is the ingrown daughter product of the parent target analyte and the parent target analyte is not present in the fraction for analysis (as in Ra-228).

0, Otherwise.

$$K = yield * vol * abund * actconv * \left(\exp^{\lambda * t0}\right)^{\mathbf{h}}$$

where:

yield = chemical yield (no units).

vol = sample size (grams, liters, m3, etc.).

abund = abundance correction, including branching ratios, from published reference data (no units).

actconv = activity units conversion factor, e.g. 2.22 dpm/pCi, to report data in pCi units.

switch h = 0, if the target analyte should not be decay corrected, usually because the specific nuclide is unknown (as in gross αβ, or Total Activity).

1, if the decay factor for the target analyte is known and is to applied (as in Sr-90, Th-228, H-3, etc.).

$$L = \left(\left(1 - \exp^{\lambda * t3}\right)/\left(-\lambda * t3\right)\right)^{\mathbf{h}}$$

where:

switch h = defined above.

IMPORTANT NOTE: In the L factor defined here,

if the g switch defined above is 0, then use the λ of the parent target analyte (as in Sr-90).

if the g switch defined above is 1, then use the λ of the ingrown progeny (as in Ra-228).

5.3 ACTIVITY CONCENTRATION

The determination of the activity concentration in a sample begins with the sample gross count rate measurement on a given instrument, such as a gas-flow proportional counter for gross α/β analyses. Various background count rate contributions, described in Sections 5.1.1 through 5.1.3 above, are subtracted from the gross count rate to yield a net count rate, which is attributable only to the actual sample activity. The standard denominator is then applied to convert the result into conventional reporting units. The final result expresses the radioactive decay rate per volume of sample material, decay corrected to the sampling date;

$$\text{Activity} = \frac{GCPM - \left[CalBCPM + \left(XTLK * a\right) + \left(ExtBCPM * b\right)\right]}{k}$$

where:

GCPM = Gross count rate (cpm)

CalBCPM = Calibrated instrument background count rate (cpm).

XTLK = Crosstalk contribution to the analyte background (cpm).

switch a = 0, if there is no crosstalk contribution in this method.

1, if there is a crosstalk contribution in this method.

ExtBCPM = External background contribution, such as the additional contribution of paper filters to a beta analysis, which is not accounted for in the base background calibration.

switch b = 0, if there is no external background contribution in this method.

1, if there is an external background contribution in this method.

5.4 UNCERTAINTY

In general, uncertainty refers to the estimated lack of accuracy and/or precision in a reported value. The uncertainty is first estimated for each individual process in the analytical method. The component uncertainties are then combined to give a Total Propagated Uncertainty (TPU) for the entire method. When accompanying the reported activity concentration, this TPU describes the range of values in which the laboratory believes that the true value of the sample lies, at the stated confidence interval.

Unless stated otherwise, the values and formulae provided below are stated at the one-sigma (1σ) confidence interval. These values, and the associate TPU, may be expressed at any other confidence interval by multiplying by the equivalent expansion factor, as described in Section 0.

5.4.1 PRIMARY COMPONENTS

Primary components of the TPU calculation are listed below, and are detailed in the Sections shown:

Analyte Count Rate Uncertainty	Section 5.4.2
Chemical Yield Determination Uncertainties:	
Radiometric Tracer Measurements	Section 5.4.3.1
ICP Mass Measurements	Section 5.4.3.2
Gravimetric Mass Measurements	Section 5.4.3.3
Analysis Uncertainties	Section 5.4.4
Preparation and Sample Handling Uncertainties	Section 5.4.5

5.4.2 ANALYTE COUNT RATE UNCERTAINTY (CU)

The analyte count rate uncertainty is the estimated deviation of the observed count rate from the true mean count rate of the analyte of interest. This component of TPU is due solely to the statistically random nature of radioactive decay.

The uncertainty of a single radiometric measurement is estimated as the square root of the total number of counts acquired. It is calculated as a count rate uncertainty, in units of counts per unit of time, as follows:

$$U_R = \sqrt{\frac{R_S}{T_S}}$$

where:

U_R = Count Rate Uncertainty

R_S = Gross Count Rate in the Sample

T_S = Duration of the Sample Count

In practice, however, a single radiometric measurement is rarely used to report activity concentrations. Instead, the gross sample count rate is background corrected by subtracting the background count rate to obtain a sample net count rate. This is known as a "paired observation", and is calculated as a count rate uncertainty, in units of counts per unit of time, as follows:

$$U_R = \sqrt{\frac{R_S}{T_S} + \frac{R_B}{T_B}}$$

where:

R_B = Count Rate in the Instrument Background Determination

T_B = Duration of the Instrument Background Count

In some analytical techniques, multiple background corrections may be made. A routine instrument background correction will be made, based on the periodic background determination ordinarily performed on the instrument. Further background adjustments may be made in cases where the basic background determination is not representative of the specific analytical technique being employed. Some examples include batch-specific adjustments to the quench curve on the liquid scintillation counter, batch-specific adjustments for the filter contribution in I-129 analyses by gas-flow proportional counting, and

sample-specific contributions to the Compton continuum in gamma spectrometry analyses.

In these cases, the contribution of the additional background determination to the overall counting uncertainty is calculated as

$$U_R = \sqrt{\frac{R_S}{T_S} + \frac{R_B}{T_B} + \frac{R_A}{T_A}}$$

where:

R_A = Count Rate in the Additional Background Determination

T_A = Duration of the Additional Background Count

Where multiple, independent measurements contribute to the additional background determination, as in the case of quench curve adjustments or I-129 blank filter counts, conservatively use the count duration of a single measurement, rather than the combined duration of all measurements. The Count Rate should, however, be the average of the individual measurements.

After calculating the Count Rate Uncertainty in units of count per unit time, that number should be converted to activity concentration units, typically pCi/gram or pCi/liter, by dividing by the appropriate conversion factors, for example:

$$\text{Counting Uncertainty (pCi/g,l)} = \frac{\text{Count Rate Uncertainty (cts/min)}}{k}$$

where:

k = the standard denominator defined in section 5.2.

It is important to note that, in potentially zero (or near zero) background counting systems such as alpha spectrometry, the calculation should guard against the erroneous production of a calculated uncertainty that is at or near zero. Reporting a counting uncertainty of zero is unacceptable, since the count is duration is limited (not infinitely long) and the failure to observe an event during the count does not guarantee that an event will never be observed. Reporting zero activity with zero uncertainty (infinite precision) is not possible.

To guard against this possibility, counting uncertainties are re-calculated by substituting the values $(3/T_S)$ for R_S, $(3/T_B)$ for R_B, and $(3/T_A)$ for R_A in the equations above, to calculate a "Zero Uncertainty"

value. If the Zero Uncertainty is greater than the calculated Counting Uncertainty, the value of the Zero Uncertainty replaces the calculated Counting Uncertainty.

The use of the constant 3 in these equations estimates a maximum true value for an observation that resulted in zero events.

5.4.3 CHEMICAL YIELD DETERMINATION UNCERTAINTIES (YU)
These will vary considerably, depending on the method used to quantify the chemical yield of a given separation procedure, as described below.

5.4.3.1 RADIOMETRIC TRACER MEASUREMENTS
Chemical yields may be determined by the analysis of a radioactive tracer added to the sample prior to chemical separation. The method for estimating the uncertainty associated with a radiometric tracer measurement is identical to the analyte count rate uncertainty described in Section 5.4.2 above, except that the tracer counts are used instead of the counts for the analyte of interest.

5.4.3.2 ICP MASS MEASUREMENTS
Chemical yields may be determined by Inductively Coupled Plasma (ICP) analysis of pre-separation vs. post-separation concentrations of a stable carrier element. The uncertainty in this yield determination is assumed to be 8.3% of the measured sample activity.

5.4.3.3 GRAVIMETRIC MASS MEASUREMENTS
Chemical yields may be determined by the measurement of the residual mass of prepared sample deposited onto a planchet or filter. In this case, the error in the yield determination may be significantly affected by interfering chemical constituents native to the sample, which the laboratory has no control over. The uncertainty in a gravimetric yield determination is conservatively estimated at 10% of the measured sample activity.

5.4.4 ESTIMATES OF INSTRUMENT ANALYSIS UNCERTAINTIES (IU)
5.4.4.1 Uncertainties associated with the instrumental analysis of radiochemical samples are assumed to be as follows:

Calibration (In-house prep. of standards): 5.0%

Calibration (Vendor-prepared standards): 2.0%

Counting Reproducibility:	1.0%
Sample Position Reproducibility:	1.5%
Counting Efficiency:	1.5%
Dead Time Estimates:	1.0%

These individual, independent uncertainty components are combined, or propagated, together by calculating the square root of the sum of the squares of the various components. This technique of combining independent uncertainties is also known as "summing in quadrature", and is shown below. This will result in a single uncertainty estimate for a procedure with multiple uncertainty contributions. Note that the same propagation technique is used to combine preparation uncertainty factors in Section 5.4.5.

5.4.4.2 Instrumental Uncertainty (for calibration with a vendor-prepared standard):

Relative Uncertainty =

$$\sqrt{.020^2 + .01^2 + .015^2 + .015^2 + .01^2}$$

$$= 0.0324 = 3.2\%$$

5.4.4.3 Instrumental Uncertainty (for calibration with an in-house prepared standard):

Relative Uncertainty =

$$\sqrt{.05^2 + .01^2 + .015^2 + .015^2 + .01^2}$$

$$= 0.0561 = 5.6\%$$

5.4.5 ESTIMATES OF CHEMICAL PREPARATION UNCERTAINTIES (PU)

5.4.5.1 Uncertainties associated with the various steps in the chemical preparation of samples are estimated to be as follows:

Gross Aliquoting (Sample Homogeneity):	5%	
Quantitative Transfers:	2.5%	#
Spike or Tracer Standard:	2.5%	
Pipetting:	0.4%	*

Volumetric Measurements	
(non-volumetric labware):	0.6% *
Mass Measurements:	0.3% *
Reagent Addition (repipetting/dispensing):	0.6% *
Aliquoting and ICP Yield Determinations	
(Section 3.3):	8.3% *
Gravimetric Yield Determinations (Section 3.3):	10%

* these uncertainty factors have been empirically determined by Paragon.

\# quantitative transfers need not be considered if a tracer or carrier used for yield determinations has already been added to the sample.

5.4.5.2 PROPAGATION OF PREPARATION UNCERTAINTIES

As described above, in Section 5.4.4.1, independent preparation uncertainties are summed in quadrature. Some generalized examples are given below, for clarification. ***Please note that these are examples only.*** Specific preparation uncertainty factors are given in the individual preparation SOPs.

Example 1: Alpha or Beta Analyses by Gas Flow Proportional Counting (GFPC)

minimal preparation, error =

$$\sqrt{(.05^2 + .004^2 + .006^2 + .003^2 + .003^2 + .025^2)} = .0565 = 5.7\%$$

Based on sample homogeneity, a single pipetting, a single volumetric measurement, two mass measurements, and a quantitative transfer.

Example 2: Liquid Scintillation Analyses

minimal preparation, error =

$$\sqrt{(.05^2 + .006^2 + .006^2 + .003^2)} = .0508 = 5.1\%$$

Based on sample homogeneity, two volumetric measurements, and a single mass measurement.

Example 3: Gamma Spectroscopy

minimal preparation, error =

$$\sqrt{(.05^{2} + .003^{2})} = .0501 = 5.0\%$$

Based on sample homogeneity and a single mass measurement.

5.4.6 CALCULATION OF TOTAL PROPAGATED UNCERTAINTY

The individual uncertainties described above are combined, or propagated, together by calculating the square root of the sum of the squares of all the individual uncertainties.

Note that, in order to combine uncertainty factors, those factors must first be in the same units, such as pCi/g or Bq/L. Uncertainty factors that are expressed as a fraction of the sample activity, such as the instrument and preparation uncertainty factors described above, must be multiplied by the sample activity concentration before proceeding with the propagation calculation.

Be sure that all uncertainty factors are in activity concentration units before performing this last step.

$$TPU = \sqrt{\mathrm{CU}^{2} + Yield\mathrm{U}^{2} + \left(I\mathrm{U} * \mathrm{Activity}\right)^{2} + \left(P\mathrm{U} * \mathrm{Activity}\right)^{2}}$$

where:

$YieldU = YU$

in cases where a radioactive tracer is employed and the yield uncertainty has been expressed as a counting uncertainty, in activity concentration units.

And:

$YieldU = \left(YU * Activiy\right)$

in cases where a stable carrier is measured by ICP, gravimetrically, or other non-radioactive yield determinations, and the yield uncertainty is expressed as a relative uncertainty.

5.4.7 EXPANSION OF THE 1σ TOTAL PROPAGATED UNCERTAINTY
As previously mentioned, the TPU calculation above is expressed at the one sigma (1σ, or 68.3%) confidence interval.

The TPU may be expressed at any other confidence interval by multiplying the 1σ TPU by the appropriate expansion factor (z), shown below.

σ value	% confidence interval	Expansion factor (z)
1.00	68.3	1.00
1.96	**95.0**	1.96
2.00	95.4	2.00
2.56	**99.0**	2.56
3.00	99.7	3.00

Additional expansion factors may be determined by calculating the relative coverage area (% confidence interval) of the normal distribution curve.

5.5 Decision Level (DL) and Minimum Detectable Concentration (MDC)
In a background-corrected nuclear measurement, in which the background count rate is expected to randomly vary with a normal distribution, the analysis of a blank sample will naturally show activity that is not necessarily zero, depending on the pairing of these randomly fluctuating count rates. The DL refers to the maximum activity concentration (at the specified confidence interval) that would be expected to be reported in a blank sample analysis.

By extension, the MDC described that level of activity that would have to be in a contaminated sample in order to give a result that is sufficiently higher than the DL, so that the sample is statistically distinguishable from one with no activity.

By convention, the DL and the MDC are expressed at the 95% confidence interval.

As described above, in Section 2.3, Paragon provides default DL and MDC calculations that follow industry convention. These default formulae assume that the background determination for the sample analysis was performed for the same duration as the sample analysis itself.

5.5.1 DL

Unless otherwise specified in documentation of specific analytical methods, instrumentation software, or client requirements, the DL shall be calculated as:

$$DL = \frac{2.33\sqrt{B}}{kT_s}$$

where:

B = the total counts in the background for the sample

T_s = the sample count duration

k = the standard denominator described in Section 5.2

5.5.2 MDC

Unless otherwise specified in documentation of specific analytical methods, instrumentation software, or client requirements, the MDC shall be calculated as:

$$MDC = \frac{4.65\sqrt{B} + 2.71}{kT_s}$$

5.5.3 REVISED DL AND MDC CALCULATIONS IN CASES WHERE THE SAMPLE COUNT DURATION DIFFERS FROM THE BACKGROUND COUNT DURATION

As described above, in Section 2.3, Paragon recognizes that there may be technical refinements to the default DL and MDC calculation, in cases where the sample and background count times differ.

These refinements, while technically sound, are generally provided only at the client's request because many clients view these changes to the calculations as a source of discontinuity to the historical record for some monitoring data. Nonetheless, the analyst should be aware of, and versed in, the revised formulae;

$$MDC = \frac{3.29\sqrt{R_B * T_s * (1 + T_s / T_b)} + 2.71}{k * T_s}$$

$$DL = \frac{2.33\sqrt{R_B * T_s * (1 + T_s / T_b)}}{k * T_s}$$

where:

R_B, k, and T_s are defined as above

T_b = the background calibration count duration

6. QA/QC

All instruments shall be calibrated according to requirements described in SOPs 704, 713, 714, 724, and 783 prior to performing these calculations.

7. REFERENCES

7.1 ANSI N42 Standards, National Committee on Radiation Instrumentation.

7.2 NIST Technical Note 1297, "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results", U.S. Dept. of Commerce, 9/94.

7.3 Knoll, Glenn F., Radiation Detection and Measurement, 3rd Ed., Wiley & Sons, 1999.

7.4 Paragon Analytics, Inc Project ID 02-15-001, "Empirical Measurements for TPU Determinations", 3/02.

7.5 Lloyd A. Curie, "Limits for Qualitative Detection and Quantitative Determination", Anal. Chem. 40, 586-93, March 1968.

7.6 National Council on Radiation Protection and Measurements, NCRP Report No. 58, 309, September 1984.

7.7 EPA 520/1-80-012, "Upgrading Environmental Radiation Data", Health Physics Society Committee Report HPSR-1, 6-26, August 1980.

7.8 Allen Brodsky, et al, "Statistical Considerations in Practical Contamination Monitoring", Radiation Protection Management, Vol. 8, No. 4, (July/August 1991), pp. 64-78.

7.9 MARLAP Manual, July 2004, Section III, Section 20.4.

8. DOCUMENT REVISION HISTORY

7/5/06: Augmented LIMS program specification references; updated format; added DOCUMENT REVISION HISTORY.

4/13/07: Added PM involvement under RESPONSIBILITIES, and DOE MDC calculation, per MARLAP, Section 7.

8/31/07: Major Revision, combined with TPU SOP 743 (will be retired). Changed Title. Also added activity calculations from individual method SOPs, and described standardized LIMS calculation.

7/18/08: Corrected the MDC and DL equations where sample and background count times differ by removing the "B" (total background counts) from both equations and replacing with "R_B" defined as the instrument background count rate.

APPENDIX A

LIMS SWITCH SETTINGS FOR SPECIFIED METHODS

ClassCode	TLAnalyte	SwitchA	SwitchB	SwitchC	SwitchD	SwitchE	SwitchF	SwitchG	SwitchH	RptHC	AbundCrit
GAB	GROSS ALPHA	1	0	1	0	0	0	0	0	-1	1.0000
GAB	GROSS BETA	1	0	1	0	0	0	0	0	-1	1.0000
GROSS_ALPH	GROSS ALPHA	1	0	1	0	0	0	0	0	-1	1.0000
GROSS_BETA	GROSS BETA	1	0	1	0	0	0	0	0	-1	1.0000
I129	I-129	0	1	0	0	0	0	0	1	-1	1.0000
I129	I-129+	0	1	0	0	0	0	0	1	-1	1.0000
GR_ALPH_CO	GROSS ALPHA	1	1	1	0	0	0	0	0	-1	1.0000
RA228	RA-228	0	0	0	0	0	0	1	1	-1	1.0000
RA228	YTTRIUM	0	0	0	0	0	0	0	1	-1	1.0000
RaTOT	BARIUM	0	0	0	0	0	0	0	1	-1	1.0000
RaTOT	RA-226	0	0	1	0	1	3	0	1	-1	1.0000
RaTOT	TOTAL RADIUM	0	0	1	0	1	3	0	1	-1	1.0000
SR89	SR-89	0	0	0	1	0	0	0	1	-1	1.0000
H3	H-3	0	0	0	0	0	0	0	1	-1	1.0000
SR90	SR-90	0	0	0	1	0	0	0	1	-1	1.0000
C14	C-14	0	0	0	0	0	0	0	1	-1	1.0000
NI63	Ni-63	0	0	0	0	0	0	0	1	-1	1.0000
Tc99	Tc-99	0	0	0	0	0	0	0	1	-1	1.0000
Rn222	Rn-222	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	PU-238	0	0	0	0	0	0	0	1	-1	1.0000
Am241	AM-241	0	0	0	0	0	0	0	1	-1	1.0000
Pu242	PU-242	0	0	0	0	0	0	0	1	-1	1.0000
Ra226_RnE	Ra-226	0	0	0	0	0	0	1	1	-1	1.0000
Np237	NP-237+	0	0	0	0	0	0	0	1	-1	1.0000
GAB_No_Att	GROSS ALPHA	1	0	0	0	0	0	0	0	-1	1.0000
GAB_No_Att	GROSS BETA	1	0	0	0	0	0	0	0	-1	1.0000
TotActivit	TOTAL BETA	0	0	0	0	0	0	0	0	-1	1.0000
Pb210_LiqS	Pb-210	0	0	0	0	0	1	0	1	-1	1.0000
Pb210	Pb-210	0	0	0	0	0	1	0	1	-1	1.0000
SR8990	SR-89	0	0	0	1	0	0	0	1	-1	1.0000

ClassCode	TLAnalyte	SwitchA	SwitchB	SwitchC	SwitchD	SwitchE	SwitchF	SwitchG	SwitchH	RptHC	AbundCrit
SR8990	SR-90	0	0	0	1	0	0	0	1	-1	1.0000
Pm147	Pm-147	0	0	1	0	0	0	0	1	-1	1.0000
Fe55	Fe-55	0	0	0	0	0	0	0	1	-1	1.0000
Ni59	Ni-59	0	0	0	0	0	0	0	1	-1	1.0000
Pu241	PU-241	0	0	0	0	0	0	0	1	-1	1.0000
TotActivit	TOTAL ACTIVITY	0	0	0	0	0	0	0	0	-1	1.0000
AmISO	CM-244	0	0	0	0	0	0	0	1	-1	1.0000
AmISO	AM-243	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	CM-244	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-232	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-238	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-233/234	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-232	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-235	0	0	0	0	0	0	0	1	-1	0.8500
ThISO	TH-229	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	TH-230	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-227	0	0	0	0	0	0	0	1	-1	0.5383
PuISO	PU-239	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	PU-242	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	PU-239/240	0	0	0	0	0	0	0	1	-1	1.0000
Am241	AM-243	0	0	0	0	0	0	0	1	-1	1.0000
AmISO	AM-241	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	CM-242	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	AM-243	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-234	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-235/236	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-235	0	0	0	0	0	0	0	1	-1	0.8500
UTOT	U-234	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-238	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	TH-228	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	TH-232	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-228	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-230	0	0	0	0	0	0	0	1	-1	1.0000

ClassCode	TLAnalyte	SwitchA	SwitchB	SwitchC	SwitchD	SwitchE	SwitchF	SwitchG	SwitchH	RptHC	AbundCrit
Th/Ac	TH-232	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-229	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	AC-227	0	0	0	0	0	0	1	1	-1	0.5383
Po210	PO-210	0	0	0	0	0	0	0	1	-1	1.0000
Po210	PO-209	0	0	0	0	0	0	0	1	-1	1.0000
Np237	NP-237	0	0	0	0	0	0	0	1	-1	1.0000
Pu242	PU-239	0	0	0	0	0	0	0	1	-1	1.0000
Ra226_RnE	BARIUM	0	0	0	0	0	0	0	1	-1	1.0000
Pm147_LiqS	Pm-147	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-233/234	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-235/236	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	Cm-243/244	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	Pu-244	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	Th-231	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	Th-234	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Am-242/243	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Am-241	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-245/246	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-247	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-248	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-244	0	0	0	0	0	0	0	1	-1	1.0000
U232TOT	U-232	0	0	0	0	0	0	0	1	-1	1.0000
U232TOT	U-238	0	0	0	0	0	0	0	1	-1	1.0000
GAB_BP	GROSS ALPHA	1	1	1	0	0	0	0	0	-1	1.0000
GAB_BP	GROSS BETA	1	1	1	0	0	0	0	0	-1	1.0000
GAB_BP_NoA	GROSS ALPHA	1	1	0	0	0	0	0	0	-1	1.0000
GAB_BP_NoA	GROSS BETA	1	1	0	0	0	0	0	0	-1	1.0000
CL36	Cl-36+	0	0	0	0	0	0	0	1	-1	1.0000
CL36	Cl-36	0	0	0	0	0	0	0	1	-1	1.0000
AmISO	Cm-242	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	Th-227	0	0	0	0	0	0	0	1	-1	1.0000

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 709 REVISION 6

TITLE: **VERIFICATION AND VALIDATION OF RADIOANALYTICAL SOFTWARE**

FORMS: **722, 724, 725**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/11/06

QUALITY ASSURANCE MANAGER _____ DATE 9/8/06

LABORATORY MANGER _____ DATE 9-10-06

HISTORY: Rev0, 10/28/92; Rev1, 3/9/93; Rev2, PCN #24, 11/10/93; Rev3, PCN #290, 12/12/94; Rev4, 10/8/99; Rev5, 8/23/02; Rev6, 9/11/06.

re-released w/o revision 3/13/09 DAS

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform validation of radioanalytical calculations and reporting software. This SOP is applicable to all radioanalytical software used at Paragon. This SOP should be used in conjunction with SOP 1400 after installation or modification of any software related to analysis of radiochemical samples. In addition, the procedures described in this SOP shall be performed and documented ***monthly*** to provide ongoing verification of reporting software.

Radioanalytical software uses a combination of complex data reduction techniques and relatively simple data calculation methods to report radioactivity concentrations in samples of various media. This SOP provides methods for independent determination of results that demonstrate correct operation of the analysis software.

2.0 SUMMARY

In order to ensure proper operation of radioanalytical software, it is necessary to perform hand calculations of the results to validate the software. When data are calculated by hand and by the software in question using the same input data, like results should be obtained. This procedure provides guidelines for each of four types of instruments: gas flow proportional counter (GFPC), liquid scintillation counter (LSC), gamma spectrometer, and alpha spectrometer.

Paragon estimates total error (Total Propagated Uncertainty) according to the methods described in SOP 743. See SOP 743 for details of additional error calculations. Calculations may be found in the method-specific SOPs.

3.0 RESPONSIBILITIES

3.1 These procedures shall be performed by personnel trained and authorized by the Department Manager or designee. It is the responsibility of the primary analyst of each instrument (LSC, GFPC, Gamma spec, and alpha spec) to perform and document the monthly verification for each analysis performed in an assigned area.

3.2 It is the responsibility of the Department Manager to ensure that this verification is being performed and documented monthly.

4.0 APPARATUS

This procedure is conducted with the use of a data package containing the benchsheet, the instrument raw data output, Laboratory Information Management System (LIMS) reports, and standard traceability information.

5.0 PROCEDURE

5.1 GAS FLOW PROPORTIONAL COUNTER

5.1.1 ANALYSIS SOFTWARE; GROSS ALPHA/BETA SAMPLES

Choose a sample counted in a batch. From the raw data instrument output, record the sample counts, counting duration, and the values of b and m from the attenuation curve equation. Also record sample ID, sample mass, reported activity in pCi/L, alpha and beta efficiency, and alpha and beta background CPM from the sample's analysis report. ***Note that samples analyzed on LB4100-A and LB4100-B systems will have different values for background, b, m, and efficiency depending on the detector used.***

Calculate the alpha and beta activity in pCi/L,g as per SOP 702. Record the result. The calculated result should match the reported result within 3% (the tolerance is due to rounding of the reported data that is not rounded in the actual calculations). If there is disagreement, notify the Department Manager. Do not use the software until the problem has been resolved and this procedure has been satisfactorily completed.

The calculations shall be performed monthly and documented. If changes are made to the software or problems are detected, then manual calculation verification shall be performed as needed.

5.1.2 ANALYSIS SOFTWARE; Sr-89/90 SAMPLES

From the data reduction sheet, obtain and record sample counts, counting duration, sample mass, reported yield, reported net CPM, beta efficiency, and beta background count rate.

Perform the calculations per SOP 707, record the results. The calculated results should match the reported result within 3% (the tolerance is due to rounding of the reported data which is not rounded in the actual calculations). If there is disagreement, notify the Department Manager. Do not use the software until the problem has been resolved and this procedure has been satisfactorily completed.

The calculations shall be performed monthly and documented. If changes are made to the software or problems are detected, then manual calculation verification shall be performed as needed.

5.1.3 MINIMUM DETECTABLE CONCENTRATION (MDC) CALCULATIONS

As a matter of convention, detection limit estimates for radioanalytical procedures are determined by a mathematical formula that takes into account sample volume, chemical recovery, instrument detection efficiency and background, and sample counting duration. Refer to SOP 708 for calculations. *Note: for purposes of detection limit estimates, minimum detectable activity (MDA) and minimum detectable concentration (MDC) are the same.*

Record the calculated value and the reported value. The calculated result should match the reported result within 3% (the tolerance is due to rounding of the reported data which is not rounded in the actual calculations). If there is disagreement, notify the Department Manager and do not use the software until the problem has been resolved and this procedure has been satisfactorily completed.

The calculations shall be performed monthly and documented. If changes are made to the software or problems are detected, then manual calculation verification shall be performed as needed.

5.2 LIQUID SCINTILLATION COUNTER

5.2.1 ANALYSIS SOFTWARE

From the hardcopy report generated by the liquid scintillation counter, obtain and record the sample CPM and blank CPM.

5.2.2 REPORTING SOFTWARE

Prepare a tritium analysis report using the sample data obtained above. Calculate the final sample activity following the calculations in SOP 704. Record the result. The calculated result should match the reported result within 3% (the allowance is due to rounding corrections). If there is disagreement, notify the Department Manager. Do not use the software until the problem has been resolved and this procedure has been satisfactorily completed.

The calculations shall be performed monthly and documented. If changes are made to the software or problems are detected, then manual calculation verification shall be performed as needed.

5.3 GAMMA SPECTROMETRY SYSTEM

Calculations for gamma spec are performed by vendor-supplied proprietary software, specifically Seeker® gamma spectroscopy software. These calculations shall be verified ***annually*** following the calculations outlined in SOP 713. The manual calculation results should match the reported results within 3%. If there is disagreement, notify the Department Manager. Do not use the software until the problem has been resolved and this procedure has been satisfactorily completed.

In addition, the total propagated uncertainty calculation is performed during data reduction. This calculation shall be verified and documented monthly or following any changes. The calculation for TPU can be found in SOP 743.

5.4 ALPHA SPECTROMETRY SYSTEM

Obtain the raw data sheet and spectrum for a sample. Manually verify the chemical yield, sample activity, uncertainty, MDA, DER, and LCS radiometric recovery. Use calculations found in SOPs 714 and 743. Record the results. The calculated results should match the reported result within 3%. The tolerance is due to rounding of the coefficients listed on the report header. If there is disagreement, notify the Department Manager. Do not use the software until the problem has been resolved and this procedure has been satisfactorily completed.

The calculations shall be performed monthly and documented. If changes are made to the software or problems are detected, then manual calculation verification shall be performed as needed.

6.0 REFERENCES

6.1 David C. Kocher, "Radioactive Decay Data Tables", DOE-TIC11-26, Appendix 5, 1981.

6.2 Lloyd A. Currie, "Limits for Qualitative Detection and Quantitative Determination", Anal. Chem. 40, 586-93, March 1968.

6.3 National Council on Radiation Protection and Measurements, NCRP Report No. 58, 309, September 1984.

6.4 EPA 520/1-80-012, "Upgrading Environmental Radiation Data", Health Physics Society Committee Report HPSR-1, 6-26, August 1980.

DOCUMENT REVISION HISTORY

9/11/06: Format updated. DOCUMENT REVISION HISTORY section added. Forms attached.

Ortec Alpha Spectrometer ***Paragon Analytics***

Alpha Spectroscopy Weekly Calibrations Log

Logbook Page / No. _____ A

Pump 1 Check pressure_____ oil OK?____
Pump 2 Check pressure_____ oil OK?____

	Energy/Efficiency		*BKG*		*Final Status*	*Cleaned Det/ Chamber?*	*Adjusted Gain?*
Det	Ct 1	Ct 2	Ct 1	Ct 2			
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							

	Energy/Efficiency		*BKG*		*Final Status*	*Cleaned Detector?*	*Adjusted Gain?*
Det	Ct 1	Ct 2	Ct 1	Ct 2			
17							
18							
19							
20							
21							
22							
23							
24							
25							
26							
27							
28							
29							
30							
31							
32							

OK = count was good
R-En = recount due to energy failure
R-Ef = recount due to efficiency failure
OL = online

Initials Analyst(s)_____

Date(s) of Calibration_____

Data Entry Done (r:\inst\alphspec\maint.xls)? _____

Alpha Spectroscopy Weekly Calibrations Log *(continued)*

Form 722r0.xls (12/9/2002)

Ortec Alpha Spectrometer ***Paragon Analytics***

Logbook Page / No. _____ B

Pump 1 Check pressure_____ oil OK?____
Pump 2 Check pressure_____ oil OK?____

	Energy/Efficiency		BKG		Final	Cleaned Det/	Adjusted
Det	Ct 1	Ct 2	Ct 1	Ct 2	Status	Chamber?	Gain?
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							
43							
44							
45							
46							
47							
48							

	Energy/Efficiency		BKG		Final	Cleaned	Adjusted
Det	Ct 1	Ct 2	Ct 1	Ct 2	Status	Detector?	Gain?
49							
50							
51							
52							
53							
54							
55							
56							
57							
58							
59							
60							
61							
62							
63							
64							

OK = count was good
R-En = recount due to energy failure
R-Ef = recount due to efficiency failure
OL = online

Data Entry Done (r:\inst\alphspec\maint.xls)? _____

Initials Analyst(s)_____

Date(s) of Calibration_____

Calibrations Log Reviewed By / Date _____

Form 722r0.xls (12/9/2002)

Summary Record of Transfer - RAD Prep. Labs to Counting Room

NOTE: This is a Duplicate record for internal tracking only (exempt from review). Official transfer of prepared samples is accomplished via the applicable benchsheet. Pagination not required. **Form 724r0.xls (1/14/06; auto**

Sequence No.	Date Transferred	Test(s) / Matrix	Workorder Nos.	Batch ID	Initials	Comments
9154						
9155						
9156						
9157						
9158						
9159						
9160						
9161						
9162						
9163						
9164						
9165						
9166						
9167						
9168						
9169						
9170						
9171						
9172						
9173						
9174						
9175						
9176						
9177						
9178						
9179						

Paragon Analytics

Sample Digestion Worksheet

Paragon Sample ID	Original sample weight (g)	As Rec'd / Dry Wt (g)	Total weight of digestate (g)	% moist	Sample Matrix	Digest.* Solution Nature	digestate size taken for analysis (g)											
							Pu	U	Th	Am/Cm	Np	Fe-55	Pu-241	Sr	a/b	H-3	C-14	other

Prep Analyst _____
Prep Date _____
Balance No. _____
QASS# _____
SOP/REV _____

* Digest solution nature = The name of digestate media (e.g., 8N HNO3) **Reviewed by** _____ **Date** _____

Form 725r2.xls (10/16/2003)

Must Discard 30 Days from _____ (date printed)

Ammended 9/27/07 (Section 7.2): Hold for 24hrs (not 16) after pH adjustment (consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57) DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 711 REVISION 7

TITLE: **PREPARATION OF WATER AND SOLID SAMPLES FOR THE ANALYSIS OF POLONIUM-210 -- EML PROCEDURE Po-01**

FORMS: **302**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 9/10/06
QUALITY ASSURANCE MANAGER _____ DATE 9/8/06
LABORATORY MANAGER _____ DATE 9/10/06

HISTORY: Rev0, 3/6/93; Rev1, PCN #147, 3/1/94; Rev2, 10/6/99; Rev3, 3/27/00; Rev4, 4/26/02; Rev5, 3/28/03; Rev6, 11/29/04; Rev7, 9/11/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used to prepare solid and water samples for the analysis of ^{210}Po using EML Procedure Po-01.

2. SUMMARY

Polonium is spontaneously deposited on a nickel disk from a 1N HCl solution. Soil samples are leached with 1N HCl. As soil samples have constituents that may interfere with the Po deposition, a smaller aliquot size for soils is recommended. Waters with high organic content must be evaporated to dryness and wet-ashed with HNO_3 prior to conversion to chloride form. The deposition is specific for Polonium and, therefore, requires no other pre-concentration or separation steps. The recovery in the procedure is monitored with a ^{209}Po tracer. Both tracer and ^{210}Po are counted by alpha spectrometry.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review or precision and accuracy tests.

3.2 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating file information indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample

preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 The presence of excessive precipitate in the final source will lead to degradation of spectral quality due to self-absorption effects.

4.2 The levels of activity taken for analysis should be minimized to prevent contamination of the detection system and overwhelming the tracer. Aliquot size should be judged according to expected activities for the samples (per pre-screening data) and should generally be less than 50pCi.

4.3 The 1N HCl solution used for nickel plating makes the deposition process specific for Polonium. Weaker acid solutions allow deposition of Bismuth and other nuclides, which can be an interference in the analysis.

4.4 The use of nitric acid-preserved samples can be problematic for this method as the mixture of nitric acid with hydrochloric acid forms dilute aqua regia which will attack the disk and can lead to very low plating yields.

4.5 The presence of significant peak activity in the spectrum other than that expected is significant cause for concern. Re-preparation or appropriate sample cleanup may be indicated. Consult a senior analyst or the Radiochemistry Manager for advice in such cases.

5. APPARATUS AND MATERIALS

5.1 steam bath (settings vary with equipment and duration)

5.2 glass hooks and support assembly

5.3 nickel disks, 3/4" diameter with 3mm hole near the edge. Clean by washing in Radiacwash™, followed by DI water. Prior to use, dip disk in conc. HNO_3, followed by conc. HCl for a few seconds, then rinse with DI water. Dip using the glass hook and avoid touching the disk once dipped.

5.4 beakers, 400mL, 600mL, and 1.5L or 2L

5.5 polypropylene cups, 100mL, 250mL

5.6 Infrared (IR) Thermometer, Raynger ST #267249, or equivalent

5.7 hot/stir plates

5.8 graduated cylinders, plastic or glass, 25mL, 100mL, 1000mL

5.9 tongue depressors

5.10 planchets, 1" diameter, stainless steel, cupped

5.11 forceps

5.12 filter paper, qualitative, fluted, Whatman 41™, or equivalent,

5.13 double-sided tape

5.14 pipet, Eppendorf™ or equivalent

5.15 balance, analytical, capable of weighing to 0.0001g

5.16 metal wire, bent into a loop

5.17 pipets, transfer, disposable

5.18 stir bars

5.19 pH paper, capable of testing at pH<2

6. STANDARDS AND REAGENTS

All chemicals and reagents must be reagent grade or better. Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

6.1 Hydrochloric acid (HCl), conc. TLV = 5ppm (ceiling)

6.2 HCL, 1M: Add 83mL conc. HCL to 917mL DI water. See 6.1 for TLV.

6.3 Ascorbic acid

6.4 Nitric acid, conc. TLV = 2ppm

6.5 Amyl acetate

6.6 Thin film solution: Add 1:1 ratio of Amyl acetate and Collodion together. Mix well. Prepare fresh weekly.

6.7 ^{209}Po tracer solution, approximately 20dpm/mL

6.8 ^{210}Po standard solution, approximately 20dpm/mL

6.9 Wash bottle, containing DI water

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Although the client is responsible for conducting the sampling process, it is emphasized that water samples be collected in a manner that addresses the considerations discussed in EPA 900.0 Section Three or Chapter Nine of EPA

SW-846, as appropriate.

7.2 Although the client is responsible for conducting water sampling for compliance purposes, it is recommended that samples be **preserved at the time of collection by adding enough 1N HCl to the sample to bring it to pH 2** (15mL 1N HCl per liter of sample is usually sufficient). If water samples are collected without preservation, they should be brought to the laboratory within 5 days and then preserved and held in the original container for a minimum of ~~14~~ 24 hrs before analysis or transfer of the sample.

7.3 The container should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 PROCEDURE FOR WATERS

8.1.1 Check that the samples are preserved to pH <2 with HCl and fill out the sample condition form (Form 302).

8.1.2 Using a graduated cylinder, measure 1000mL of the sample into a labeled 1.5 or 2 L beaker. Filter suspended solids, if present, using qualitative filter paper.

8.1.3 Add 50mL conc. HCl.

8.1.4 Add ^{209}Po tracer solution with a calibrated mechanical pipet. Typical activity is 20dpm, or as directed by the primary instrument operator.

8.1.5 Evaporate on a hot plate to near dryness. Transfer to a 250mL polypropylene cup and dry completely.

8.1.6 If the sample was preserved in HNO_3, add 10mL of conc. HCl and dry completely to convert to a HCl system. If the sample was preserved with HCl, proceed directly to following Step.

8.1.7 Redissolve the residue in 100mL of 1N HCl. Heat in a steam bath to aid in dissolution.

8.1.8 Add about 100mg ascorbic acid (estimate on a tongue depressor tip). Swirl to dissolve the ascorbic acid.

8.1.9 Proceed to Section 8.3, nickel deposition.

8.2 PROCEDURE FOR SOILS AND SOLIDS

8.2.1 Weigh out 0.5g of sample in a 250mL polypropylene cup and add appropriate tracers and spiking solution.

8.2.2 Add 25mL of 1N HCl to each sample and place samples in the steam bath using a 100mL polypropylene cup as a lid. Heat the samples for a minimum of four hours, preferably overnight.

8.2.3 After leaching, take the samples from the steam bath and rinse the lids with 1N HCl and allow them to cool.

8.2.4 Using Whatman 41™ filter paper or equivalent, filter samples into a clean, labeled polypropylene cup. Rinse the cup and filter paper with 1N HCl. Bring to 100mL with 1N HCl.

8.2.5 Add ~100mg of ascorbic acid (estimate on tip of tongue depressor), then proceed to Section 8.3, nickel deposition.

8.3 NICKEL DEPOSITION

8.3.1 Clean nickel disk by washing in Radiacwash™. Rinse with DI water. Prior to use, dip disk in conc. HNO_3 followed by conc. HCl for a few seconds, then rinse with DI water. Dip using the glass hook and avoid touching the disk once dipped.

8.3.2 Equilibrate a water bath to ~55°C by placing DI water in a 600mL beaker and placing the beaker on a stirring hot plate to heat.

8.3.3 Put a small, clean (see SOP 720) stir-bar in each sample cup. Place the sample cups in the prepared water bath and allow 10-20 minutes for the temperature to re-stabilize.

8.3.4 Suspend a cleaned nickel disk in each solution using a glass hook.

8.3.5 Note the decay date and time on the benchsheet.

8.3.6 Maintain the water bath at ~55° C and mechanically stir for 4 hours.

8.3.7 After 4 hours, remove the disks and rinse with DI water. Allow disks to air dry. Be careful to hang the disks in the same order as the beakers to avoid confusing their identifications.

8.3.8 Label the back of a 1" stainless steel planchet for each disk with ^{210}Po, the sample ID and batch number. Apply a small piece of double-sided tape to the center of the front of each planchet.

8.3.9 Using forceps, remove each disk from its glass hook and center the planchet on the tape.

8.3.10 Add approximately 250mL of DI water to a 400mL beaker.

8.3.11 Place a metal wire loop into the DI water, making sure the entire loop is covered by the DI water. Bend the arm of the wire loop over the beaker to hold the loop in place.

8.3.12 Place 1 drop of the Thin film solution into the beaker. Allow 30 seconds for the thin film to cure, then remove and allow to dry.

8.3.13 Once dry, place thin film over the planchet.

8.3.14 Repeat Steps 8.3.10 through 8.3.13 above until all samples have thin films placed over them.

8.3.15 Arrange the planchets in a petri dish and label the petri dish with the analyte, sample ID's and batch number. Submit the prepared samples and the updated benchsheet to the Counting Lab. Mark the status sheet "C" for prep complete. The Counting Lab will analyze and ultimately dispose of the planchet and disk in the manner described in SOP 714.

9. CALCULATIONS

9.1 TPU FACTORS. As defined in SOP 743, the following 1 σ preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty:

9.1.1 Water samples require a preparation uncertainty factor of 0.0615. This is based on one gross aliquoting (sample homogeneity), one volumetric measurement, one tracer addition, and one quantitative transfer. See the following equation:

$$0.0615 = \sqrt{0.05^2 + 0.006^2 + 0.025^2 + 0.025^2}$$

9.1.2 Solid samples require a preparation uncertainty factor of 0.0613. This is based on one gross aliquoting (sample homogeneity), one mass measurement, one tracer addition, and one quantitative transfer. See the following equation:

$$0.0613 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2}$$

9.1.3 In practice, these values are substantially equivalent. For simplification in reporting, the first factor of 0.0615 may be used for both matrices.

10. QUALITY ASSURANCE

10.1 A blank and laboratory control sample (blank spike, LCS) is run for each batch. Both are run at a 5% minimum frequency. Each is taken through the entire procedure as specified for the matrix.

10.2 The LCS (blank spike) is spiked with 5-10dpm of ^{210}Po standard solution using a calibrated pipet.

10.3 DI water is used as the matrix for all blanks and blank spikes. Use the same volume as specified for the sample matrix.

10.4 Sample duplicates are run at a 10% minimum frequency. If enough sample is not provided to do duplicates, an LCS duplicate is prepped and analyzed.

11. DEVIATIONS FROM METHOD

This is a Paragon proprietary method. Therefore, there are no deviations from promulgated methods.

12. SAFETY HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.2 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

12.1.3 Gloves, safety glasses and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals. Use care when handling strong acids (e.g. HNO_3, HCl, etc.).

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.3 below.

12.1.5 All non-original containers used to hold reagents (e.g. wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.1.6 Care should be taken when diluting acids. Unless the method explicitly directs you to do otherwise, **always add acids to water**, not water to acids.

12.2 WASTE DISPOSAL

12.2.1 The analytical process liquid effluent has been determined to not be hazardous in other than corrosivity. This material may be discharged into the Paragon wastewater treatment facility. Here the solution will be neutralized prior to discharge and the activity will be monitored to ensure compliance with Colorado Rules and Regulations pertaining to

Radiation Control Part 4 regarding discharges to sanitary discharges to sanitary sewers.

12.2.2 Solids and filtered residues should be air-dried in a beaker in the fume hood. Solid radchem waste is to be placed in the Radioactive waste/Contact waste bucket in the Actinides Lab.

13. REFERENCES

13.1 Environmental Measurements Lab (EML) Procedure Po-01, "Polonium in Water and Urine", rev. 2/92, Vol. 1, 27th Edition.

13.2 EPA Eastern Environmental Radiation Facility (EERF) “Method Po-01”, Radiochemistry Procedures Manual, EPA 520/5-84-006, December 1987.

13.3 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.4 Paragon SOP 743 “Estimating Total Propagated Uncertainties for Radiometric Analyses”.

DOCUMENT REVISION HISTORY

9/11/06: LIMS program specification language augmented. Updated responsibilities. Clerical changes made. DOCUMENT REVISION HISTORY added. Form attached.

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 712 REVISION 14

TITLE: **DETERMINATION OF TOTAL ALPHA-EMITTING RADIUM ISOTOPES IN DRINKING WATER -- EPA METHOD 903.0 AND SW9315**

FORMS: **302, 313, 631**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/4/07

LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 12/09/92; Rev1, PCN # 160, 3/0/9/94; Rev2, PCN # 233, 6/02/94; Rev3, PCN # 398, 2/25/95; Rev4, 3/15/96; Rev5, 7/17/97; Rev6, 2/14/00; Rev7, 10/12/00; Rev8, 3/01/01; Rev9, 9/24/01; Rev10, 3/02/02; Rev11, 12/04/02; Rev12, 9/22/03; Rev13, 2/27/06; Rev14, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- EPA Method 903.0 and SW-846 Method 9315 -- are applicable to the measurement of total soluble alpha emitting radioisotopes of radium -- namely radium-223, radium-224 and radium-226 -- in drinking water and other environmental waters. It is primarily a screening method for radium-226.

2. SUMMARY

The radium in the drinking water sample is collected by co-precipitation with barium and lead sulfate, and purified by co-precipitation from EDTA solution. Citric acid is added to the drinking water sample to ensure that complete interchange occurs before the first precipitation step. The final $BaSO_4$ precipitate which includes radium-226, radium-224 and radium-223, is alpha counted, per SOP 724, to determine the total disintegration rate of the radium isotopes. The radiometric results are corrected for chemical yield on a sample-by-sample basis using the results of inductively coupled plasma atomic emission spectrometry (ICP-AES) determination of Ba recovery.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 This test will show high bias for radium-226 in the sample results if other alpha emitting isotopes of radium are present in the sample (especially Ra-224 and Ra-223). Reanalysis of the sample following a decay period equal to five half lives of the interfering isotope will provide a more accurate measurement of the Radium-226 concentration of the sample. In cases where radium-224 activity is likely, a decay period of 18 days is appropriate. Where radium-223 is suspected, 57 days is appropriate.

4.2 The presence in the sample matrix of significant natural barium or large quantities of sediment and particulates in the sample may cause interference by elevating the planchet residual mass. The mass on the planchet must be within the efficiency calibration range. Otherwise corrective action, usually re-preparation with a reduced aliquot, must be taken. The matrix interference and corrective actions taken should be clearly documented in a QASS (Form 302), approved by the Department Manger, and disclosed in the case narrative.

4.3 Yield corrections are calculated by ICP measurement of the pre- and post-separation concentrations of barium in the sample. If high barium concentrations are known to be present in the sample matrix, reduced aliquots may be taken without addition of barium to the sample.

4.4 In certain cases it may be advantageous to generate chemical yield data from samples spiked with Ba-133 tracer. The concentration of the tracer is determined by gamma spectroscopy and used in lieu of the chemical yield determined by ICP.

4.5 The presence of sediment or particulate matter in the sample is not accounted for by this method. Failure to remove insoluble particulates from the sample could cause a high bias in activity results, due to alpha emitting radionuclides. Samples

containing significant amounts of sediment will be filtered prior to analysis.

4.6 In cases where "dissolved" analysis of radium is requested, the sample must be filtered in the field and immediately preserved by addition of nitric acid to pH < 2, prior to shipment.

Where the samples have not been filtered and preserved in the field, a non-conformance report (NCR, Form 313) is generated by the analyst and the client is immediately notified. With the client's approval, sediments are removed by filtration, and the sample is subsequently preserved by addition of nitric acid to pH < 2. In this case, the resulting potential low bias in the final analytical results are noted on the NCR and in the case narrative.

4.7 Where drinking water protocols are required by the client, samples will not be filtered prior to analysis. Samples will be run as received through Step 8.1.14 and filtered into a clean centrifuge tube. Proceed directly to Steps 8.1.16 and 8.1.17, then repeat Step 8.1.14 and continue with the procedure.

4.8 Where filtration has been performed, a note must be made on the benchsheet and a narrative comment must inform the client that the sample was filtered and that the final result does not include undissolved particulates that may have been present in the sample.

5. APPARATUS AND MATERIALS

5.1 Counting planchets, stainless steel, 2" diameter

NOTE: Although it is common practice to clean planchets used in the laboratory, cleaning the planchets is not conducive to obtaining an even distribution utilizing this method. Therefore, the planchets used for this method only will be used as received from the manufacturer. Method blank results for each batch will be used to monitor the efficacy of this practice.

5.2 Stir bars, magnetic

5.3 Hot plate, electric, stirring

5.4 Aspiration apparatus

5.5 centrifuge tubes, polypropylene, 50mL

5.6 Analytical balance

5.7 Graduated cylinder, 1L

5.8 Beakers, 1500 or 2000mL

5.9 Hot water bath, 90-100 °C

5.10 Vortex mixer

5.11 Watch glasses

5.12 Cups, Polypropylene, 250mL and 100mL

5.13 Permanently labeled glass beakers, 100mL, or equivalent

5.14 Filter paper, Whatman® #42 (90 mm), or similar

5.15 Parafilm™

5.16 Test tubes, 15mL, disposable, with caps

5.17 Spatulas, plastic

6. REAGENTS

NOTE: TLV and other hazard information may also be given here. As stated in section 12.1.3 of this SOP, any chemical with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Glacial Acetic Acid (CH_3COOH_2), 17.4N, conc.: 99.8 percent, ACS reagent grade. TLV = 10ppm (TWA). Irritant.

6.2 Ammonium Sulfate, 200mg/mL: Dissolve 200g reagent grade $(NH_4)_2SO_4$ in a minimum of water and dilute to 1L.

6.3 Barium carrier, 16mg/mL (approximately 28mg/mL $BaSO_4$ yield, standardized)

6.3.1 Place a 1000mL Class A volumetric flask on a stir plate, add a stir bar and ~500mL of DI water.

6.3.2 Add 28.46g $BaCl_2 \cdot 2H_2O$ and stir until completely dissolved.

6.3.3 Then add 5mL 16N HNO_3.

6.3.4 Remove stir bar, rinsing with DI water, and dilute to 1000mL with DI water.

6.3.5 Transfer to a clean, labeled 1L poly container.

6.3.6 Document the preparation of this carrier in the Reagent Prep Logbook.

6.3.7 Standardization of Ba carrier by ICP analysis

Prepare in triplicate a 1000-fold dilution of the Ba carrier using the ICP solution described in Section 6.14 below. Submit to the metals lab for analysis. Average the results and record in the Reagent Prep Logbook.

TLV = 0.5 mg Ba/m^3 = 0.06ppm (TWA). Irritant.

6.4 Citric acid, 1M: Dissolve 210g reagent grade $C_6H_8O_7 \cdot H_2O$ in water and dilute to 1L.

6.5 Deionized (DI) water, ASTM Type II or better.

6.6 EDTA reagent, basic, 0.25M: Dissolve 20g reagent grade NaOH in 750mL water, heat and slowly add 93g disodium ethylenedinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$). Heat and stir until dissolved.

6.7 Hydrofluoric acid (HF), 48.0-51.0 %, conc.
TLV = 3ppm (ceiling). Irritant, burns, bone, teeth, fluorosis.

6.8 Lead carrier, 15mg/mL: Dissolve 24g reagent grade $Pb(NO_3)_2$ in water. Add 5mL 16N HNO_3 and dilute to 1L with water.
TLV = 0.05mg/m^3 (= 0.004ppm) as elemental Pb.

6.9 Sodium hydroxide, 6N: Dissolve 240g reagent grade NaOH in 800mL water and dilute to 1L.
TLV of NaOH = 2 mg/m^3 (= 1.22 ppm) (ceiling). Irritant.

6.10 Sulfuric acid, 18N: Cautiously mix one volume reagent grade 36N H_2SO_4 (conc.) with one volume of water.
TLV = 1 mg/m^3 (= 0.25ppm) (TWA). Irritant. Note- A face shield and rubber apron must be worn while handling concentrated sulfuric acid.

6.11 Sulfuric acid, 0.1N: Mix one volume 18N H_2SO_4 with 179 volumes of water.
TLV = 1 mg/m^3 (= 0.25ppm) (TWA). Irritant.

6.12 Non-Ionic Surfactant. Triton X-100® or equivalent.

6.13 Diluted surfactant solution: Dilute 1 drop of non-ionic surfactant in 100mL DI water. Mix thoroughly.

6.14 ICP Diluting Solution, 5% HNO_3 / 2.5% HCl: Carefully add 50mL of concentrated HNO_3 and 25mL of concentrated HCl to 925 mL of DI water. Mix thoroughly.

TLV = 2ppm for conc. HNO_3 (TWA), and 5ppm for conc. HCl (ceiling). Both irritant, corrosive.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 LIQUID SAMPLES

7.1.1 A representative sample must be collected from a free-flowing source of water and sufficient volume be collected so that adequate aliquots may be taken in order to meet the required Minimum Detectable Activity (MDA).

7.1.2 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to effect a pH of 2 (15mL 1N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.1.3 The sample should be collected in a plastic container.

7.1.4 A regulatory holding time has not been specified by the EPA.

7.2 SOLID SAMPLES

Preservation is not required. A representative sample of 25-50 grams should be submitted for analysis.

8. PROCEDURE

8.1 PREPARATION OF AQUEOUS SAMPLES

NOTE: See Sections 4.2, 4.5, 4.6, and 4.8 regarding dissolved and suspended solids prior to aliquoting samples.

8.1.1 Verify and record (on Form 631) the pH of the sample according to SOP 733.

8.1.2 Using a graduated cylinder, aliquot the sample into a labeled 1.5L or 2L beaker. A sample aliquot of 1L is typical for this method, but may need to be reduced due to matrix interference. All samples should be brought to a final volume of 1L. Add a stir bar to each beaker and place on a stirring hot plate.

8.1.3 Prepare quality control (QC) samples according to Section 10.

8.1.4 How to take initial ICP aliquot:

8.1.4.1 Prior to adding any reagents, spikes, or carriers to the sample, use a calibrated pipette to remove 1mL of sample and place into a clean test tube filled with 9mL of ICP diluting solution and labeled with the sample ID and “i”, to indicate the initial ICP aliquot. Cover with a test tube cap and invert tube several times to mix thoroughly. Set aside until final ICP aliquot has been taken.

8.1.4.2 A “reference carrier” (RC) must be prepared by adding 1mL Ba carrier to 1L of DI water. Mix thoroughly, remove 1mL of solution and dilute to 10mL as stated above for samples. Submit with samples for ICP analysis to provide a reference

concentration for the yield calculations.

8.1.5 To each sample add 1 to 2 drops non-ionic surfactant, 5mL 1M citric acid, 1mL lead carrier, 1.0 mL barium carrier, and spiking solution per Section 10. Use a Class A pipette or calibrated micropipet to deliver the Barium carrier and spiking solution.

8.1.6 Stir and heat to boiling.

8.1.7 Slowly add 25mL 18N H_2SO_4.

8.1.8 Boil for ten minutes. Remove from heat and retrieve stir bar, rinsing with 0.1N H_2SO_4.

8.1.9 Cover and let stand overnight.

8.1.10 Aspirate the supernatant. The supernatant can be disposed of down the laboratory sink. Refer to Section 12.2.1 of this SOP. Transfer the precipitate to a centrifuge tube, rinsing the beaker with 0.1N H_2SO_4.

8.1.11 Centrifuge at 3500 RPM for 12 - 15 minutes. Discard the supernatant into the laboratory sink and flush with plenty of cold tap water.

8.1.12 Wash the precipitate with 15mL 0.1N H_2SO_4. Centrifuge as above and discard wash into the laboratory sink.

8.1.13 Dissolve the precipitate by adding 25mL basic EDTA reagent. Heat in a hot water bath. Additional basic EDTA can be added in 5mL increments until the precipitate dissolves completely. If necessary, add 6N NaOH dropwise until dissolution is complete.

8.1.14 Once the samples are completely dissolved, remove the tubes from the steam bath and allow the samples to cool.

8.1.15 How to take final ICP aliquot:

8.1.15.1 Vortex the sample to mix thoroughly. Using a calibrated pipette, aliquot 0.1mL of sample into a clean, labeled test tube containing 9.9 or 10mL of DI water (record the volume of water used). Cover with Parafilm™, and invert several times to mix completely. With a calibrated pipette, aliquot 1.0mL of the diluted sample into another clean test tube labeled with the sample ID and "f" and containing 9.0mL of ICP diluting solution. Cover with a test tube cap and mix well. Submit the initial and final test tubes to the metals lab with proper bench sheets for analysis.

8.1.15.2 Upon the return of ICP sample fractions to the radiochemistry lab, and after satisfactory review of the chemical yield data including LIMS validation of the benchsheet, the ICP fractions may be discharged into the PA waste water treatment facility (i.e., down the laboratory sink with plenty of cold tap water). The test tubes may be soaked in a Radiacwash™ solution, rinsed with tap water and discarded into the sanitary trash. The tubes containing the intermediate, DI water diluted, sample may be disposed of in the same manner.

8.1.16 To the remaining sample in the centrifuge tube, add 1 mL ammonium sulfate solution per 50mL of EDTA solution and mix thoroughly by vortexing. Add glacial acetic acid dropwise until precipitation begins. Then add an additional 2mL of glacial acetic acid. **Note the time and date of this precipitation on the benchsheet.** Mix with a vortex mixer or equivalent. Heat in the hot water bath ten minutes.

NOTE: The pH of the precipitation (4-4.5) is absolutely crucial to the success of the separation between lead and barium/ radium. Over-acidification of the solution will cause lead to coprecipitate with barium/radium and may lead to a high planchet mass.

8.1.17 Centrifuge and discard the supernatant into the Pb/Ba waste container.

8.1.18 Wash the precipitate with 15mL water and centrifuge. Discard the wash into the laboratory sink, followed by plenty of cold tap water. Refer to Section 12.2.2 of this SOP.

8.1.19 Label and weigh stainless steel flat-bottomed planchets. Record the weight on the benchsheet. Place planchets on a hot plate.

8.1.20 To transfer the sample to the planchet, add ~4mL of DI water to the centrifuge tubes and vortex until all of the precipitate is suspended. Working quickly to avoid precipitate settling, remove cap, rinse once with DI water, and pour into the planchet. Rinse the centrifuge tube with DI water and add to the planchet. Sample should be evenly distributed on the planchet.

8.1.21 Used centrifuge tubes may be soaked in Radiacwash, rinsed in tap water, then discarded in the sanitary trash.

8.1.22 Dry on a hot plate set at 2 or 3.

8.1.23 It is essential that the (Ba, Ra)SO_4 be evenly distributed on the planchet. Sometimes the sample will separate when it is near dryness.

To correct this, approximately 1mL of diluted surfactant solution is applied to the planchet using a transfer pipet. Carefully swirl the planchet to distribute the precipitate. Repeat as necessary, adding as little of the surfactant solution as possible, as it may add mass to the planchet.

8.1.24 Cool to ambient temperature.

8.1.25 Weigh to the nearest ± 0.1mg on an analytical balance. Record weight on the benchsheet for the calculation of the total weight of the solids on the planchet in mg.

8.1.26 Transfer the planchets to the desiccator in the instrument lab, with the appropriate benchsheets. The planchets will be analyzed and ultimately disposed of as described in SOP 724.

8.2 PREPARATION OF SOLID SAMPLES

8.2.1 Verify and record (on Form 631) the condition of the sample.

8.2.2 Weigh 1 gram of dried, pulverized soil into a permanently labeled 100 mL glass beaker. Typical aliquot size is 1.0 g but may be adjusted due to MDA or matrix interference considerations. Record the sample weight and beaker number on the benchsheet.

8.2.3 Prepare QC samples according to Section 10.

8.2.4 To each sample add 1.0mL barium carrier. Add the appropriate spiking solution amount to any samples that require it, per Section 10. Use a Class A pipette or calibrated micropipet to deliver the barium carrier.

A “reference carrier” must be prepared by adding 1.0 mL Ba carrier to 1L of DI water. A 1mL aliquot is removed from the RC for ICP analysis, as stated in Section 8.1.4.2.

8.2.5 Dry the uncovered beakers on a hotplate set at 2 (samples must be completely dry prior to muffling). Cover the beakers with a watch glass and muffle at 600°C for at least 4 hours.

8.2.6 Transfer the sample to a 250mL polypropylene cup, using at least 20mL conc. HNO_3 to rinse the beaker. Scraping with a plastic spatula may be necessary to remove all of the soil from the beaker.

8.2.7 Add 20mL HF, cover with a 100mL polypropylene cup, and heat for 4 hours on a steam bath.

8.2.8 Remove the 100mL cup and evaporate to dryness. The 100mL cups

may be rinsed off with tap water and discarded into the sanitary trash.

8.2.9 Add 10mL 8N HNO_3 to the samples while they are on the steam bath to facilitate the dissolution.

8.2.10 Transfer the solution to a 1L graduated cylinder, rinsing the polypropylene cup with DI water.

8.2.11 Bring the sample to a volume of 1L with DI water.

8.2.12 Transfer the sample to a labeled 1.5 or 2L beaker, add a stir bar, place on a stirring hotplate, and proceed to Step 8.1.4, without adding barium carrier in Step 8.1.5.

8.3 PREPARATION AND ANALYSIS OF CALIBRATION STANDARDS

8.3.1 Preparation of Efficiency Calibration Standards

8.3.1.1 Spike five 1 liter DI water samples with approximately 1 mL Ba carrier and 2,000 to 5,000 dpm NIST-traceable Ra 226 standard per sample. Follow the same procedure for the preparation of aqueous samples (see Section 8.1).

8.3.1.2 Ingrowth-corrected efficiency calibrations for Total Alpha-Emitting Radium isotopes are performed per SOP 724, with the modifications described below.

8.3.1.3 Ingrowth-corrected efficiency planchets should be relinquished to the instrument lab as soon as possible after separation since the first count of the planchets will be used to extrapolate the base of the efficiency curve as stated in Section 8.3.1.4.2.

8.3.1.4 Newly prepared calibration planchets may be counted repeatedly to obtain total efficiency determinations at various stages of ingrowth.

8.3.1.4.1 Assume that the total efficiency has two distinct components: 1) the base Ra-226 efficiency, that is always used at its full value, and 2) the aggregate efficiency of the three ingrown alpha emitting daughter products, which is used in proportion to the degree of ingrowth.

8.3.1.4.2 By adjusting the estimated base efficiency for Ra-226, the residual efficiency for each calibration count is calculated as the arithmetic difference between the observed total efficiency

and the estimated base efficiency. Theoretically, if the estimated base efficiency is correct, the residual (progeny) efficiency will be the same for all stages of ingrowth. In practice, enter the raw count data into a spreadsheet and allow the Excel "Solver" utility to set the base efficiency such that the variance in the individual residual efficiencies over the ingrowth period is minimized.

8.3.1.4.3 The calculated total efficiency is determined as the base Ra-226 efficiency plus the Ra progeny efficiency, ingrowth corrected. Per Paragon's Laboratory Quality Assurance Plan (LQAP), the calculated total efficiency values are acceptable if they are within 10% of the actual efficiency values observed during the calibration counts.

8.3.2 Preparation of Mass Attenuation Calibration Standards

8.3.2.1 Supply the instrument lab with a series of planchets containing a range of $BaSO_4$ mass from ~10 mg to ~125 mg, including a duplicate for each specified mass. To accomplish this, prepare 14 samples using DI water and spike with approximately 2,000 to 5,000 dpm of Ra-226 standard per sample. Add the proper amount of Ba carrier to each sample to obtain the desired mass on the planchet. The target masses are: 10 mg, 20 mg, 40 mg, 60 mg, 80 mg, 100 mg, and 125 mg. Proceed with the standard aqueous sample preparation method (Section 8.1). Submit planchets to the instrument lab immediately upon completion.

NOTE: Prior to preparing calibration standards, be sure to coordinate with the instrument lab to ensure that detector or time issues can be resolved.

8.3.2.2 Mass attenuation calibrations for Total Alpha-Emitting Radium isotopes are performed using the calibration planchets, prepared as described above, with final masses of barium sulfate ranging from approximately 10mg to 125mg. Every planchet is counted in every detector and the data are composited to create a single yield corrected mass attenuation correction curve.

8.3.2.3 The data is fitted in the traditional method, with the equation taking the form bm^x, where x is the residual mass of the

sample planchet, in mg. This equation would normally provide a mass correction to a zero-mass efficiency calibration. Total radium efficiency calibrations, however, are performed with planchets that have approximately 30mg $BaSO_4$ residual mass. Consequently, the final mass attenuation correction will take the form bm^{x-x°, where x° is the average residual mass of the efficiency calibration planchets.

9. CALCULATIONS

9.1 Calculate the actual volume, V_A, of sample analyzed for samples (accounting for volumes of sample removed) as follows:

$$V_A = V * \frac{V_i - icp_i}{V_i} * \frac{V_f - icp_f}{V_f}$$

where:

V = sample aliquot (L, g)

V_i = sample final dilution volume (mL)

icp_i = initial aliquot taken for ICP (mL)

V_f = sample volume in EDTA (mL)

icp_f = final aliquot taken for ICP (mL)

9.2 Calculate the barium chemical recovery for aqueous samples, Y, as a percentage, as follows:

$$Y_i = V_i * ICP_i * DF$$

$$Y_f = V_f * ICP_f * DF$$

$$Y_{RC} = V_{RC} * ICP_{RC} * DF$$

$$Y = \frac{Y_f}{Y_i + Y_{RC}} * 100\%$$

where:

Y_i = barium recovery from initial ICP aliquot (µg)

ICP_i = initial barium concentration measured by ICP (µg/mL)

DF = dilution factor

Y_f = barium recovery from final ICP aliquot (µg)

ICP_f = final barium concentration measured by ICP (µg/mL)

Y_{RC} = barium recovery from RC aliquot (µg)

V_{RC} = RC final volume (mL)

ICP_{RC} = RC barium concentration measured by ICP (µg/mL)

NOTE: The barium chemical recovery calculations for solid samples are the same as those for aqueous samples, except that Y_i is compared to Y_{RC} to determine which to use in calculating the barium yield, since barium carrier was added prior to taking the initial ICP aliquot. If $Y_i > Y_{RC}$, Y_i is used in the calculation in place of $(Y_i + Y_{RC})$. If $Y_i < Y_{RC}$, Y_{RC} is used in the calculation in place of $(Y_i + Y_{RC})$ and a "low bias" flag is noted on the benchsheet.

9.3 TPU FACTORS

As defined in SOP 708, the following one-sigma (1σ) preparation uncertainty factors should be applied during the final reporting stage of analysis, as a component of the Total Propagated Uncertainty (TPU):

9.3.1 Aqueous Samples require a (1σ) preparation uncertainty factor of 0.107. This is based on one gross aliquot, one volumetric measurement, one ICP determination, one spike/carrier addition, two quantitative transfers, one pipetting and two reagent additions:

$$0.107 = \sqrt{0.05^2 + 0.006^2 + 0.083^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.004^2 + 0.006^2 + 0.006^2}$$

9.3.2 Solid Samples require a (1σ) preparation uncertainty factor of 0.112. This is based on one gross aliquot, one mass measurement, one spike/carrier addition, one volumetric measurement, one ICP determination, one pipetting and two reagent additions, and four quantitative transfers.

$$0.112 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.006^2 + 0.083^2 + 0.004^2 + 0.006^2 + 0.006^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2}$$

In practice, these two preparation uncertainty factors are substantially equivalent. To simplify the data reporting procedure, the greater of the two (0.112) may be used for both matrices.

10. QUALITY CONTROL

Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.1 A blank, prepared with one liter of DI water, acidified to a pH of less than 2 with concentrated nitric acid, for aqueous samples, and a Whatman™ filter paper for solid samples, must be analyzed with each batch of 20 or fewer field samples (i.e.,

at a five percent frequency).

10.2 One blank spike (LCS), prepared with one liter of DI water, acidified to a pH of less than 2 with concentrated nitric acid, for aqueous samples, and a Whatman™ filter paper for solid samples, must be analyzed with each batch of 20 or fewer field samples (i.e., at a 5 percent frequency). The spiking level for LCSs should be at least 4-10 times the requested MDA, or 100 dpm, whichever is larger. The source used to spike the LCS should be a second independent source from the source used for calibration (*required* for DOD samples per LIMS program specification).

10.3 Duplicate sample analyses will be performed at a minimum frequency of ten percent. If there is insufficient sample volume for this frequency of duplicates, LCS duplicates may serve as a measure of batch reproducibility.

11. DEVIATIONS FROM METHOD

11.1 This SOP meets the requirements of and is substantively equivalent to EPA Method 903.0. In addition to describing a procedure for aqueous samples, this SOP describes a procedure for determining total alpha emitting radium in soil, which the laboratory employs at a client's request. Also, this SOP provides procedure for determining the chemical yield by ICP as an addition to EPA Method 903.0. This measurement increases the accuracy of the method.

11.2 In order to completely dissolve the precipitate, 25mL of basic EDTA reagent is added rather than 15 mL stated in EPA Method 903.0 (see Section 8.1.13 of this SOP).

11.3 Only 1.0 mL of barium carrier, instead of 2.0mL, is added to aqueous samples. The lesser amount of carrier facilitates dissolution of the precipitate in EDTA. Since Ba yield is determined by ICP, this amount is more than sufficient for (Ba, Ra)SO_4 precipitation and Ba chemical recovery measurement.

11.4 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ± 20%, irrespective of the lab's internally derived acceptance criteria.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

12.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals. A face shield and a rubber apron are required when handling

concentrated sulfuric acid.

12.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

12.1.4 Any non original containers be used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

12.2 WASTE DISPOSAL

12.2.1 The total radium process effluent has been determined to not be hazardous except by corrosivity. This material may be discharged into the laboratory wastewater treatment facility.

12.2.2 The total radium analytical process effluent has been determined to not be hazardous in other than corrosivity, except the Pb containing supernatant. This supernatant must be segregated into the Pb waste container supplied by waste management staff.

12.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

13. REFERENCES

13.1 Alpha-Emitting Radium Isotopes in Drinking Water, Method 903.0, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032.

13.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.3 SW846, 3rd edition, Method 9315, Alpha-Emitting Radium Isotopes, Revision 0, September 1986.

DOCUMENT REVISION HISTORY

8/31/07: Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Section 7.1. Removed activity calculations from Section 9 and referenced SOP 708 instead. Added comment Section 10 that acceptance limits for quality control parameters may vary per client specifications, consult applicable LIMS program specification. Added use of independent second source for LCS spiking (Section 10.2). Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Paragon Analytics

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 713 REVISION 10

TITLE: ANALYSIS OF GAMMA EMITTING RADIONUCLIDES BY GAMMA SPECTROSCOPY -- METHOD EPA 901.1

FORMS: 754 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER Renee Kellogg DATE 7/21/08

QUALITY ASSURANCE MANAGER Deb Schenk DATE 7/20/08

LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: Rev0, 6/1/92; Rev1, 7/27/93; Rev2, 10/15/93; Rev3, 4/26/96; Rev4, 5/16/96; Rev5, 3/20/00; Rev6, 6/15/01; Rev7, 8/24/02; Rev8, 4/7/03; Rev9, 4/10/06; Rev10, 7/20/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform gamma emissions analysis of samples of various media using high purity germanium (HPGe) high-resolution intrinsic gamma spectrometry. This procedure is applicable to all gamma spectrometry analyses performed at Paragon. The procedures outlined in this SOP are based on EPA Method 901.1 and DOE/EML Procedure 4.5.2.3.

2. SUMMARY

Gamma emissions from radionuclides are detected by a semiconductor germanium crystal, which provides a small electronic pulse for each gamma interaction where the pulse height is proportional to the gamma incident energy. This electronic data is converted to digital data by an analog to digital converter (ADC) and stored in a multichannel buffer (MCB). The data collected by the MCB is subsequently interpreted by a complex software program, generating results in units of radioactivity per unit sample volume. The gamma spectroscopy analysis software program that Paragon uses is Seeker®, Version 2.2, a product of Vertechs Software Solution, Inc.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of a proficiency test sample.

3.2 Upon receipt of a new or repaired detector, it is the responsibility of the technician to follow the steps outlined in Appendix D, 'General Gamma Detector Operations', prior to data acquisition.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Manager or designee. Initialing and dating the processed data indicates that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

The physical shape of the source and its proximity to the detector is critical to the efficiency calibration. These factors define the "counting geometry". The calibration geometry and the sample geometry must match within ±0.5cm of the line on the sample container.

5. APPARATUS AND MATERIALS

This procedure is conducted with the use of installed gamma detection and analysis equipment consisting of multiple intrinsic germanium gamma spectrometers mounted in lead shields for the reduction of ambient background radiation, a personal computer analysis system with multichannel analyzer interfaces, three NIM-bin based multichannel buffers, gamma analysis software, and associated nuclear electronics and cabling.

6. REAGENTS

No reagents are used by this procedure. The operator should be aware, however, that water samples are preserved to pH <2 with Nitric Acid (HNO_3).

7. PROCEDURE

7.1 OPERATING CONDITIONS

The gamma spectrometry systems shall be operated with detector bias as specified by the detector manufacturer and amplifier and MCB settings as required to obtain a nominal 0.5keV/channel energy calibration across a range of approximately 40 to 2000keV. The operating conditions shall be verified daily by performance of the daily quality control checks (described in Section 8 below).

7.2 SPECTRUM ACQUISITION

7.2.1 The detector must be calibrated for the geometry of the sample to be analyzed. Efficiency calibration procedures are defined in Section 8 below. A list of current geometries, calibration date and the dates the calibrations expire, as well as standards used for calibration is posted in the instrument lab. This list is maintained by instrument lab personnel

and is exempt from 'Operator Aid' policies, as it is an integral part of gamma operations and is updated on an on-going basis.

Samples shall be placed directly on the detector, inside the lead shield, and in a manner that is level and centered over the detector, unless noted otherwise on a Quality Assurance Summary Sheet (QASS) or other supporting documentation.

7.2.2 After samples have been loaded on the detectors, select the desired detector in the Spectral Display Control menu. Next, select the 'TOOLS' icon, which will then prompt for the ID and the desired live time or count time.

Enter the sample ID as it appears on the sample benchsheet, followed by a space, and then the batch ID (e.g., 0011222-3 GSyymmdd-n). After the ID has been entered, select the 'ID SET' icon to save the sample ID.

Enter the desired count time in seconds in the box labeled 'LIVE TIME' and then select the 'PRE SET' icon to save the count time. Sample count times depend on the sample volume, geometry, and the client's required minimum detectable concentration (MDC). An outline of the geometries and their respective matrix and/or volume can be found in Appendix C of this SOP. LCS samples are typically counted for 1800 seconds (30 minutes) and blank samples will be counted for as long as the longest sample count time.

7.2.3 After the sample ID and count time have been entered and saved, clear the previous spectrum by selecting the 'ERASE' icon.

7.2.4 Begin spectrum acquisition by selecting the 'GO' icon and exit the 'TOOLS' window by selecting 'DONE'.

7.2.5 Enter all samples that are analyzed in the gamma spectroscopy logbook (Form 754). Use the current page with the date that the sample is counted. *Ensure that the detectors being used have passed the Daily QC checks (see Section 8 below).* Necessary information recorded in the gamma spectroscopy logbook includes:

- Paragon sample ID
- detector number
- geometry, including sample orientation and the use of a positioning (puck), if appropriate
- duration of the count
- count start time

- operator's initials
- spectrum file name
- position verification check

7.3 SPECTRUM ANALYSIS

Upon completion of the sample count, the data must be transferred to the workspace and analyzed, using the procedures described below:

7.3.1 Select the appropriate detector, then select the appropriate analysis/application type, based on the sample geometry, from the Application Select menu. Next select 'Read MCA' on the menu bar. By "reading the MCA", the data acquired during the analysis count is transferred to the workspace and default settings and files from the application are applied (i.e., efficiency, library, units, etc.).

When 'Read MCA' is selected, the analysis parameters screen is displayed. At this time the file name is automatically generated. Record this file name in the gamma spectroscopy run log (Form 754).

The analyst will need to verify, enter, or edit the following sample parameters:

Sample ID: This should be automatically transferred in the format described above, but corrections can be made here.

Spec. Code: This field is left blank.

Sample Size: Enter the volume, weight, or number of filters as appropriate.

Units: This will be transferred automatically as a default, but can be changed as needed.

Sampling Start and Stop: This is normally the same date and time for both the start and stop. Enter the collection date of the sample in both boxes. The time of day is generally 12:00:00 for all samples.

Efficiency File: This line should be generated automatically by the computer and is in the form:

$$(D_{xx})(S_{GG}).EFF$$

where:

xx is the detector number

GG is the geometry of the sample.

If changing the efficiency file, make sure the detector of the efficiency file is for the detector the sample was counted on and that the efficiency file has not expired.

After all the parameters and values are satisfactory, select 'OK' to exit the 'Read MCA' window. By selecting 'OK', all of the parameters and values are saved under the file ID and can be retrieved later to further analyze. By selecting 'CANCEL', all of the parameters are lost and the file ID is not saved.

7.3.2 Next, the spectrum must be analyzed to identify peaks at the various energies. To do this, select 'PEAK SEARCH' on the menu bar and the software will apply the resolution calibration to the acquired spectrum to define peaks and peak height. This will prompt the next window, which allows the analyst to see all of the peaks identified, and the counts acquired for each peak.

The analyst shall review the peak search results to identify peak shifts, multiplets, etc. After the peak search results are considered to be satisfactory, select 'DONE' to exit the peak search results window.

7.3.3 To calculate activity concentrations, select the 'CALCULATE' icon under 'ACTIVITY' on the menu tool bar. This will prompt an activity report parameters window. Then perform the following:

Select the desired library to be used in the column labeled 'LIBRARY FILE'. Next select the background file to be used according to the detector and the count date. Background files are named so that the first two numbers correlate to the detector, the next two correlate to the month the background was counted, and the next two correlate to the day of the month. *Background files can be used for one week after counting (i.e. sample counts must be started before the day and time that the background calibrations were completed on the previous week.)*

The LSF File should remain as 'NONE'.

The 'RESULTS FILE' and the 'PRINTOUT FILE' should be the same as the .SPC file, except ending in .RES and .TXT, respectively.

Select 'OK' after the correct library and background have been selected and the Library Search Results window will be shown. This allows the analyst to review peaks that have been matched to specific peaks in the library.

To **finish the calculations**, select 'OK' to prompt the raw data printout. This window allows the analyst to review all of the parameters used in the analysis.

To **save the data**, select the 'SAVE' icon, which calls up the "SAVE" window. For general analyses the fields are automatically populated. The default values (yynnnnD##.RES) are accepted, except where multiple analyses of a spectrum are performed, as described below.

Select "SAVE" again to store the results in the defined .RES file.

Print the raw data by selecting the 'PRINTER' icon.

In some cases, reanalysis of the same spectrum may be required to apply different geometry calibrations or analytical libraries. To perform multiple analyses on the same spectrum, select "SPECTRUM" on the menu bar, then select "EDIT" and return to step 7.3.1, beginning with the "Efficiency File" specification, with the following exception:

> Multiple analyses of a single spectrum require a unique identifier appended to the default file name (yynnnnD##**A**.RES, yynnnnD##**B**.RES, etc.). The unique file name must be defined prior to saving the .RES file, to **prevent overwriting previous files**.

8. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Standards for Daily QC Checks need not be traceable to the National Institute for Standards and Technology (NIST). All Daily QC monitoring shall be recorded in the gamma spectroscopy run log (Form 754). **QC parameters must meet the established limits defined in the instrument software.**

8.1 QC MONITORING

8.1.1 DAILY QC ENERGY CALIBRATION CHECKS

A daily QC check involves performing an energy calibration, as well as monitoring the detector resolution (FWHM) and efficiency. Each detector has a labeled calibration standard. Center the appropriate calibration standard on the corresponding detector. Count each daily check standard as described in the procedure above for 20 minutes using the sample ID "Daily Check".

When the count is complete, select 'DAILY CHECK' under the Application Select menu, then select 'Read MCA' to prompt the edit parameters screen. Select 'OK', as the parameters should be the default.

On the menu bar select 'PEAK SEARCH' as described above, then select 'Q.C.', then 'DETECTOR'. The calibration parameters screen is then prompted. Make sure that the 'ENERGY' bullet is selected.

Select 'OK', choose 'MERGE PSR', then select 'CURVE FIT', then select 'SAVE'. This will save the energy calibration for that day. The program then compares the results of the energy recalibration to the Q.C. parameters (found in the Q.C. editor) established for the specified detector.

8.1.2 CORRECTIVE ACTION FOR DAILY QC FAILURES

If a detector is not within established control limits for any of the bounds tests, corrective action must be taken. The first course of action is to re-run the QC check. If the observed parameter is still outside normal acceptance criteria after the second analysis, the procedure is as follows:

- If one of the centroid exceeds the bounds test (e.g., 662keV), the peak location should be adjusted. This is done by placing a calibration source on the detector (preferably a Laboratory Control Sample, LCS) and starting the detector.

  Clear the current spectrum by typing 'F4' (Clear). The acquisition can then be started by typing 'F2'.

  Move the cursor to the appropriate centroid (e.g., 662keV) and check the actual location. The peak can be moved by adjusting the fine gain, located on the amplifier. *Note that it only requires a minute adjustment (one click) to move the peak three to five keV.* After the peak has been moved to the correct location, re-run the energy calibration.

- If the failure includes one of the other parameters (e.g., FWHM or efficiency), the daily QC can be re-run. If the QC fails for a second time, the detector is taken off-line and the lab Supervisor is contacted.

  NOTE: A pole-zero adjustment can be conducted in the case of a FWHM failure, using the following procedure:

  First, **attach a co-axial cable** from the "1 Meg" port associated with the vertical input on the oscilloscope to the "uni" output on the amplifier.

Next, **set the scope settings** as follows:

Volts/Div(Vertical) = 0.1

Polarity = DC

Trigger Selector = EXT(-)

Mode = DC

Triggering Level = 0

Stability = Preset

Time/Div = 20μs

Variable = Calibrated

Next, **place a source on the detector** and **adjust the signal** so that it is as close to the baseline as possible by using the 'PZ ADJ' dial found on the amplifier.

The energy calibration can now be run again. If any parameter still fails, tag the detector out of service (SOP 317) and notify the lab Supervisor.

All calibration operations must be recorded in the run log, including fine gain adjustments, bounds re-calculations with start and end dates, and calibration re-runs.

8.2 EFFICIENCY CALIBRATION PROCEDURES

Standards for efficiency calibrations shall be traceable to the National Institute for Standards and Technology (NIST). Standards will normally be of the mixed-gamma, multiple-energy type available from several commercial suppliers. The analysis systems shall be calibrated for each physical form of sample to be analyzed (e.g., water, soil, filter, etc.) at least annually. A FWHM calibration shall also be performed at least annually. Note that there is only one FWHM calibration per detector, and it is not geometry specific. Before starting an efficiency calibration, consult with a Senior Instrument Technician. Record all efficiency calibrations in the gamma spectroscopy run log (Form 754).

8.2.1 SPECTRUM ACQUISITION

Place the calibration source for the appropriate geometry on the detector to be calibrated. The efficiency calibration will be initiated like that of a sample count. First, an internal workorder number must be obtained from the current non-client workorder notebook (located in the radium/strontium lab). Use this workorder number and follow the same procedure used to count a sample. Be sure to enter the appropriate dates and time for the calibration standard (2 hours and/or a

duration long enough to acquire 10,000 cts/per energy line that will be used in the calibration). For calibrations where 10,000 cts/per energy line cannot be acquired, Supervisory approval is required.

8.2.2 SPECTRUM ANALYSIS

8.2.2.1 After the acquisition is complete, the MCA of the sample spectrum should be read. In the edit parameters screen, enter the standard calibration origin date, and the appropriate volume/sample size. Select 'PEAK SEARCH', then 'CALIBRATE'. The types of calibrations prompted are: Energy, FWHM and Efficiency. Make sure that the 'EFFICIENCY' bullet is selected. The calibration parameters screen is prompted, at which time the operator must choose the appropriate calibration standard, aliquot size and the appropriate fit formula for the efficiency curve (exponential fit is used in most cases).

Select 'OK' to prompt the calibration workspace. Transfer the peak search results by selecting 'MERGE PSR', then 'CURVE FIT'. View the results of the calibration.

The % difference for the measured efficiency should be less than +/- 5% for all nuclides, but may be up to 10% with specific written approval from the instrument lab Supervisor. If the measured difference exceeds this criterion, the calibration will have to be redone. If efficiency limits are met, select 'OK', then 'SAVE', and then print the calibration.

This calibration should be done annually or when maintenance has been conducted on the detector.

8.2.2.2 If the observed efficiencies need to be adjusted to optimize the fit of the calibration curve, this may be done with the approval of the lab Supervisor. *Do not adjust the Cs-137 efficiency.* If the other efficiencies need to be adjusted, manually calculate the new efficiency, by either increasing or decreasing by a known percentage (usually 5 to 10%).

DO NOT MANUALLY ADJUST EFFICIENCIES WITHOUT FIRST CONFERRING WITH A SENIOR INSTRUMENT TECHNICIAN.

After adjusting a peak, re-start the calibration process (choose the print to screen option until the efficiencies have been accurately adjusted). Manual adjustments are

conducted in the calibration work space.

In all cases, manual adjustments of peak efficiencies will be noted on the calibration output page.

8.2.2.3 After the calibration has been stored, analyze an LCS with the appropriate geometry for 1800 seconds to verify the calibration. This analysis must pass normal LCS acceptance criteria.

8.3 WEEKLY BACKGROUND CALIBRATION

8.3.1 A background calibration is performed weekly. Use the general form, "yymmdd-## Weekly Bkgd", for the sample ID.

8.3.2 Make sure there is no sample in the detector shield. Consult the gamma spec maintenance logbook to see if the detectors have been cleaned within the past month, if not, the detectors need to be cleaned per Section 8.3.5 below.

8.3.3 Start the counts for 1000 minutes (60000 seconds) for each detector in service. Geometry and aliquot are irrelevant.

8.3.4 Record detectors that have been started in the logbook. After the counts are complete, "Read the MCA" and do a 'PEAK SEARCH' as described above. At this point, review the acquired spectral data for evidence of peak-fit errors and/or gain shift. If the spectral quality is acceptable upon review of the 'PEAK SEARCH' results, save the background calibration by selecting 'SAVE AS BKGSUB'. Save each background file as DET##MMDD.BKG, where '##' is the detector number and 'MM' and 'DD' are the month and day the background was started. Then select 'BACKGROUND' under 'QC' on the menu bar. Select 'OK' to analyze the background and see if the count is within control limits. Record any failures in the run log, clean the detector (see 8.3.5 below), and restart the background calibrations.

8.3.5 WEEKLY CALIBRATION FAILURES

The inside of the detector must be thoroughly cleaned with a paper towel dampened with Radiacwash®, or an equivalent EDTA solution. Then wipe the detector with a paper towel dampened with DI water. Record the cleaning date in the gamma spec maintenance logbook.

After this has been done, the background calibration can be run again. If the detector fails after cleaning, the lab Supervisor must be notified and the detector must be tagged out of service (SOP 317) until the problem is resolved.

8.4 QC SAMPLES

One LCS and blank, per geometry, are to be analyzed with every batch of not more than 20 samples.

9. INTERPRETATION OF DATA

The spectrum analysis capabilities of the analytical software are only as good as the software set up. It is essential that appropriate analysis geometries, efficiency files, and library files be used to ensure accurate analyses. Results data must be reviewed as soon as it becomes available to ensure that the calibrations are correct, that the spectral quality is adequate, and that all Q.C. acceptance criteria have been met.

All unknown peaks greater than 5 times the listed critical level must be qualitatively identified in the case narrative. The spectrum must also be reviewed to ensure that characteristic peaks, such as K-40 at 1460keV, and the annihilation peak at 511keV, do not show evidence of a gain shift. A gain shift may show up as a secondary peak slightly offset from all the normal characteristic peaks in the spectrum. A spectrum that shows evidence of a gain shift must be rejected and the sample re-counted. The detector showing the gain shift must have the fine gain on the amplifier adjusted as described previously in Step 8.1.2.

10. PERIODIC MAINTENANCE

Each detector has a Dewar filled with liquid nitrogen to keep the germanium detector cold. Twice per week, the detector Dewars must be filled with liquid nitrogen. Allow 15 minutes after filling before resuming data acquisition.

If a Dewar runs out of liquid nitrogen between fillings, the red bias display, located on the 'BIAS SUPPLY' control board, will be shutdown. If this occurs, tag the detector out of service, and do not operate the detector until the Dewar can be re-filled. The detector may need to be cycled through ambient room temperature before being re-cooled. The lab Supervisor must be notified before proceeding.

To fill the Dewar, follow the steps below:

- After the nitrogen lines have been attached to the 'LIQUID' output of the new tank, flip the 'SOLENOID CONTROL' switches to the 'ON' position. This switch is located on the 'AUTO FILL EXPANSION CONTROL' board. Then depress the red 'MANUAL' fill button on the 'AUTO FILL CONTROLLER'.
- Once the Dewars have been filled, the red LED read-out on the 'AUTO FILL CONTROLLER' should read "168.0", which indicates the number of hours until the next fill should be done.
- If a tank has not been completely filled, an alarm will sound. To silence the alarm, depress the 'ALARM RESET' button on the 'AUTO FILL CONTROLLER'. Once the alarm is shut off, check the 'AUTO FILL EXPANSION CONTROL' board to see which detector LED lights are on

(note that the 'SOLENOID CONTROL' switch will still be in the 'ON' position if a Dewar has not been completely filled).

- To re-fill a partially filled Dewar, depress the two red 'ERROR RESET' buttons on the 'AUTO FILL EXPANSION CONTROL' board and then depress the 'MANUAL' fill button.

- Each detector is equipped with an overflow line. If this line appears to be bleeding an excessive amount of liquid nitrogen, the 'SOLENOID CONTROL' switch should be turned to the 'OFF' position.

- Record all liquid nitrogen fills and re-fills in the gamma LN2 fill logbook.

11. DEVIATIONS FROM THE METHODS

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the lab's internally derived acceptance criteria.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Normal laboratory safety procedures (gloves, safety glasses, and lab coats, where necessary) must be complied with during the conduct of this procedure.

12.1.2 Bias applied to detectors is typically in the range of 1000 to 4000 volts DC. This can result in electric shock if bias cables are disconnected while bias is applied. To minimize the possibility of electric shock, bias shall be turned off to any detector before any cabling is disconnected.

12.1.3 The liquid nitrogen used to fill the Dewars is at -196°C. Exposure to the skin can cause severe frostbite. Use insulated gloves when handling frozen lines, valves, etc.

12.1.4 Large liquid nitrogen spills can displace room oxygen and cause asphyxiation. In case of a large liquid nitrogen spill, open the lab doors and allow the liquid nitrogen to dissipate before re-entering the lab.

12.2 WASTE DISPOSAL

12.2.1 The gamma spec instrument technician is responsible for returning the samples to the sample custodian or to the sample storage area after analysis, completing the internal chain of custody (SOP 318).

12.2.2 Some samples will be returned to the client after analysis. Samples or sample wastes containing radioactive materials, which are not being returned to the client, must be disposed of according to Paragon's

procedures for disposal of radioactive materials. Contact the Waste Disposal Coordinator for more information.

13. REFERENCES

13.1 ANSI N42.14, American National Standards Institute, Calibration and Usage of Germanium Detectors for Measurement of Gamma Ray Emission of Radionuclides, April 1978, Reaffirmed April 1985.

13.2 EPA-600/4-80-032, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, "Method 901.1, Gamma Emitting Radionuclides", August 1980.

DOCUMENT REVISION HISTORY

4/10/06: Made procedural clarifications involving operation of the Seeker® software. Added LIMS Program Specification directive to 'Responsibilities' Section. Added DOCUMENT REVISION HISTORY.

7/20/08: (4/9/07) Minor clerical changes. Added reference in RESPONSIBILITIES to Appendix D and added Appendix D - General Gamma Detector Operations. (6/9/08) Added comment about ingrowth requirement for geometry 17 samples to Appendix B. (7/20/08) Added Operator's Aid exemption text to 7.2.1.

APPENDIX A
COMMON GAMMA ENERGIES AND CHANNEL LOCATIONS

This Section is provided to assist in determining proper channel locations during calibrations and QC checks.

NUCLIDE	ENERGY (keV)	TARGET CHANNEL
Am-241	59.54	120
Cd-109	88.04	176
Co-57	122.06	244
Cs-137	661.65	1324
Y-88	898.04	1796
Co-60	1173.22	2346
Co-60	1332.49	2664
Y-88	1836.06	3672

NOTE: Paragon uses a 2.0keV matching tolerance for nuclide/energy matching; this will allow up to a 4 channel deviation from target channels. In addition, the daily QC checks perform energy versus channel calibrations each time they are run, correcting for small changes in peak channel locations.

APPENDIX B
GEOMETRY/EFFICIENCY LIST

Geometry Number	Geometry Description	Default Count Time (min.)	Efficiency file/Standard file number
01	1 liter H_2O in 2 liter Marinelli	300	01
07	47mm Filter	60	07
08	Five 10 cm filters	1000	08
09	Hi-Q charcoal cartridge	60	09
13	500g Solid	30	13
11	100g Solid	30	11
*17	215g Solid	30	17
18	1350g Solid	120	18
*26	215g Solid (Ra-226)	30	26
27	1332g Solid (Ra-226)	120	27

* Unless otherwise directed, samples packed for Geo17/26 will be ingrown 21 days before analysis to allow Rn222 to approach equilibrium with its progeny.

APPENDIX C

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency Check	Daily	Within derived control limits, as established in instrument software.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Peak Resolution Check	Daily	Within derived control limits, as established in instrument software.	Recount, re-evaluate, perform pole-zero adjustment, if necessary, and repeat daily performance checks.
Energy Calibration	Daily	Within derived control limits, as established in instrument software.	Recount, re-evaluate, perform fine gain adjustment, if necessary, and repeat daily performance checks.
Peak Background Calibration	Weekly	Within derived control limits, as established in instrument software.	Clean detector, recount, re-evaluate, or document why condition is acceptable.
Efficiency Calibration	Yearly, for each counting geometry.	Each fitted value is within 5% of the observed value. Subsequent LCSs pass within normal acceptance criteria. *	Tag geometry off-line. Determine and correct problem; verify source activity; recount and/or recalibrate. With supervisors written approval, fitted values may be within 10% of observed value.
Peak Resolution (FWHM) Calibration	Yearly	Each fitted value is within 10% of the observed value. Subsequent LCSs pass within normal acceptance criteria. *	Perform pole-zero adjustment, if necessary, and repeat.
Gain shift	Each sample	Review each spectrum to ensure that characteristic peaks @ 511, 1460 KeV are present, not shifted during the count, and properly ID'd by software.	Recount sample after daily performance checks are successfully performed.

NOTE: This SOP and SOP 715 contain acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

* as established in the applicable LIMS nickname (e.g., Paragon Standard or as created for a specific client

Paragon Analytics

Gamma Spectrometer Calibration Log

Date: _____ Reviewed By/Date: _____

Det. No.	Out Of Service	Background		Source Check			Repeat Source Check			
		Started	OK	Started	OK	Failed Parameter(s)	OK	Failed Parameter(s)	Corrective Action Taken **	Removed from Service
1.										
2.										
3.										
4.										
5.										
6.										
7.										
8.										
9.										
10.										
11.										
12.										

. Corrective Action:**

Paragon Analytics

Gamma Spectrometer Run Log

Date: _____ Reviewed By/Date: _____

Sample ID	Ver[1]	Det. No.	Geo[2]	Count Dur. (min.)[3]	Start Time	Analyst	File ID/Comments	Saved?

[1] Analyst will verify the position, detector, and geometry when the sample is removed from the detector.

[2] Calibration geometry.

[3] Count duration.

KEY: * sample was counted on a puck
↑ sample was counted with air flow arrow pointing up
↓ sample was counted with air flow arrow pointing down

_____ **B**

Form 754r11b.doc (6/13/2005)

APPENDIX D

GENERAL GAMMA DETECTOR INTALLATION NOTES

Upon receipt of a new or repaired detector the following steps must be taken prior to data acquisition.

1) Inspect the detector for damage during transit.
2) Review accompanying documentation to ensue the following;
    a. Quality Assurance Data Sheet. This documents the detector performance after repair/manufacture.
    b. Spectrum Printout: Supplements the QADS.
    c. Repair Analysis Report (if detector was repaired). This documents the problems identified with the detector and any corrective action/repairs that were undertaken.
3) Cool the detector.

NOTE: The detector must be cooled overnight before applying bias. Do not connect the detector cabling until the assembly has cooled in LN overnight.

a. Inspect the nitrogen dewar to be used, if necessary.

    Note: In all cases, the dewar should not be placed directly on the floor. Insert some vibration absorbing material between the dewar and the floor to minimize microphonic noise (low frequency harmonics) in the detector.

b. Fill the dewar with LN, to within 3-4” of the top of the neck. Do not allow the LN to overflow or to contact the latex collar, though the collar will be cold after filling.
c. Allow the collar to warm for 20-30 minutes to allow enough flexibility to insert the detector cryostat.
d. At this step it is helpful to have a second technician waiting underneath the shield to receive the detector cables and to adjust the position of the dewar, as necessary.
e. Feed the long grey pre-amp cable through the top of the opening in the shield.
f. Carefully insert the cryostat through the shield, into the LN dewar. After inserting the cryostat partway, feed the detector leads through the opening. It may be necessary to move the dewar slightly to one side to accomplish this.
g. After all the cables are clear of the shield and collar, center the dewar and insert the cryostat completely into the LN.
h. The initial cooling of the detector may use a significant volume of LN. After the detector has cooled for 2-3 hours, top off the LN, filling the dewar until the LN spills out of the overflow port.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 714 REVISION 11

TITLE: **ANALYSIS OF ALPHA EMITTING RADIONUCLIDES BY ALPHA SPECTROMETRY**

FORM: **746, 302** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/31/07

QUALITY ASSURANCE MANAGER _____ DATE 8/31/07

LABORATORY MANAGER _____ DATE 8-31-07

HISTORY: Rev0, 9/18/91; Rev1, 7/27/93; Rev 2, 10/21/93; Rev3, 5/20/96; Rev4, 4/7/98; Rev5, 10/24/99; Rev6, 10/18/01; Rev7, 1/4/02; Rev8, 1/2/03; Rev9, 6/18/04; Rev10, 9/11/06; Rev11, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform spectroscopic analysis of alpha emissions on samples of various media using high-resolution ion implanted silicon alpha spectrometry. This procedure is applicable to all alpha spectrometry analyses performed at Paragon. The target analytes are routinely separated from liquids (primarily aqueous) and solid samples (primarily soils, wastes, filters) following equilibration of the sample with a suitable isotopic tracer, and mounted by micro-precipitation onto 25mm, 0.1 micron (µm) pore sized filters, fixed into 31mm stainless steel planchets. Analyte activity is derived from the relative count rates of analyte and tracer isotopes and the known activity of tracer added. When no suitable nuclide is available for use as an isotopic tracer (e.g., ^{237}Np), splits of each sample are prepared following addition of a known quantity of NIST-traceable tracer solution of the target analyte. The chemical yield data generated from split sample analysis is used for the calculation of sample results.

2. SUMMARY

Alpha emissions from radionuclides are detected by an ion-implanted semiconducting silicon wafer, which transfers the energy deposited into a small electronic pulse for each alpha interaction, where the pulse height is proportional to the incident alpha energy. The 600mm^2 ion implanted silicon detectors are mounted in vacuum chambers and operated at or below 500 milliTorr absolute pressure to minimize loss of alpha particle energy during the path from the sample to the detector. The data collection and processing is performed through the AlphaVision32©, v5.3 software package.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. The Alpha Spectroscopist is responsible for day-to-day operations, calibrations, troubleshooting, repair of the instrument, and related details

3.2 It the analyst's responsibility to ensure that the activity of the calibration sources are properly verified at least annually by comparison to an independent source. In addition, it is the analyst's responsibility to ensure that the independent source has been verified by a NIST-traceable laboratory within a year of use. In practice this means that the independent source can be sent off-site for re-verification at an interval of just less than two years.

3.3 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715.

3.4 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.5 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.6 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the report components and review checklists indicate that reviews for precision, accuracy, completeness, and reasonableness are complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.7 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager or designee.

4. INTERFERENCES

4.1 The presence of excessive precipitate in the final source will lead to degradation of spectrum quality due to self-absorption effects. Excessive tailing, poor peak separation or visible evidence of unusual amounts of solids on the final source may necessitate cleanup of the sample (by dissolving LaF_3–analyte precipitate in boric/nitric acid, co-precipitating as a ferric hydroxide, dissolving $FeOH_3$ in HCl and repeating the microprecipitation steps. Additional column separation may be necessary to remove various interfering constituents).

4.2 The levels of activity taken for analysis should be minimized to prevent contamination of the detection system and overwhelming the tracer. Aliquot size should be judged according to expected activities for the samples (refer to pre-screening data available in the work order folder) and should generally be held within the range of less than 30-50pCi.

4.3 For the alpha spectrometry system, a sample with elevated activity is defined as one that has more than 200 total disintegrations per minute (DPM) deposited on the planchet. This includes all requested analytes of interest as well as the tracer analyte. When such a sample is encountered, the Preparation Lab and Instrument Lab Supervisors must be notified so that they can investigate the possibility of equipment contamination. At the instrument, a background check of the detector used to count the sample must be performed before any subsequent samples may be counted by that detector. This is performed to ensure that detector contamination did not occur, which could bias subsequent analyses on that detector. Generally, a 1000-minute background calibration is run in order to fulfill the background check requirement. If the new background calibration passes quality control criteria, this calibration replaces the previous weekly background calibration until the next weekly background calibration is performed. If the new background calibration fails to meet quality control criteria, consult the Department Supervisor for corrective action. Please refer to Section 11 of this SOP for background quality control criteria.

4.4 The Paragon default minimum detectable concentration (MDC) formula referenced in this SOP 708 conservatively assume that background count times equal or exceed sample count times. If extended count times are necessary to meet data quality objectives (DQOs), it is advisable that dedicated background counts be conducted immediately prior to the count to both ensure that count time parity is achieved, and to minimize the potential effect of detector contamination.

4.5 The presence of significant peak activity in a spectrum other than that expected (e.g., thorium peaks in a plutonium spectrum) is significant cause for concern. Re-preparation or appropriate sample cleanup may be indicated. Consult with the Department Manager for advice in such cases.

4.6 Detectors are segregated into U/Th/Np only and Am/Cm/Pu/Np/Po only due to the progeny resulting from U/Th samples. The U/Th progeny will cause an interference in Am/Cm/Pu measurements.

4.7 In some cases, the addition of normal tracer analytes will cause interference in other analytical regions of interest (ROIs). For example, ^{229}Th activity generally "tails" into the ^{230}Th ROI, and ^{243}Am may have measurable ^{241}Am activity present. These potential interferences must be accounted for in the analytical procedure.

4.8 In some cases, two requested analytes may be indistinguishable by alpha

spectrometry (e.g. ^{233}U and ^{234}U). In these cases, the combined ROI is reported as a single result for both analytes (e.g. $^{233/234}$U).

5. APPARATUS, MATERIALS AND REAGENTS

This procedure is conducted with the use of installed alpha detection and analysis equipment consisting of ion implanted silicon detectors mounted in combination vacuum chambers/spectrometers. These spectrometers are controlled by a personal computer based analysis system with multi-channel analyzer interface, integral multi-channel analyzers (MCAs), alpha analysis software, and associated cabling. Currently, the analysis software used to analyze samples is AlphaVision32©, Version 5.3, by EG&G Ortec Corporation. The alpha detectors used to count samples are Ortec "U-024-600-AS" 600mm^2 ULTRA_AS ion-implanted detectors, or equivalent. In addition, the following materials are used for routine maintenance of the detectors.

5.1 KimWipe™ lint-free wipes

5.2 cotton balls

5.3 Methanol, reagent grade
TLV=200ppm

5.4 canned (pressurized) air

6. SAMPLE HANDLING

6.1 All samples received by the radiochemistry Instrument Lab must be checked in within one business day, using the LIMS internal chain of custody (SOP 318).

6.2 Generally, samples with long count times (greater than 360 minutes) are loaded at the end of the day. Samples with shorter count times (less than 360 minutes) may be loaded throughout the day, as time allows

6.3 Generally, samples are prioritized for counting based on the client requested due date.

6.4 Polonium is generally volatile under the vacuum conditions used in this analysis. Samples for polonium analysis are sealed with a thin film covering to prevent detector contamination. The planchets should be carefully handled on the outside of the planchet, with a gloved hand rather than forceps, to prevent puncturing of the thin film.

6.5 In some cases, short-lived analytes or interfering progeny may require samples to be analyzed as quickly as possible. For example, ^{227}Th has an 18.72 day half-life and significant delays in counting will result in elevated detection limits. Also, the ^{232}U- progeny, ^{228}Th ingrows with a half-life of 1.9 years and significant delays in counting will result in ^{228}Th interference in the ^{232}U ROI.

6.6 Uranium and thorium analyses, particularly those in high activity samples, should be removed from the detector as soon as possible after the completion of the count to prevent recoil and progeny contamination of the detector.

6.7 Standard verifications and proficiency demonstrations should be analyzed and processed within 48 hours of receipt from the prep lab due to the pressing production needs of the Department.

6.8 Planchets will be stored in the Instrument Lab for a minimum of three months prior to disposal to allow for reanalysis if necessary.

7. PROCEDURES

Instructions are given for the AlphaVision32© program, Version 5.3. Throughout the text of this document, < > defines a computer keystroke, ___ defines a window header, and [ ] defines a menu option on the AlphaVision software. Basic technician-level access to AlphaVision can be obtained through the user name "user" and the password "user". See the Department Manager for administrator- and supervisory-level access.

7.1 OPERATING CONDITIONS

The alpha spectrometers are operated in a low vacuum system, less than 500milliTorr absolute pressure, at detector bias voltages of typically 30-50 volts DC. The operating conditions shall be verified weekly by running energy/efficiency and background calibrations on each detector. See Section 11 for quality control procedures.

7.2 SAMPLE PREPARATION

Samples are prepared by radiochemical separation applicable to the radionuclide(s) being evaluated. Samples are prepared in the Actinides Preparation laboratories using chemical separation and deposition processes (refer to the radiochemistry preparations procedural SOPs for specific information). The samples are received in the Instrument Lab in the form of a filter mounted on a labeled planchet or as in the case of ^{210}Po, as an electroplated disk to be counted.

7.3 DATA ACQUISITION AND ANALYSIS

7.3.1 Each alpha spec detector is separately contained in a metal housing with an o-ring sealed door hinged at the bottom of the housing. Forceps are used to handle planchets. Planchets are loaded into detectors that are calibrated and have passed all QC checks. Planchets for Uranium or Thorium analysis are loaded only into those detectors that are designated for U/Th. Detector numbers are recorded in the appropriate place on the benchsheet. To load the planchets into the detectors after the vacuum has been properly released from the chamber (see below): Open the door, slide out the tray, place the planchet on the tray, slide the tray back in. Make sure the filter paper on the planchet is centered under the detector. Close the door. *Note that the tray position within the chamber should always be in the position of the current calibration; currently that position is the default (top) position in the chamber.*

7.3.2 Before the analysis can be started, the detector chambers must be evacuated. There is one vacuum line connected to each tower. To evacuate a chamber, turn the knob under the door to the 'PUMP' position. However, once the knob has been turned to apply vacuum to a chamber, all other chambers that are connected to the same vacuum line will temporarily lose vacuum and bias. *If bias to chambers is lost during active counting of samples, the data quality will be compromised!*

On the AlphaVision (AV) grid displayed on the computer, certain colors are set to indicate the status of the chambers:

- **Green** indicates an idle chamber.
- **Red** indicates a detector that is offline.
- **Yellow** indicates a chamber with an active count running.

Therefore, before applying vacuum, chambers where data is being acquired must have the vacuum put on hold by turning the knob under the door to the 'HOLD' position. For example, to start a count in a detector or group of detectors with other samples counting in the same tower (and thus sharing the same vacuum manifold), the vacuum must be put on 'HOLD' for detectors containing the samples that are already counting.

Now it is safe to turn the knobs to the right to 'PUMP' to evacuate all detectors that have been loaded. It is necessary to manually check that all detectors have been properly evacuated. This is done by selecting 'MCA VIEW' by right clicking on that detector with the mouse. Once the spectrum window has opened, select [ACQUIRE] and [ADJUST CONTROLS…]. The vacuum pressure, bias voltage, and current can now be viewed. Once it has been verified that all detectors are pumped down, the detectors that have been placed on 'HOLD' can now be turned to 'PUMP'.

7.3.3 Record the Detector Number, Analytical Run, Sample ID, Analyte Type/Matrix, Count Duration, and Analyst's Initials and in the Alpha Spectroscopy Run Log (Form 746).

7.3.4 After samples have been loaded, and the counting chambers evacuated, start spectrum acquisition as follows:

7.3.4.1 From the AV menu bar select [PROCESS] then [BATCH].

7.3.4.2 Under General, enter the analytical run (i.e., UAS0608100-

2_A) and select the correct template (i.e., iso U or U default) from the drop down menu. Select, [NEXT] which will move to the next screen.

7.3.4.3 In the Batch screen, select the current month and analyte type. Select [NEXT], which will move to the sample screen.

7.3.4.4 In the Sample screen, select [ADD]. A new small screen will open. Enter sample ID of first sample of analytical run only. Select [OK] to close the small screen. Enter the correct sample units (g, L) and sample aliquot size (This may be done in whole numbers instead of entering exact aliquot volumes. In order for LIMS to perform the final calculations, it queries aliquot volumes from the benchsheet, not from the aliquot entry in AV. Therefore, rounding of aliquot sizes in AV does not impact data quality). Select [NEXT], which will move to the Acquisition screen.

7.3.4.5 In the Acquisition screen, enter the run time in minutes. Select [NEXT], which will move to the Analysis Setup screen.

7.3.4.6 In the Analysis Setup screen, select the correct nuclide library, ROI set, and Tracer set from the drop down menus. Enter the Tracer amount from the benchsheet.

7.3.4.7 Select [PREVIOUS] to return to the Sample screen. Enter the remaining sample IDs from the analytical run. Select [FINISH], which will open a screen showing all sample IDs that have been entered.

7.3.4.8 To assign detectors, select a desired detector and drag over to the appropriate sample ID. When all detectors have been assigned, select [START NOW].

7.3.5 When unloading samples, release the vacuum as slowly as possible by turning the knob counterclockwise from ‘Pump’. Turn the knob slowly the rest of the way to vent. *Air should not be heard rushing into the detector to any appreciable extent as air current stirs up particles and potentially contaminates the detector and chamber.*

7.3.6 When removing the samples from the detector chambers, verify the position by checking the sample removed from the detector against the

detector # recorded on the benchsheet. Any discrepancy should be noted on a QASS and/or the benchsheet and the raw data printout. If a discrepancy is found, the sample may need to be re-analyzed.

7.4 SPECTRUM ANALYSIS

Each nuclide emits alpha particles at distinct energies characteristic of the decaying species (see attached Table 1 for a short list of energies). When an alpha particle is incident on the detector, an electrical pulse is generated, the signal produced is analyzed according to pulse height, and is stored as a count in the appropriate channel of the given MCA buffer. As the number of counts stored increases, peaks for each radionuclide begin to form. AV is programmed to conduct an ROI analysis of the spectrum from the data gathered during the count and information that was previously entered (i.e., tracer DPM, target nuclides and relative ROIs, recovery type, etc.). The results of the analysis are then summarized in a raw data results report and a graphical hardcopy printout of the spectrum is produced. The raw data results are also written to the AV database.

7.4.1 After sample acquisition has been started, it is possible to examine the spectrum "live" to make a real-time estimate of chemical yield expected for that sample (note that sufficient time must have elapsed for the spectrum to be discernible, 10-15 minutes is usually sufficient).

7.4.1.1 This may be accomplished by selecting the detector with the mouse, right clicking and choosing [MCA VIEW]. At this point, the chemical yield can be estimated from the net area of the peak. The detector may also be manually analyzed in order to get a printout to determine preliminary chemical yields. See Section 9 for the appropriate calculation.

7.4.1.2 Alternately, select the "spectrum" line in the sample entry in the upper right window, right-click the mouse and select [INTERIM ANALYSIS]. This will perform a normal analysis, as described in Section 7.4.2 below, using the data acquired thus far. The analysis report will show calculated yields, activities, etc. as well as a printout of the interim spectrum.

7.4.2 When the preset live time has elapsed, the detector icon turns solid green to indicate that the full count duration has elapsed. The spectrum and analysis data is then reviewed prior to printing the raw data and saving the .pdf image.

7.4.2.1 In some cases the software fails to recognize the tracer peak in the spectrum and the analysis sequence is stopped

before completion. In this case, at the analyst's discretion, the analytical sequence may be manually taken to completion. Select the analytical parameters by right-clicking the mouse on the spectrum entry in the upper right window. Select [ANALYZE]. In the Analysis window, uncheck the "Shift With Tracer" box, then select [OK]. ROIs may then be evaluated, as described below.

7.4.2.2 Select the "analysis" line in the sample entry in the upper right window. This displays the spectrum and ROIs in the "Spectrum" tab. Specific analytical considerations for evaluating and adjusting ROIs are discussed below. *NOTE – due to limitations in the AlphaVision software, if ROI adjustments need to be made, first select [INTERACTIVE ROI ANALYSIS]*. Adjust ROIs as necessary. ROIs can be adjusted by dragging the ROI boundaries left and right. Finally, select [INTERACTIVE ROI ANALYSIS] again.

7.4.2.3 Select the "Report" tab at the bottom left of the report window to display the raw data report. Select the printer icon at the top left, which will call up the default PDF Factory program. Save the image under the file name designated on the LIMS Instrument Worksheet (e.g., U81925D.PDF), then print a hard copy for further review.

7.4.3 After samples have finished counting, perform a cursory review of the raw data printouts to ensure that chemical yield, duplicate error ratio(s) (DER), minimum detectable activity (MDA), tracer counts, blank activity, and laboratory control sample (LCS) values all satisfy applicable data quality objectives. Check the spectra for peak shifts and peak resolution. Verify that a raw data printout and spectrum is present for all counted samples. Determine if there are samples to be recounted or re-prepared. This will give the Preparation Group adequate time to complete a re-extraction if any of these parameters fail to pass acceptance criteria.

7.4.4 In the absence of client-specific yield requirements, a sample that has between 15-30% yield recovery may be reported in some cases. In such cases, spectral quality must be acceptable in the analyst's judgment and all other QC criteria must be met. The sample is flagged with a "Y2" flag, a narrative comment is made, and the results are reported, with Supervisory oversight.

Samples with chemical yields below 15%, those with yields below client-specific yield requirements, or those that do not meet the spectral

quality requirements listed above require corrective action. An NCR will be initiated (see SOP 928) and sample re-extraction may be necessary. Samples with low yields may still be reported when a sample is of an uncommon matrix, if re-extraction would not be expected to produce improved chemical yield, or if a second extraction of a sample shows repeated poor chemical yield (generally an indication of matrix interference). Low yield is always documented in a case narrative, and an explanation is included if the sample was not re-analyzed. Consult with the Department Manager and the Project Manager before reporting results for a sample that has shown poor yield.

7.4.5 DER values are calculated using the formula found in SOP 715. Compare blank activities to established limits and, if applicable, to client/project-specific data quality objectives. Compare LCS results to the known values for a particular radionuclide for appropriate spikes. The known values are found on the benchsheet; crosscheck this against the standard verification worksheet.

7.4.6 Sample measurements are routinely determined by internal addition of isotopic tracer to each sample prior to separation. Samples are traced with adequate activity and counted for a sufficient period of time such that counting uncertainties of approximately 5% (1 sigma) are obtained for the tracer peak (approximately 400 net tracer counts). Samples that do not achieve approximately 400 tracer counts may be counted longer or are re-prepared to achieve the target uncertainty. However, if tracer counts fall below 400 and all other QC criteria are met and assuming that the additional uncertainty is clearly reflected in the reported TPU or clearly documented in the case narrative, then the samples may be reported, with Supervisory oversight.

7.4.7 ROIs are areas that encompass spectral peaks. Default values have been set based on the expected energies defining the channels between which specific nuclide peaks are expected to fall. Occasionally, slight adjustment of the ROI by a few channels may be necessary to ensure good fit with the acquired data before a final report can be generated. To adjust the ROI, the general guidelines used consist of:

7.4.7.1 For routine Isotopic Uranium, set the boundaries for ^{238}U and ^{234}U so that they are the same distance from the centroid as they are for the tracer, ^{232}U. The ^{235}U ROI will encompass an energy range from approximately 4217keV to 4396keV. The count data for this ROI will be abundance corrected for 85.1% of the total alpha activity measured. This technique minimizes the high bias to the

^{235}U results due to tailing of the ^{234}U peak.

For Isotopic Uranium where $^{235/236}$U is requested, set the boundaries for ^{238}U and ^{234}U so that they are the same distance from the centroid as they are for the tracer, ^{232}U. The area between the right boundary of ^{238}U and the left boundary of ^{234}U represents $^{235/236}$U. The ^{238}U, $^{235/236}$U, and ^{234}U regions should be directly adjacent to each other with no space in between.

7.4.7.2 For Plutonium and Americium, when there are no peaks for the nuclides and the tracer peak resolution is good, ROIs are set to correspond to energies listed in Radioactive Decay Data Tables, David C. Kocher (reference available on Paragon network). Set the ROI for the missing nuclide between the higher and lower energies.

7.4.7.3 Samples analyzed for Isotopic Thorium concentrations have a radioactive tracer, ^{229}Th, added to allow for chemical yield determinations in the separation process. A limitation of this method is that all client and QC samples demonstrate the presence of a small amount of characteristic activity in the ^{230}Th region of interest (ROI) that is attributable to ^{229}Th activity. Peak resolution at this level is inherently limited by methodology and software capabilities.

In order to avoid a high bias to the reported ^{230}Th activity concentrations, an arithmetic correction is made to the count rate in the ^{230}Th ROI. A population of method blank samples, which is assumed to be free of ^{230}Th contamination, is analyzed and the average net contribution to the ^{230}Th ROI is used to make the arithmetic correction. The current blank population (established in April 2006) showed the ^{230}Th correction to be 2.73% of the counts acquired in the ^{229}Th ROI. This value is re-evaluated yearly.

The adjusted number of ^{230}Th background counts is, therefore, calculated as (^{230}Th ROI Calibrated Background Counts) + (0.0273 * ^{229}Th ROI Net Counts). This adjusted background count number is used in all the usual calculations for Net Activity, Counting Uncertainty, and Minimum Detectable Concentration.

This adjustment to the ^{230}Th background counts is made automatically by entering the correction value (2.73%) in the "Contaminated Tracer" box of the "Tracer Information" screen in AlphaVision. This information should only be entered under the supervision of the Department Manager.

For Thorium samples without ^{230}Th activity, set the ROI for the LCS first. This defines the shape of the peaks and gives an idea of the location and the size of the tracer peak. Note the channel for the middle of the tracer peak of the LCS. Additionally, note the channel for the lower energy end of the ROI for the tracer peak of the LCS. The difference in channel number will be used to set the ROI for samples without appreciable ^{230}Th activity. Samples with ^{230}Th activity will have enough peak resolution in order to accurately set ROI boundaries. For a sample without significant ^{230}Th activity, determine the channel number for the middle of the tracer peak, subtract the number of channels determined from the LCS, and set the lower energy ROI at the new channel.

7.4.8 The full width at half maximum (FWHM) is defined as the width of the peak distribution at a level that is half the maximum ordinate of the peak. Except for isotopic thorium analyses, in determining acceptable resolution, the tracer FWHM shall be between 40 and 100keV. Consult the Supervisor for samples that do not meet this criterion. If the deviation is minimal and all other criteria are met, results are reported with a narrative comment and supervisory approval.

7.4.8.1 Due to limitations in the AV software, the FWHM may need to be manually confirmed, if the reported value falls outside the 40–100 keV range.

7.4.8.2 Find the channel inside the peak with the greatest number of counts. Divide this number of counts by 2 to obtain the "half max" value.

7.4.8.3 Find the left-most channel of the peak that has counts less than the "half max" value. Move the cursor to the right, counting the number of channels, until the right-most channel of the peak that has counts less than the "half-max" value is selected. Multiply this number of channels by the slope of the energy calibration (nominally 10.0 kev/CH) to obtain a conservative estimate of the FWHM value, in keV.

7.4.8.4 If greater precision in the FWHM estimation is necessary, calculate the partial channels associated with either side of the spectrum by fitting a straight line between the two channels that bound the "half-max" value, and interpolating the precise point at which the "half-max" value is obtained.

For example, suppose that the half-max value is 80 counts, and left-hand side of the peak includes channel 123 with 70 counts, and channel 124 with 95 counts. The slope of the number of counts per channel is 25 cts/CH (i.e., 95cts-70cts).

Determine the portion of the channel where the peak crosses the 80-count level. This point is calculated as (80 cts –70 cts)/(25 cts/CH) or 0.4 channel. Repeat this process for the right side of the peak.

To calculate the FWHM for this peak begin with an initial value of 0.4 CH, start at channel 124 and count to the right as described above, stopping at the channel that has counts greater than the "half-max" value, and add the fraction of a channel calculated for the right side of the peak. Convert this to keV units by multiplying by the slope of the energy equation.

7.4.9 Isotopic Thorium uses ^{229}Th as a tracer analyte. Because ^{229}Th occurs at emission energies from approximately 4800-5100keV at various branching ratios, this peak is expected to be much broader than other isotopic tracer peaks. Therefore, the calculated FWHM value is expected to be greater than that for other analyses, and spectral quality is still sufficient for accurate quantification. Inspection of thorium spectra from analyzed quality control samples (method blanks and laboratory control samples) indicates that a FWHM value equal to or less than 160keV still provides adequate spectral quality. Therefore, for thorium analyses, 160keV is used as the upper FWHM limit. As with the other analytes, if deviation from 160keV is minimal and all other criteria are met, results are reported with a narrative comment and Supervisory approval.

7.5 MAESTRO (MCA CONTROL OPTION IN ALPHAVISION)

Maestro is used to examine a live spectrum (one that is in the process of being acquired). Maestro can be accessed in AlphaVision by selecting the detector on the grid, right click on the mouse, and select [MCA VIEW]. Data acquisition can be stopped and started, and the buffer cleared with the normal menu options. After viewing the spectrum, exit Maestro to return to AlphaVision.

7.6 DATA REPORTING

7.6.1 For the final data package, individual results forms, QA results forms, and results summaries are generated. These reports are created in LIMS after uploading data from the AV database in the R:\USER directory. The data is uploaded by double-clicking on the "LIMS DATA TRANSFER" icon, located on the desktop of the AV computer.
REVIEWING HARD COPY REPORT FORMS
Review all forms for completeness. Crosscheck raw data to the Raw Data Report form. Check yields, activity values, MDC values, and other data quality control parameters. Note any flags that require an explanation in the narrative.

7.6.2 NARRATIVES
For most clients, a general narrative template may be used.

The narrative template gives a summary of the samples included in the data package, including preparatory information, any anomalous situations encountered, any quality control deviations, or any other applicable information which may affect data quality. .

7.6.3 NARRATIVE COMMENTS

- Any time there is a Non-Conformance Report (NCR), a narrative comment and a copy of the NCR is required. Any time data quality objectives have not been met, but the deviation is not great enough to prohibit reporting (i.e., activity in the blank, but not greater than the requested MDC; $1.42 < DER < 2.13$ (warning versus control limits, see SOP 715); requested MDCs not met as a result of small sample aliquot size), a narrative comment is required.
- Minor anomalous situations that have no effect on results usually do not require a narrative comment, but should have a Quality Assurance Summary Sheet (QASS, Form 302). If in doubt, ask the Department Manager regarding the proper way to narrate an anomalous situation.
- **Gross QC failures cannot be narrated without proper NCR documentation!** If any of these types of situations are discovered at the time of reporting, notify the Department Manager and Project Manager immediately. The following types of situations require an NCR and most likely will require a re-extraction: LCS exceeds control limits; activity in blank greater than requested MDC; DER failure > 2.13; contamination of the sample; chemical yield outside the control

limits.

8. CALCULATIONS

Alpha spectra are interpreted and analyzed by a sophisticated mathematical routine that provides for peak identification, peak area analysis, and peak energy determination. Details of calculations performed by the AlphaVision software can be found in the AlphaVision Software Reference Manual (see References Section below, 15.1). Paragon's routine alpha spectroscopic analysis of samples employs an ROI approach to spectrum analysis.

The following raw data generated by the AV system are used for sample calculations: Analyte and Tracer Net Counts and Count Time; associated Background Counts for each ROI; Background Count Time and Detector Efficiency. Further data (including Sample Aliquot, Split and Dilution Data, Percent Solids Data, Tracer Concentration and Amount Added, and Estimates of Total Uncertainty as described in SOP 708) from the preparation and standards spiking process, is taken from the electronic benchsheet and merged with the count data during the data reduction step during reporting. Total Efficiency calculations assume that the nuclide used for the tracer is not native to the sample.

Total uranium (a modification of EPA 908.0 by alpha isotopic summation) is calculated using the isotopic uranium results. The net counts are summed and the background counts are summed for ^{234}U, ^{235}U and ^{238}U. The equations depicted in Sop 708 are then used, substituting the 'summed net counts' for 'net counts' and 'summed background counts' for 'background counts', to determine the total uranium (TU) results:

where:

$$\mathbf{SmplNtCts_{TOT}} = SmplNtCts_{234} + SmplNtCts_{235} + SmplNtCts_{238}$$

$$\mathbf{BkgCts_{TOT}} = BkgCts_{234} + BkgCts_{235} + BkgCts_{238}$$

9. RESULTS INTERPRETATION

9.1 It is essential that appropriate analysis volume and units, tracer information, efficiency files and library files be used to ensure accurate analyses. Results must be reviewed to ensure that the sample type used was appropriate to the analysis type (e.g., Pu, U, Th, etc.) and the report reflects proper sample volume and units.

9.2 All target analyte peaks in the spectrum must be matched to the appropriate radionuclide, and, where applicable, the presence of a given radionuclide should be supported by the presence of other significant alpha emissions from that radionuclide.

9.3 Although most of the analyses are routine, it is important to note that each radionuclide has a different peak shape. This is especially evident when dealing with high level samples, and radionuclides that do not exhibit clear and defined

peak shapes.

9.4 Peak shape is most often negatively affected by an unusual sample matrix, which may contribute to the attenuation of alpha particles. This attenuation can cause the spectrum to be interspersed with small non-descript peaks, which must be accounted for when adjusting ROI's. If there is any question as to the placement of ROI's see the Alpha Spectoscopist or the Department Manager.

9.5 The radionuclide of interest can also effect the spectrum. For example, thorium spectra usually exhibit more non-descript peak shapes, especially in the ^{229}Th and ^{230}Th ROIs. A typical thorium spectrum is included in Appendix A of this SOP. The other radionuclides analyzed by alpha spectrometry exhibit defined and similarly shaped peaks (i.e., plutonium, uranium, americium, curium, and neptunium). Typical plutonium and uranium spectra are also included.

10. PERIODIC MAINTENANCE

10.1 VACUUM PUMP

The vacuum pump shall be checked weekly. The pressure of both vacuum pumps should be below 100 milliTorr. If the pressure is not below 100milliTorr, see the Department Manager. Note in the Alpha Spec Calibration Log Book, the date and pressure of both vacuum pumps. The pump oil level should be above the "MIN" level mark on the pump. Inform the Primary Alpha Spectroscopist if one or both of the vacuum pumps is above 100milliTorr. Changing the oil in the vacuum pump usually will bring the vacuum pressure down to or below 100milliTorr. The vacuum pump oil should be changed annually to prevent any unusual wear on the vacuum pump. Note the oil change date in the Alpha Spec Maintenance Log.

10.2 AIR FILTERS

Air filters are located at the bottom of the MCA NIMBIN. The air filters need to be cleaned annually or as needed by removing and vacuuming. Note the filter cleaning date in the Alpha Spec Maintenance Log Book.

10.3 DETECTOR AND CHAMBER CLEANING

The detector and chamber should be cleaned annually or as indicated by the results of periodic background measurements. Periodic cleaning to reduce background contamination may be performed at any time. To clean the detectors and chambers, always wear gloves to prevent contamination. Remove the detectors with a 5/16" open-end wrench. *Do not attempt to remove the detectors by hand. This can damage the microdot connection!* Clean the chamber using a clean cotton ball and alcohol. The connection between the detector and the chamber needs to be thoroughly cleaned. Using a clean cotton ball and alcohol, clean the detector window, then the top and sides of the detector. Clean the connection on the top of the detector thoroughly. The detector calibrations (Energy, Efficiency, and Background) must be re-calibrated following cleaning of the chamber, sample tray, or detector.

11. QUALITY CONTROL

11.1 CALIBRATION PROCEDURES

Note that the procedure for acquiring any calibration spectrum is the same as that of a normal sample acquisition. All calibrations must be documented in the Alpha Spec Calibration Log. Calibrations for the alpha spec include energy, efficiency, and background calibrations, and are done each week.

11.1.1 ENERGY AND EFFICIENCY CALIBRATION

Eight electroplated sources are used that consist of ^{241}Am and ^{234}U with a small amount of ^{235}U activity. The sources are counted for approximately 35 minutes. The naming convention for these sources is Paragon source ID 97-19-103-XX, where XX is equal to source 01, 02, etc. The energy/efficiency calibrations are typically done first, before the background checks. When the count is finished, the program will compare the locations of the ^{241}Am, ^{234}U and ^{235}U peaks to the primary emissions energies and perform a linear fit of the energy per channel data. This data will then be stored in the appropriate detector file for reference by the analysis program during sample analyses.

11.1.1.1 Load calibration planchets into an octet

11.1.1.2 Pump down detectors

11.1.1.3 Open AlphaVision

11.1.1.4 Click on the black calibration button to the upper left on the AlphaVision screen

11.1.1.5 Right click on detector you are analyzing and select [MCA VIEW]

11.1.1.6 Click [CLEAR], then [GO] for all detectors you are analyzing in that octet

11.1.1.7 Go back to the first detector and press [CTRL]+[LEFT or RIGHT ARROW] to move the cursor to the ^{241}Am peak at channel 249, make sure the peak is at channel 249 +/- 1

11.1.1.8 If the peak is within range select [STOP], then [CLEAR]

11.1.1.9 If the peak is not within range use the small standard screwdriver to move the “e-cal” potentiometer slightly left or right. Repeat Steps 11.1.1.7 and 11.1.1.8 until the ^{241}Am peak is within range.

11.1.1.10 Exit “MCA view”

11.1.1.11 Click [PROCESS] and then [CALIBRATION]

11.1.1.12 In the General screen enter calibration name (Cymmddxx) and template number (the number on the planchet loaded into the detector)

where:

C = Calibration

y = last digit of the year

mm = month

dd = day

xx = detector number

11.1.1.13 Click on finish

11.1.1.14 After 35 minutes, a small window will appear. Select [CALIBRATION] from drop down menu, then select [CALIBRATE], [SAVE], then [CLOSE]. Repeat for each detector. This saves preliminary calibration data to the database.

11.1.1.15 To analyze the calibration, select detector and click on [SPECTRUM] tab on lower left of report window.

11.1.1.16 Zoom in on each peak by clicking and dragging a box around the peak, then right click and select [ZOOM IN].

11.1.1.17 Move the peak identifier of each peak to the top point of the peak by clicking and dragging the identifier.

11.1.1.18 Due to limitations in the AV software, both the peak identifier and the ROI must be adjusted in order for both the energy and efficiency coefficients to be properly saved. Consequently, move any ROI edge over and then back to its original position.

11.1.1.19 Right click and select [INTERACTIVE ROI ANALYSIS].

11.1.1.20 Repeat Steps 11.1.1.15 through 11.1.1.19 for all detectors in the octet.

11.1.1.21 Go back to first detector in the octet and select the [REPORT] tab at the bottom left of the report window.

11.1.1.22 Select [PRINT] icon in upper left of the report window.

11.1.1.23 In the screen that appears, save under calibration name Cymmddxx in the calibration folder.

11.1.1.24 Repeat Steps 11.1.1.21 through 11.1.1.23 for remaining detectors in the octet.

11.1.2 QA TEST FOR ENERGY/EFFICIENCY CALIBRATIONS
The QA test must be completed before reporting any samples through LIMS, otherwise the calibration report page will not show the correct calibration date.

11.1.2.1 Select [QA/QC] button to the upper left on the AV screen.

11.1.2.2 Select the detector number from list on the upper left and select [CALIBRATION ENERGY].

11.1.2.3 Select [CHART] tab from lower left of the report window.

11.1.2.4 Select [QA] from the menu options, then [CALIBRATION].

11.1.2.5 Select [QA], [DISPLAY], [CUSTOM], then [QUARTER]. Make sure that a dot appears on the chart in correct date.

11.1.2.6 Select [REPORT] tab at bottom left of window, then [PRINT] and minimize PDF factory screen.

11.1.2.7 Select [CALIBRATION EFFICIENCY].

11.1.2.8 Select [CHART] tab from lower left of the report window.

11.1.2.9 Repeat Step 11.1.2.5 and select [REPORT] tab at bottom left of window, then [PRINT]. Save as CCymmddxx. Where the "CC" indicates a calibration control chart and all other factors are as defined above.

11.1.2.10 Repeat Steps 11.1.2.2 through 11.1.2.9 for remaining detectors in octet.

11.1.2.11 Record the results of the calibration in the Alpha Spec Calibration Logbook.

11.1.3 BACKGROUND CALIBRATIONS
A blank filter paper is placed on a numbered planchet, one for every detector. The filter paper is counted for 1000 minutes, typically following the energy/efficiency calibrations. Filter papers and

planchets are replaced at least annually.

11.1.3.1 Place the numbered, detector specific, blank filters into the detector chambers. Close the doors and apply vacuum to the chambers.

11.1.3.2 Open AlphaVision. Using the mouse, select the detector(s) that will be started. From the menu bar, choose [PROCESS] then [BACKGROUND].

11.1.3.3 Under General screen, Enter the batch filename as follows: Bymmddxx

where:
B = Background
y = last digit of the year
mm = month
dd = day
xx = M1, M2, M3, etc...for MCB number

11.1.3.4 Select the proper template from the drop-down menu, depending on whether the Octete is designated for U/Th analysis or Am/Pu analysis.

11.1.3.5 Under General screen, Select [NEXT].

11.1.3.6 Under Sample screen select [ADD] and enter sample ID of samples as Bymmddxx, where xx = detector number.

11.1.3.7 Click on [FINISH].

11.1.3.8 A new window will appear with all samples on it. Click and drag desired detector to sample ID. Select [START NOW].

11.1.3.9 After 1000 minutes, a window will appear for each detector.

11.1.3.10 Select [SAVE]. Save as Bymmddxx in calibration folder, where xx = detector number.

11.1.4 QA TEST FOR BACKGROUND CALIBRATIONS
The QA test must be completed before reporting any samples through LIMS, otherwise the calibration report page will not show the correct calibration date.

11.1.4.1 Select [QA/QC] button to the upper left on the AV screen.

11.1.4.2 Select the detector number from list on the upper left and select [BACKGROUND].

11.1.4.3 Select [CHART] tab from lower left of the report window.

11.1.4.4 Select [QA] from the menu options, then [BACKGROUND].

11.1.4.5 Select [QA], [DISPLAY], [CUSTOM], then [QUARTER]. Make sure that a dot appears on the chart in correct date.

11.1.4.6 Select [REPORT] tab at bottom left of window, then [PRINT]. Save as BCmmddxx, where BC = Background Control Chart.

11.1.4.7 Record the results of the calibration in the Alpha Spec Calibration Logbook.

11.2 CALIBRATION ACCEPTANCE CRITERIA

Because calibrations are performed weekly and the accumulation of 30 data points would be impracticable, acceptance criteria for alpha spec calibrations are based on an initial calibration set rather than a mean and standard deviation of a historical population. Acceptance criteria are updated, at a minimum, when detectors are replaced, or when major service to the Octete is performed.

11.2.1 BACKGROUND ACCEPTANCE CRITERIA

For U/Th detectors, the warning limit is set at 500 counts, and the control limit at 750 counts, over the entire spectrum. Since the background calibration is evaluated over the entire spectrum, elevated counts due to ^{228}Th daughter products (expected progeny) will therefore elevate the entire count. Since these progeny occur at energies higher than most analytes of interest, they do not interfere with data quality, with the exception of ^{228}Th. However, as an additional quality assurance measure, any detectors that exceed the warning limit will be evaluated by the instrument operator to assure that all standard Paragon data quality objectives will still be achieved under normal operating conditions.

For all other detectors, the warning limit is 100 counts and the control limit is 150 counts.

11.2.2 BACKGROUND CALIBRATION CORRECTIVE ACTIONS

If the background determination does not pass acceptance criteria, clean the detectors thoroughly. Most frequently, short-lived decay

products are responsible for the failure. Cleaning a detector will often help expedite the process of returning the backgrounds to normal levels. Repeat the background determination. In some cases, the department manager may OK a detector for use if the background counts are elevated as long as the background peaks do not interfere with the analysis performed on that detector. This decision should be clearly documented in the Instrument Calibration Logbook.

11.2.3 ENERGY CALIBRATION ACCEPTANCE CRITERIA
For energy calibrations, the energy calibration equation is used to calculate the energy in keV of the middle channel of the spectrum (256). The initial calibration is used as baseline and the warning limits are set ±40 keV from the initial value. Control limits are set ±50 keV from the initial value.

11.2.4 CORRECTIVE ACTION FOR ENERGY CALIBRATION
With the calibration source in place, manually adjust the E-cal pot. on the front of the chamber until the ^{241}Am peak centroid lies in channel 249. At this point the energy calibration must be repeated.

11.2.5 EFFICIENCY CALIBRATION ACCEPTANCE CRITERIA
The initial calibration is used as baseline and the warning limits are set at 3.33% of the initial value. Control limits are set 5% of the initial value.

11.2.6 CORRECTIVE ACTION FOR EFFICIENCY CALIBRATION
If it is determined that the instrument response has drifted relative to the point of initial calibration, the weekly operating limits and specific method calibrations will be re-established prior to analysis of further samples.

11.3 QC MONITORING
Please refer to SOP 715 for further details regarding preparation and monitoring of method blanks, laboratory control samples, duplicates, and chemical recoveries in samples.

12. DEVIATIONS FROM METHOD

This SOP describes a confidential, proprietary procedure developed by Paragon Analytics. Therefore, there are no deviations from a promulgated method.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 SAFETY
Normal laboratory safety procedures must be followed during this procedure. No special safety requirements are mandated by this procedure.

13.2 HAZARDS
There are no special hazards associated with the conduct of this procedure.

13.3 WASTE DISPOSAL
Samples or sample wastes containing radioactive materials that are not being returned to the client must be disposed of according to Paragon's procedures for disposal of radioactive materials. Contact the site Waste Management Officer for more information.

14. REFERENCES

14.1 AlphaVision Software Reference Manual, Model A-36-BI, Version 5.3.

14.2 ANSI Standard P-N42.23-D2, Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories, Final, February 10, 1995.

14.3 Paragon SOPs 708 and 715.

DOCUMENT REVISION HISTORY

9/11/06: Incorporates instructions for the use of AlphaVision32 version 5.3, removed LIMS reporting instructions, added reference to LIMS program specifications, and referred to the re-verification of calibration sources. Added DOCUMENT REVISION HISTORY. Attached Forms.

8/31/07: Removed most actual calculations from Section 8 and referenced SOP 708 instead.

TABLE 1

COMMON ENERGIES AND APPROXIMATE CHANNEL LOCATIONS
(to assist the user during calibrations, QA checks and initial spectral interpretation)

Nuclide	Energy (keV)	Target Channel
Am-241	5485	249
Am-243	5275	228
Cm-242	6112	311
Cm-244	5805	281
Pu-242	4900	190
Pu-238	5499	250
Pu-239	5155	216
Th-228	5423	242
Th-229	4845	184
Th-230	4687	169
Th-232	4010	101
U-232	5320	232
U-234	4775	178
U-235	4396	140
U-238	4196	120

NOTE: Actual Target Channels will vary slightly for each detector; peak energy and channel matching is done weekly with the energy calibration process in AlphaVision.

TABLE 2

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Energy Calibration	Weekly	The initial calibration is used as baseline Warning limits are set ±40keV from the initial value Control limits are set ±50keV from the initial value	Record failure in the Alpha Spectroscopy Maintenance Log. Check source integrity, detector configuration, recount and reprocess: Tag detector off-line; Determine and correct problem; or Narrate why condition is acceptable
Efficiency Calibration	Weekly	The initial calibration is used as baseline Warning limits are set at 3.33% of the initial value Control limits are set 5% of the initial value	Record failure in the Alpha Spectroscopy Maintenance Log. Check source position and integrity, detector configuration, recount and reprocess; Tag detector off-line; Determine and correct problem; or Narrate why condition is acceptable
Background Calibration	Weekly long background	U/Th detectors - the warning limit is set at 500 counts & the control limit is set at 750 counts, both over the entire spectrum. All other detectors - the warning limit is 100 counts and the control limit is 150 counts.	Clean chamber and detector, repeat check; Tag detector off-line; Determine and correct problem, re-establish limits; or Narrate why condition is acceptable
Vacuum check	Weekly	<100 milliTorr	Check/replace seals; locate and repair leak; or call service
Chemical Yield	Each sample	Each sample meets current control limits for analysis	Re-prep; or Qualify or Narrate why condition is acceptable
Regions of Interest (ROI)	Adjust ROI as needed	ROI is properly set, tailing does not compromise quantitiation	Adjust ROI's to fit identified peaks; For tailing, cleanup or re-prep and recount affected samples, consult with Supervisor; Qualify or Narrate why condition is acceptable
Spectral Interferences	Evaluate each spectrum for spectral interferences	Interfering activity does not compromise quantitation	Recount; Clean-up, re-prep/ recount affected samples; Consult with Supervisor or Department Manager; Determine and correct problem; or Qualify or Narrate why condition is acceptable

NOTE: SOP 715 contains acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

APPENDIX A

SAMPLE SPECTRA

The following three spectra examples demonstrate a typical uranium, thorium and plutonium spectra. Note that americium, curium, and neptunium spectra are somewhat similar to the plutonium spectrum, in relation to their peak shapes.

The thorium spectrum contains four analytes. The difficulty with the placement of the ROI's for ^{229}Th and ^{230}Th is due to close proximity of the two peaks. The small peaks to the right of the ^{228}Th peak are ^{228}Th daughter products, which are expected progeny.

The plutonium spectrum contains three analytes, with no other obvious peaks present. Note that uranium, americium, curium, and neptunium spectra should also contain no other peaks, other than those accounted for by existing ROIs.

In detectors used for Uranium and Thorium analyses, persistent background peaks are typically seen in the higher energy regions of the spectra. These peaks are associated with natural decay progeny and do not interfere with U and Th analyses except in the case of ^{228}Th, where the increased detector background is unavoidable and typically results in elevated ^{228}Th MDC values.

Paragon Analytics

FORM746r7.xls (2/13/06)

Alpha Spectrometer Instrument Run Log

Date:_____

Detector	Batch ID	Sample ID	Iso/Matrix	Duration	Initial	Print/ Reviewed

Detector	Batch ID	Sample ID	Iso/Matrix	Duration	Initial	Print/ Reviewed

Notes:

Reviewed by:
Date:

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 715 REVISION 15

TITLE: REVIEW OF RADIOANALYTICAL DATA

FORMS: 302, 313, 631, 15001, 15002, 15003, 15004, 15005 **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7/21/06
QUALITY ASSURANCE MANAGER _____ DATE 7/21/06
LABORATORY MANAGER _____ DATE 7-21-06

HISTORY: Rev0, 9/17/92; Rev1, 10/29/92; Rev2, 5/3/93; Rev3, 7/27/93; Rev4, PCN #14, 10/15/93; Rev5, PCN #95, 1/19/94; Rev6, PCN # 205, 4/5/94; Rev7, PCN #272, 9/20/94; Rev8, 4/7/96; Rev9, 4/29/97; Rev10, 10/8/99; Rev11, 3/26/02; Rev12, 8/26/02; Rev13, 3/28/03; Rev14, 5/17/04; Rev15, 7/24/06.

re-released w/o revision 3/13/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform data review and evaluate the overall quality of results generated by radiochemistry analysis systems, including: gamma spectrometry, alpha spectrometry, alpha scintillation, liquid scintillation and low background alpha/beta analyses. This procedure is applicable to all radiochemistry analytical results generated at Paragon.

2. SUMMARY

Radiochemistry analysis results are generated by the Paragon Laboratory Information Management System (LIMS), from raw data for each of several types of radioactivity measurement devices at the conclusion of the analysis procedure. The data undergo a series of redundant reviews by qualified analysts according to appropriate data review checklists before the final report is released to the client.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to the appropriate SOP and to complete all documentation required for review.

3.2 It is the responsibility of the analyst performing the review to be familiar with the Paragon LIMS Program Specifications, which provide the lab's default acceptance criteria as well as any client-specific requirements.

3.3 At least one of the redundant reviews is to be carried out by a senior analyst who is cognizant of the capabilities and limitations of the procedure under review. All data review is performed by personnel in the laboratory who have demonstrated the familiarity with and the ability to carry out this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the tracking sheet and data review checklist, indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented in either a Quality Assurance Summary Sheet (QASS; Form 302) or Non-Conformance Report (NCR; Form 313), which must then be reviewed and approved by the appropriate Supervisor or Department Manager.

4. APPARATUS AND MATERIALS

This procedure requires access to the Work Order, Project Specific Requirements, any work order change forms, the benchsheet associated with the samples, and any QASSs, NCRs, or Sample Condition Forms (Form 631). Additionally, the instrument raw data, calibrations, report forms, and Data Review Checklists are required (Form 15001, 15002, 15003, 15004 or 15005). A calculator may be needed to perform manual calculations during the review process.

5. REAGENTS

Not applicable.

6. PROCEDURE

6.1 This procedure begins upon completion of the preparation of the samples. This procedure requires the use of the data review checklists, attached to this SOP. Review items on the checklist that are self-explanatory must be completed, but are not discussed further in this SOP. Items that require further explanation or interpretation are discussed below.

6.2 Before proceeding, the analyst must review the LIMS program specifications to ensure compliance with either the Paragon default requirements or the client's project-specific requirements, as appropriate.

6.3 The data review checklist is generally initiated by the preparation technician, prior to delivering samples to the instrument lab. The checklist accompanies the analytical documentation throughout the analysis and reporting process. Before counting, instrument lab personnel should perform a second review of the preparation section of the checklist. Likewise, each section of the review checklist should receive both the first and second reviews before the work described in the next section is initiated.

6.4 Review the benchsheet for completeness and correctness. Generally, this review is done to ensure that the benchsheet accurately reflects the work performed on the samples.

6.4.1 The benchsheet should contain appropriate entries in all necessary fields. Otherwise the value "NA" should be entered, or the field should be "Z'd out".

6.4.2 On the first iteration of the benchsheet where the analyst's initials appear in a given field, the initials must be hand-written to authenticate the LIMS record.

6.4.3 The Quality Assurance Summary Sheets (QASSs), Non-Conformance Reports (NCRs), and Sample Condition Forms should be reviewed to ensure that they are technically and procedurally reasonable, and that they reflect the work that was actually performed on the samples.

6.4.4 Sufficient supporting documentation should accompany the benchsheet so that all entries can be properly verified. These may include "Percent Moisture" determinations, Drying/Grinding Sheets, Distillation Logs, etc.

6.4.5 Any non-routine calculations, such as those done with a common digestion and subsequent splitting of the digestate for multiple analyses, must be verified manually before proceeding.

6.5 Following instrument analysis, a review of the count data is performed.

6.5.1 In addition to the specific questions asked on the data review checklist, the analyst is responsible for ensuring that the calibrations factors used in the analysis appropriately correspond to the presentation of the sample (e.g. ringed planchet calibrations for ringed planchet sample prep, etc.).

6.5.2 All data entered into the instrument, such as collection date for gamma spec, or residual mass for Gas Flow Proportional Counting (GFP), must be verified against the workorder or benchsheet, as appropriate.

6.5.3 The analyst must ensure that all data quality objectives, whether Paragon standard requirements or client-specific requirements, have been met. This may include the evaluation of chemical yields, spike recoveries, blanks activity, negative activity results, duplicate results, etc, as described below. It is important that this verification be performed as soon as possible after analysis, so that any necessary

corrective action can be expedited. Out of control results shall normally be cause for re-extraction and re-analysis of an analytical batch and shall be recorded on a NCR (SOP 928). Where EPA drinking water methodologies are required, LCS and matrix spike recoveries are to be within ±20% of expected values.

6.6 Calculations for Review.

6.6.1 The LCS accuracy:

$$LCS\% = \frac{OBS * 100}{KNV}$$

where: OBS = observed value
KNV = known value.

6.6.2 The Matrix Spike Accuracy:

$$\text{MS\%} = \frac{(MS - SR)}{SAV} * 100$$

where: MS = matrix spike result
SR = native sample result
SAV = spike added value

The above LCS and Matrix Spike values are decay corrected to common reference dates (usually sample collection date for the matrix spike and the count date for LCS) and reported in consistent units for the associated sample or batch.

To avoid confusion with calculated chemical yields, the analyte spike recovery may sometimes be requested to be reported in terms of "Relative Bias". This term is calculated by subtracting 100% from the "% accuracy" results calculated above. The terms "relative bias" and "% accuracy" are equivalent and can be used interchangeably, with equivalent adjustments to established control limits.

6.6.3 Method Blank

6.6.3.1 The sample specific minimum detectable concentration (MDC) will be used to determine the acceptability of blank results. When a batch of samples contains sample volumes that are of comparable size, the blank result will be calculated using the mean aliquot for the batch. On the other hand, the blank volume will be reported as a volume of 1 (one) when a batch of samples contains samples of variable volume (i.e. an order of magnitude difference). A narrative comment will be made directing the client to evaluate the validity of the blank result relative to the individual sample volumes in the case of a wide range of sample volumes. The following is the suggested wording for the narrative comment:

> "Various aliquot sizes were taken for the preparation of these samples. By convention, the results for the batch blank and LCS are determined based on a 1.0g/L aliquot size. Therefore, the blank results are not directly comparable to the sample results. Mathematically dividing the reported blank activity and MDC by a given sample's 'final aliquot' will convert the blank results to a comparable form for that sample."

6.6.3.2 If the blank activity falls above the calculated MDC, the effect on the data will be assessed. An NCR shall be initiated for any samples showing activity less than 5 times the blank activity. These samples shall generally be prepared for reanalysis, except by direction from the department manager. Any samples showing activity less than the client's requested MDC may be reported as acceptable results, with a narrative comment.

6.6.4 Review the precision of results for duplicate(s) in the sample batch and the corresponding sample(s).

The 2σ duplicate error ratio (DER) is calculated as:

$$DER = \frac{/S - D/}{2 * \sqrt{\sigma_S^2 + \sigma_D^2}}$$

where: S = Sample Result
D = Duplicate Result
σ_S = The One-Sigma Sample Total Propagated Uncertainty (TPU)
σ_D = The One-Sigma Duplicate TPU

A 2σ duplicate error ratio in excess of 1.42 shall be noted in the report narrative as being in the warning range. A 2σ duplicate error ratio in excess of 2.13 shall be considered to be out of control and is cause for re-extraction or re-analysis of the sample(s), unless extenuating technical circumstances prevail and are noted in the narrative.

For gamma spectroscopy analyses where several nuclides are reported, 75% of the nuclides must meet the DER requirements.

6.6.5 At the client's request, where the sample result is greater than five times the associated MDC, the duplicates may be analyzed by the Relative Percent Difference (RPD), which is calculated as:

$$RPD = \frac{(|Sampleresult - Duplicateresult|)}{\left(\frac{Sampleresult + Duplicateresult}{2}\right)} * 100$$

An RPD greater than the client's requested acceptance criteria shall be noted in the report narrative. Paragon does not control on RPD. Where the sample activity is less than five times the calculated MDC, the RPD report will be flagged "NC" for "not calculated". This situation should also be narrated.

For gamma spectroscopy analyses where several nuclides are reported, 75% of the nuclides must meet the RPD requirements.

6.6.6 Negative sample results are compared to the associated Total Propagated Uncertainty (TPU).

6.6.6.1 If the magnitude of the negative result is greater than the associated 2σ TPU and less than the 3σ TPU, a narrative comment is made bringing this fact to the client's attention and stating the expected statistical frequency of this event.

6.6.6.2 If the magnitude of the negative result is greater than the associated 3σ TPU the result may be reported, with the approval of the department manager, and with a narrative comment explaining the situation and any limitations to the

usability of the data. At the manager's discretion, an NCR may be initiated and corrective action taken.

6.6.7 A reported zero "0" value for the MDC requires a narrative comment.

Following ANSI N42.23, the TPU is reported to two significant figures. The MDC is rounded to the same decimal place as the TPU. In practice, in samples with significant activity including the LCS, this can result in a reported value of "0" for the MDC.

6.7 Before reporting the data, a complete second review is performed. All steps outlined in Section 6.5 are repeated. The data review checklist is initialed and dated.

6.8 After the data is reported, per the appropriate analytical SOP, the case narrative is written, which summarizes the analytical process. It should address situations requiring a QASS and NCRs. Data qualifiers should be addressed. The narrative should be signed and dated.

6.9 After the data package is complete, the data compiler completes, initials and dates the data review checklist, which is then independently reviewed, initialed and dated by another qualified analyst.

6.10 MANUAL RE-CALCULATION OF REPORTED RESULTS

6.10.1 Once per month, manual calculations are performed on a sample for each method. The results are stored separately from the batch. The exception is where calculations are performed by vendor-supplied, proprietary software that is inaccessible to the analyst. In these cases, such as the SEEKER® gamma spec software, the manual calculation is performed annually.

6.10.2 Non-routine prep situations require a manual calculation to be performed with the analytical batch. This calculation should remain with the batch and should be filed with the work order.

6.11 Upon satisfactory completion of the final review, the final review analyst will sign the narrative and forward the data package to Reports Management.

6.12 REVIEW OF INTERNAL PROFICIENCY DEMONSTRATION DATA
Blank spike trials are performed for the demonstration of method proficiency. A memorandum from the primary operator should accompany the results stating that the results for the specified method meet Paragon standard limits and are acceptable. Upon approval from the Department Technical Manager, the

memorandum and accompanying data are given to the QA Department, with copies to the applicable Supervisor.

7. QUALITY CONTROL

Sample results shall not be considered final until the first and second reviewers have approved the results by initial and dating the data review sheet and the case narrative has been signed. All necessary supporting data shall be forwarded with the results to Reports Management. An electronic copy of the completed data review checklist and in-house documentation, as well as a copy of the final report, will be kept by the laboratory and will be made available internally as needed.

8. REFERENCES

This is a proprietary procedure developed by Paragon. No deviations from a promulgated method are to be noted.

DOCUMENT REVISION HISTORY

7/24/06: Data review checklists now controlled and included as attachments (some items addressed in the checklists are no longer discussed in the body of the SOP). Other clerical editing performed. DOCUMENT REVISION HISTORY section added.

APPENDIX A

TABLE 1

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per batch or 5% frequency	Activity less than MDC, RMDC or 1/5 associated sample activity	Recount; re-prep and/or recount affected batch or samples; determine and correct problem; or qualify or narrate why condition is acceptable
Laboratory Control Sample (LCS)	One per batch or 5% frequency	Meets established control limits	Recount; re-prep and/or recount affected batch or samples; determine and correct problem; or qualify or narrate why condition is acceptable
Duplicate Sample (DUP)	One per batch or 10% frequency	Warning range: 2 sigma DER >1.42 and Control limit: 2 sigma DER >2.13	Narrate 2 sigma warnings; re-prep and/or recount affected samples for 2 sigma failures; determine and correct problem; or qualify or narrate why condition is acceptable
Matrix Spike (MS)	One per batch for analyses which do not otherwise have chemical yield determination	Paragon does not control on matrix spike samples. Matrix spikes are used only as an indication of matrix interference	Narrative comment
Chemical Yield	Each sample	Meets established control limits	Re-prep; notify client; qualify or narrate why condition is acceptable

APPENDIX B

RADIOCHEMISTRY DATA QUALIFIERS (FLAGS)

J – The reported result is an estimated value.
R – The result is rejected by the laboratory, but is included in the report.

U – The reported activity is less than the calculated MDC.
LT –The reported activity is greater that the calculated MDC, but is less than the client's requested MDC.

M – The client's requested MDC was not met, and the sample activity is below the achieved MDC.
M3 – The client's requested MDC was not met, but the sample activity is above the achieved MDC.

B – The activity in the method blank is greater than the calculated MDC.
B3 – The activity in the method blank is greater than the calculated MDC, but less than the client's requested MDC.

H – The LCS recovery is above the upper control limit.
L – The LCS recovery is below the lower control limit.
P – The LCS passes the established control limits.

N – The matrix spike recovery is outside the established acceptance criteria.

W – The Duplicate Error Ratio is above the 1.42 warning level, but below the 2.13 control level.
D – The Duplicate Error Ratio is above the 2.13 control level.
+ – The Relative Percent Difference exceeds the established acceptance criteria.
NC – Not calculated.

Y1 – Chemical yield is in control at 100 – 110%. Quantitative yield is assumed.
Y2 – Chemical yield is outside established control limits.
LB – The initial sample fraction for ICP yield analysis contains less than the amount of carrier known to be added to the sample, between 85% and less than 100% of the known value. To minimize the potential low bias in the final sample results the chemical yield is calculated using the amount of carrier known to be added to the sample.
15% - The initial sample fraction for ICP yield analysis contains less than the amount of carrier known to be added to the sample, less than 85% of the known value. To minimize the potential effect on the data quality the chemical yield is calculated using the amount of carrier known to be added to the sample.

Z – In the initial ICP determination of the carrier analyte, before the carrier is added to the sample, the calculated result is less than zero. To minimize a low bias in the final radioanalytical results, a value of zero is used in the calculations.

* - Aliquot basis “as received”, report basis “dry weight”
# - Aliquot basis “dry weight”, report basis “as received”

Flags specific to Gamma Spectroscopy
SI – Spectral interference.
SQ – Poor spectral quality.
TI – The nuclide is tentatively identified, as it does not meet one or more of the normal identification criteria.
NR – Not reported.
G – The sample density is outside the ±15% comparison to the calibration standard.

APPENDIX C
FORMS & CHECKLISTS

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAI W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

NCR # _____ *Paragon Analytics*

NON-CONFORMANCE REPORT

Initiated by _____ Date _____ Method/Procedure _____

Reason: ___ Non-Conformance Work Orders Affected _____

___ Client Inquiry Batches Affected (optional) _____

___ Other _____ Clients _____

SECTION I TYPE OF EVENT (circle as appropriate) Explanation: _____

___ 1. LCS / Surrogate / IS / Tracer or Chemical Yield Criteria Not Met

___ 2. Calibration Criteria Not Met (ICAL, ICV, CCV)

___ 3. Method Requirements Not Met (HTV, MB, ____)

___ 4. Deviation from LQAP/SOP (i.e., PAR criteria not met)

___ 5. Client Criteria Not Met (MDC, DER, _____)

___ 6. Equipment Failure or Laboratory Incident / Error

___ 7. Other _____

Actions to Prevent Recurrence (Retrain, etc.): _____

SECTION II NOTIFICATION

Client Contacted? (Y / N) Name:_____ Date:_____ Time: _____

SECTION III CORRECTIVE ACTIONS

___ 1. Submit for Re-Prep. or Clean-up

___ 2. Re-analyze

___ 3. Resubmit Data (hc, edd, narrative)

___ 4. Document in Narrative

___ 5. Other _____

Approved by: _____ DPM _____ PM

SECTION IV REQUEST FOR REWORK

Initial Batch ID: _____ Date: _____

Reworked Batch ID: _____ Date: _____

Outcome: _____

Approved by: _____

Matrix Effect or Elevated / Sample Activity Suspected? (circle applicable)

SECTION V DISPOSITION **Use as is** **Repair** **Reject**

SECTION VI COMMENTS _____

SECTION VII APPROVAL SIGNATURES

Project Manager (PM) _____ Date _____

Department Manager (DPM) _____ Date _____ (Verification of Disposition)

QA Manager _____ Date _____

SECTION VIII DISTRIBUTION ____ PM ____ Dept. Manager ____ Lab Director ____ Rpt.Group or ____ Rad

FORM 313r15.doc (7/18/04)

Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Actinides Preparation / Alpha Spectroscopy Tracking Sheet & Data Review Checklist

Form 1500 Tr 1 (7.07.06)

	Tests(s)			
Prep Batch ID	Am241	IsoCm/Am	IsoPu	IsoTh
	IsoU	Np	Po	Th/Ac
Analytical Batch ID	Pu242	Th229	U232	U-Tot

Matrix		
Water	Soil	Sludge
Liquid	Solid	Filter
Other:		

As Applicable (Check WIP)
IsoPu 239/240
IsoU 233/234
IsoU 235/236

QC Associated with which WO?

QC #	PA WO	Client / Project	Fax Due Date	Ship Due Date	Requested MDC	Calculated Count Time	Report Level	CC	ROI Check/ Adjust	Reported	Forms	Pkg Made	Narr	Final Rev Complete	Date Received in Lab & misc. comments

Preparation and Pretreatment 1st Review _____ Date _____ 2nd Review _____ Date: _____

_____ Project Instructions, Work Orders & WO Changes included and followed? _____
_____ If necessary, were multiple QC batches created? (diff projects/clients/MDCs/analytes of interest, etc.) _____
_____ Do these clients require: Dup - MS - MSD? _____ Nuclide ID
_____ Have all the requested samples (all matrices) been prepared? If no, then explain_____ _____
_____ Appropriate method blanks(5% freq)/LCS(5% freq.)/Dup (10%freq)? _____
_____ Have all documents (benchsheets, worksheets, etc.) been filled out completely and reviewed? _____
_____ Spiking/Tracing solutions: Human initials, exp dates written out? _____
_____ Are all QASS 's noted on the benchsheet and included? _____ Tracer _____ _____
_____ Are all NCR's noted on the benchsheet, completed, approved and copy included? _____
_____ Current SOP #'s used and documented on benchsheet (w/ rev #'s)? _____ Spike _____ _____
_____ Non-routine pretreatment performed, documented and referenced on benchsheet? _____
_____ Are sample volumes/aliquots cross-checked, correct, and entered in benchsheet? _____
_____ Matrices, units and reporting basis correct? If not, are they documented & QASS included? _____
_____ Is a sample condition form/grinding sheet/drying sheet included with benchsheet? _____
_____ Were the samples relinquished & received properly in the LIMS internal COC? _____
_____ Has the status sheet been updated to C?

Raw Data Review 1st Review _____ Date _____ 2nd Review _____ Date: _____

_____ Position check performed and all samples correctly loaded? _____
_____ Sample ID and Batch ID correct and in the correct format? _____ Yield Summary Sheet Done?_____
_____ Does the ROI Set Name = Program Spec requirements? _____
_____ Does the Nuclide Library = ROI Set Name? _____
_____ Is the FWHM for the tracer 40-100 keV (Thorium = 40-160 keV)? _____
_____ Tracer counts >than 400? If no, has dept mgr. approved? _____
_____ Bkg, Calib file names valid/current ? Calibration equation: offset = 3000 +/- 100 keV; gain = 10 +/- 1? _____ Run Log Date Page
_____ Is the spectrum free of gain shift / other spectral quality issues ("Branching Ratio" = 99.5 - 100.5%)? _____
_____ Is the dead time < 5%? _____
_____ Have the detection limit requirements been met? _____
_____ Chemical yield and QC parameters checked?(Blank,LCS,DER,etc) _____ _____ _____
_____ ROI's correctly fitted to spectral data? _____
_____ Are unknown peaks present? If so, do they compromise qualification/quantification? _____ _____ _____
_____ Is the Th-230 "contaminated tracer" function properly applied? Correction factor = _____. _____
_____ Instrument QASS/NCR's & anomalous situations documented? _____
_____ Were any samples recounted? Notation regarding reason of recount made on benchsheet? _____ _____ _____
_____ Run log present, correct, and complete? _____
_____ Has the data been transferred to LIMS?
_____ Has the status sheet been updated to CC?

Reporting/Packaging 1st Review _____ Date _____ 2nd Review _____ Date: _____

_____ Project Instructions/Specs, Work Orders & WO Changes followed? _____
_____ Narrative proofread and signed? _____
_____ QASS/NCR's & anomalous situations documented in narrative? _____
_____ Client Name, Project Name and Number correct? _____
_____ Is results summary included ? Are sample ID and dates correct? _____
_____ All results for requested samples present? _____
_____ Matrices, units and reporting basis correct? _____
_____ Are there samples with negative activity? Is negative activity > 2σ TPU (NARR) / > 3σ TPU (NCR)? _____
_____ Are there any samples with an MDC of zero caused by ANSI rounding of the TPU? _____
_____ Raw data summary included? Are the count rates, yields, count times correct? _____
_____ Does the raw data match the data summary? _____
_____ Benchsheet completed properly (Z-out, supercede/in-conjunction with, NCR#'s recorded, etc.)? _____
_____ Packaging correct for client report level? _____
_____ Data package inventory sheet prepared, printed, and included with package? _____
_____ For non-routine prep, analysis: is a successful manual calculation provided (within 3%)? _____
_____ Has the status sheet been updated to F ?

General Comments:

Gas Flow Proportional Counting Tracking Sheet & Data Review Checklist

Batch ID _____

Analysis:

Gross α/β	Cl-36	I-129	Sr-89/90	Other:
Ra-228	Sr-90	Ra-226	Total Ra	

Matrix:

Water	Soil	Solid	Other:
Sludge	Liquid	Filter	

QC #	PAI WO#	Client	Due Date	Req. MDC	Rpt Lvl	C C	PD	Final	Done	Comment

Preparation and Pretreatment **Form 15002r1 (7/7/06)**

1st review____ **date**_____ **2nd review**____**date**_____

____ ____ Project Instructions, Work Orders & WO changes included and followed?
____ ____ Benchsheet completed and reviewed?
____ ____ Are there multiple QC associations in this batch? If so, are they indicated at the top of the page?
____ ____ Do these clients require additional QC (LCSD, MS, MSD) ?
____ ____ Appropriate frequency of LCS(s) (1/20), Blank(s) (1/20), and Duplicate(s) (1/10) per batch?
____ ____ Non-routine pretreatment performed, documented and referenced on benchsheet?
____ ____ Anomalous condition(s) requiring QASS/NCR?
____ ____ Is residue mass within calibrated limits for Gross α/β? Within limits for Tot. Rad?
____ ____ If Gross Alpha/Beta, do EPA drinking water protocols apply? (Res. Mass: ___mg<x< 100mg; Th230; 72 hrs desiccation)
____ ____ Matrices, units, and reporting basis correct? If not, are they documented & QASS included?
____ ____ Are all the samples prepped for this WO/matrix? If not, explain_____
____ ____ If applicable, are the chemical recoveries within control limits? ICP Data Reviewed?
____ ____ Are the Sample Condition Form/grinding sheet/drying sheet complete/present/reviewed?
____ ____ Current SOP #'s used and documented on benchsheet?
____ ____ Were the samples relinquished & received properly in the LIMS internal COC?
____ ____ Were the planchets visually inspected upon receipt? If so, is there uneven deposition/unusual appearance?
1. ____ ____ Is the expiration date of the spiking standard entered on the benchsheet?
2. ____ ____ Do these samples require ingrowth? (Tot. Rad or Sr) COUNT DATE: _____
3. ____ Is the status sheet updated with a C?

Raw Data Review

1st review____ **date**_____ **2nd review**____**date**_____

____ ____ Runlog complete and included in package?
____ ____ Sample position on runlog, benchsheet, and raw data agree?
____ ____ Does Daily QC pass for the detectors used?
____ ____ Are the detectors used for analysis calibrated?
____ ____ Residual mass entered correctly for applicable analyses?
____ ____ Are Weekly BKG calibrations current and in control?
____ ____ Efficiency and Attenuation logfile(s) current & proper for the analysis?
____ ____ For Beta only analyses, are alpha CPM < 10X alpha BKG CPM? If not, QASS/NCR required.
____ ____ Were any samples recounted? Notation regarding reason of recount made on benchsheet? File names to be used marked below?
____ Is the status sheet updated with a CC?

Reporting / Packaging **Analytical Run ID:** _____

1st review____ **date**_____ **2nd review**____**date**_____

____ ____ Have all columns on the raw data report been verified?
____ ____ Are LCS(s) and Method Blank(s) within control limits?
____ ____ DER(s), MS within control limits?
____ ____ Client name, Project Name, matrix, units, and sampling dates correct?
____ ____ All results for requested samples present?
____ ____ Calculation Verification? Manual/Spreadsheet (Date:_____)
____ ____ Do sample MDC's meet client's requested MDC?
____ ____ Is there an MDC=0? If so, include in narrative.
____ ____ Are there samples with negative activity? Is the magnitude of the negative activity > 2σ TPU (NARR) / >3σ TPU (NCR)?
____ ____ Does the narrative accurately and completely describe the analytical process? Applicable QASS/NCR documented in narr.?
____ ____ For non-routine prep, analysis: is a manual calculation provided (within 3%)?
____ Is the status sheet updated with a F?

Gamma Spectroscopy Tracking Sheet & Data Review Checklist (Form 1500Sr1, 7/7/06) **Batch ID** _____

Test(s)		
	Gamma Spec	Ra-226
	Other:	

Matrix		
Water	Soil	Sludge
Liquid	Solid	Filter
Other:		

	qc #	PAI WO	Client / Program	Prelim Due Date	Final Due Date	Special MDC	Count Time	Report Level	prep	frms	pkg	nalr	final	done	Library & Comments
1															
2															
3															
4															
5															*PDF due* __/__/__
6															

Preparation and Pretreatment **1st Review** _____ **Date** _____ **2nd Review** _____ **Date:** _____

- ____ Project Instructions, Work Orders & WO Changes included and followed? ____
- ____ Are all samples present? Are all samples logged in for all test nicknames? (i.e. Geo. 17 & 26) ____
- ____ Do these clients require additional QC? ____
- ____ Appropriate method blanks(5% freq)/LCS(5% freq.)/Dup (10%freq)? ____
- ____ Has the benchsheet been filled out completely and reviewed? ____
- ____ Does the benchsheet give the correct sample geometry? Spike & spike volume listed? ____
- ____ Are all QASS 's and NCR's noted on the benchsheet and included? ____
- ____ Current SOP #'s used and documented on benchsheet (w/ rev #'s)? ____
- ____ Non-routine pretreatment performed, documented and referenced on benchsheet? ____
- ____ Are sample volumes/aliquots correct and entered in benchsheet? ____
- ____ Where required, are the % moisture determinations provided? ____
- ____ Matrices, units and reporting basis correct? If not, are they documented & QASS included? ____
- ____ Is a sample condition form/grinding sheet/drying sheet/prep wrksht included with the benchsheet? ____
- ____ For Ra-226 ingrowth is complete on (date)_____ ____
- ____ Were the samples relinquished & received in the LIMS internal COC? Status sheet updated? ____
- ____ Has the status sheet been updated to C?

Raw Data Review **1st Review** _____ **Date** _____ **2nd Review** _____ **Date** _____

- ____ Are Blank/LCS in control? Recovery checked by spreadsht, samples taken to sample closet? ____
- ____ Is there 'Dead Time' >10%? ____
- ____ Is a peak shift evident from the 911KeV, 1460KeV, 511KeV or other peak in the pk srch results? ____
- ____ Requested detection limits been met? ____
- ____ Blank counted as long as longest sample count? ____
- ____ Are the instrument performance checks current and within control limits? ____
- ____ Has the benchhsheet been filled out completely and properly? ____
- ____ Have all the requested samples been analyzed? ____
- ____ Are the Sample IDs and Batch ID correct? Format Correct? ____
- ____ Are the sampling dates correct (start/stop)? ____
- ____ Does the Sample Size value match the benchsheet? ____
- ____ Matrices, units, and reporting basis correct? ____
- ____ Spc. File match run log? ____
- ____ Is the run log completed properly? Does it match the benchsheet? ____
- ____ Does the runlog note puck used? (Geo. 7 & 8) or is orientation of sample noted? (Geo. 9) ____
- ____ Energy Cal date = Ct. Date? FWHM Date < 1yr. old? ____
- ____ Sensitivity = 1.00? Sigma Multiplier= 2.00? Search Range= 80 - 4000? Collection Effic. = 1? ____
- ____ Bkg. File Correct? Bkg Date < 1 week old ? ____
- ____ Efficiency File Correct? (DXX)(ShXX).eff < 1 yr old? ____
- ____ Library correct? ____
- ____ Are spectra included for BJC/LANL ESH17 filter samples? ____
- ____ Are the unknown peaks => 5 times the critical level identified? ____
- ____ Has the status sheet been updated to CC?

NARR. COMMENTS:

# samples	
DUP on	
M or M3	
Analytes:	
neg-ACT	
TI	
G, BIAS	
SI	
J	
ingr. Start	
ingr. Stop	
D,W,NR	
RPD	

ANALYTICAL RUN ID:

Reporting/Packaging **1st Review** _____ **Date** _____ **2nd Review** _____ **Date:** _____

- ____ Are the QC parameters in control? (Blank, LCS, DER) ____
- ____ Are all anomolous conditions recorded on an NCR or QASS? ____
- ____ Is the calibration and traceability data included for high level packages? ____
- ____ Are there samples with negative activity? Is negative activity > 2σ TPU (NARR) / > 3σ TPU (NCR)? ____
- ____ Are the client name. project ID and sample IDs correct? ____
- ____ Are the spec. codes the same as on the raw data? ____
- ____ Flags OK? TI, SI ____
- ____ Is there an MDA of 0? If so, is it documented in narrative? ____
- ____ Does the narrative note if a duplicate count was performed due to limited sample volume? ____
- ____ QASS/NCR's & anomalous situations documented in narrative? ____
- ____ Has inventory sheet been printed? Is PDF created if needed? ____
- ____ Has the narrative been proofread and signed? Is W.O. track. sheet complete/turned in? ____
- ____ Has the status sheet been updated to F?

Liquid Scintillation Tracking Sheet & Data Review Checklist (Form 15004r1, 7/7/06)

Prep Batch ID _____

ANALYSIS:

H-3	C-14	Tc-99	Ni-63	Other:
Pb-210	Pm-147	Pu-241	TotAct	
Fe-55	Rn-222			

MATRIX:

Water	Soil	Solid	Other:
Sludge	Liquid	Oil	

QC #	PAI WO#	Client	Req. MDC	Count Time	Due Date	Rpt Lvl	C C	P D	N	F	D	Comment

Preparation / Pretreatment

(1st Review _____Date _____) (2nd Review _____Date _____)

____ ____ Has the benchsheet been filled out completely?
____ ____ Does the benchsheet accurately reflect non-routine sample volumes and aliquots?
____ ____ Have all the requested samples (matrices) been prepared? If no, then explain_____.
____ ____ Are all the samples present that are listed on the benchsheet?
____ ____ Is a sample condition sheet/grinding sheet/drying sheet included with the benchsheet?
____ ____ If the samples are solid matrix, does a %Moisture worksheet accompany the benchsheet?
____ ____ If necessary, is yield data included, reviewed, and signed?
____ ____ Are the necessary QASSs included and documented on the benchsheet?
____ ____ Appropriate reagent blanks(per method)/method blanks(5% freq)/LCS(5% freq.)/Dup (10%freq)?
____ ____ Does the client require any additional QC?
____ ____ Is the tritium run log present, completed, and properly reviewed for all samples in this batch?
1.1.1. ____ ____ Is the expiration date of the spiking standard entered on the benchsheet?
____ ____ Are there multiple QC associations in this batch? If so, are they indicated at the top of this page?
____ ____ Were the samples relinquished/received in the LIMS internal COC? Was status sheet updated?
____ Is the status sheet updated with a C?

Raw Data Review

(1st Review _____Date _____) (2nd Review _____Date _____)

____ ____ Is the run log filled out properly? Does a copy accompany the raw data?
____ ____ Is the raw data included for all samples on the benchsheet?
____ ____ Is the %LUMEX <5% for LS6000/6500 or <10% for Quantulus?
____ ____ Was an automatic LUMEX correction performed? If not, was the sample(s) recounted?
____ ____ Is the quench factor in control for the current calibration being used?
____ ____ Is a separate efficiency determination necessary? If so, is the proper QASS included?
____ ____ Are window settings the same for calibration and sample analysis?
____ ____ Is efficiency correct for the method/geometry/inst?
____ ____ Is the count rate above the analyte window in control?
____ ____ If there is a raw data file available, is it noted on the raw data hardcopy?
____ ____ Were any samples recounted? Notation regarding reason of recount made on benchsheet? File names to be used marked below?
____ ____ Is the daily check data in control?
____ ____ Is the instrument background rate for this method in control?
____ Is the status sheet updated with a CC?

Reporting/Packaging

(1st Review _____Date _____) (2nd Review _____Date _____)

Analytical Run ID: _____

____ ____ Have all columns on the Raw Data Report been verified?
____ ____ Are there samples with negative activity? Is the negative activity > 2σ TPU (NARR) / (>3σ, NCR)
____ ____ Are the necessary QASSs/NCRs included with the data package?
____ ____ Was the requested MDC achieved?
____ ____ Are the method blanks/LCS/MS/DER/RPD in control?
____ ____ Date of last calc. verification _____ (monthly).
____ ____ Have all the requested samples been reported?
____ ____ Is the client name/project ID/client IDs correct?
____ ____ Are the collection dates and analysis dates correct?
____ ____ Are the matrices, units, and reporting basis correct?
____ ____ Does the narrative accurately and completely describe the analytical process?
____ Is the status sheet updated with a F?

Ra-226 by Radon Emanation (903.1) - Tracking Sheet & Data Review Checklist (Form 15005r1, 7/7/06)

Prep Batch ID _____ **Analytical Batch ID** _____ **Matrix** _____

QC #	PAI WO#	Client	Req. MDA	Ct. Time	Due Date	Rpt Lvl	C C	D R	D P	P C	N	F	D	Comment

Preparation/Pretreatment

1st review_____ **date**_____ **2nd review**_____**date**_____

____ ____ Project Instructions, Work Orders & WO changes included and followed?
____ ____ Are all the samples prepped for this WO/matrix? If not, list other batch IDs:
____ ____ Is a Sample Condition Form/Grinding Sheet included?
____ ____ Appropriate frequency of LCSs (1/20), Blanks(1/20), and Duplicates(1/10) per batch?
____ ____ Appropriate frequency of MS's (1/20) included for soil matrices?
____ ____ Do these clients require additional QC (DUP, LCSD, MS, MSD) ?
____ ____ Current SOP #'s used and documented on benchsheet?
____ ____ Non-routine pretreatment performed, documented, and referenced on benchsheet?
____ ____ Are the sample volumes/aliquots correct?
____ ____ Are the QASSs/NCRs listed on the benchsheet?
____ ____ Matrices, units and reporting basis correct? If not, are they documented & QASS included?
____ ____ Is the expiration date written on the benchsheet?
____ ____ Are there multiple QC associations in this batch? If so, are they indicated at the top of the page?
____ ____ Does the first purge date and time on the benchsheet match the hand written benchsheet?
____ ____ Does the second purge date and time on the benchsheet match the hand written benchsheet?
____ ____ Is the ICP raw data included with the benchsheet?
____ ____ Are the chemical recoveries within control limits?
____ ____ Benchsheet completed and reviewed?

Raw Data Review

1st review_____ **date**_____ **2nd review**_____**date**_____

____ ____ Has each detector/cell combination been used less than 20 times since calibration or verification?
____ ____ Are the detector performance checks within control limits? Are these control limits included with the data?
____ ____ Is the background count time the same as the sample count time?
____ ____ Are the sample counts bracketed with passing checks?
____ ____ Is the run log present for all samples in this batch?
____ ____ Has the run log been completed and properly reviewed?
____ ____ Are there at least 4 hours between the second purge time and sample count time?
____ ____ Do the flask, and detector IDs on the benchsheet match the run log?
____ ____ Do the background counts on the benchsheet match the run log?
____ ____ Does the counting date and time on the benchsheet match the run log?
____ ____ Do the sample counts on the benchsheet match the run log?
____ ____ Do the detector efficiencies match the calibration summary?
____ ____ Is a manual calculation verification provided? If not, when was the last one performed? _____
____ Is the status sheet updated with a CC?

Reporting / Packaging

1st review_____ **date**_____ **2nd review**_____**date**_____

____ ____ Are LCS(s) and Method Blank(s) within control limits?
____ ____ DER within control limits?
____ ____ Have the requested MDCs been met?
____ ____ Have additional client-requested QC guidelines been met?
____ ____ Are there results for all the requested samples?
____ ____ Are there samples with negative activity? Is negative activity >2σ TPU (NARR) / >3σ TPU (NCR)?
____ ____ Are the Client Name, Project ID, Matrix, Units and sampling Dates correct?
____ ____ Is there an MDC = 0? If so, is a narrative comment included?
____ ____ Has the narrative been proofread and signed?
____ ____ Does the narrative accurately and completely describe the analytical process?
____ Is the status sheet updated with a F?

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 724 REVISION 10

TITLE: ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES BY GAS FLOW PROPORTIONAL COUNTER -- METHOD EPA 900.0

FORMS: 780 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/2/07

LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 5/10/93; Rev3, 7/29/93; Rev4, PCN #149, 3/02/94; Rev5, PCN #466, 4/25/95; Rev6, 3/24/00; Rev7, 1/4/02; Rev8, 4/07/03; Rev9, 8/24/06; Rev10, 8/31/07.

1. SCOPE AND APPLICATION

This procedure describes the steps necessary to perform alpha and beta emissions analysis of samples of various media using the Tennelec LB 4100-W and Tennelec LB5100-W gas flow proportional counting (GFPC) systems. Samples will normally be liquids (primarily water) and solids (primarily soil or sand) evaporated onto planchets or precipitated onto filters. This procedure is applicable to all gross alpha/beta analyses, alpha analyses (such as Total Radium) and certain specific beta analyses (such as ^{90}Sr) performed on the Tennelec LB4100-W and LB5100-W by Paragon.

2. SUMMARY OF METHOD

Alpha and beta particle emissions from the sample produce ionizations in a gas-filled chamber, generating a small electronic pulse for each interaction. The pulse height is dependent upon the incident energy of the particle. Since alpha and beta particles are normally emitted at widely separated energies, the instrument is able to discriminate between the alpha and beta particle interactions. The instrument provides raw counting information to a computer and spreadsheet-based analysis program. This information is then transferred to Paragon's Laboratory Information Management System (LIMS) for further data reduction and reporting. This procedure provides the calibration, data collection, and analysis portions of EPA Method 900.0.

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of Paragon's internally derived acceptance criteria. In addition, gross alpha analysis of EPA drinking water samples is limited to a residual mass of 100mg on the planchet.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and

interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 It is the responsibility of the instrument operator to coordinate counting activities with preparation lab activities to ensure timely analysis of samples with short-lived radionuclides or other time-sensitive concerns.

3.3 It is the responsibility of the instrument analyst to ensure optimum instrument capacity through the timely performance and documentation of calibrations, daily performance checks, routine maintenance, etc., as described in Table 1.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples utilizing this method to note any anomalous or out-of-control events associated with the preparation and analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES / DISCUSSION / COMMENTS

4.1 Low background gas proportional counters generally monitor both alpha and beta activity simultaneously. In beta-specific analyses, such as ^{90}Sr, the alpha channel must be monitored for evidence of interfering radionuclides that might cause a bias to the analyte of interest. A count rate in the alpha channel greater than 10 times the crosstalk-corrected background count rate is cause for concern and must be further evaluated by the Department Manager for potential impact on the data quality. Further, these beta-specific analyses should not be performed on detectors that do not meet both the alpha and beta normal performance criteria,

except with the approval of the Department Manager (as in cases where the data quality is not affected).

4.2 Instrument response is greatly affected by the residual mass of the sample on the planchet. This residual mass is generally recorded on the LIMS benchsheet, and must be maintained at a constant weight to allow for the proper mass-attenuation correction. Some samples may absorb moisture from the air (hygroscopicity), making the residual mass unstable. All planchets must be stored in a desiccator to prevent hygroscopicity. The residual mass of planchets that are stored outside a desiccator, awaiting disposal, must be re-verified prior to any requested re-analysis.

4.3 Instrument response is also greatly affected by the distribution of sample residue on the planchet. Planchets must be inspected upon receipt to ensure even deposition of material, generally equivalent to the calibration planchets for that method.

4.4 On gas proportional counters with active guard detectors, the guard detector count rate must be monitored to ensure that that count rate is below established control limits. Elevated guard count rates are potentially indicative of other electronic problems that may bias the final results.

4.5 For samples analyzed by the gas flow proportional counter, an elevated level sample is defined by either a beta count rate of over 5,000 counts per minute (cpm) or an alpha count rate of over 1,000cpm. If a particular sample exceeds either of these parameters, the detector used to count that sample must be evaluated to ensure that no contamination of the detector has occurred. This evaluation is performed by analyzing a blank sample on the detector for a count duration that equals or exceeds the expected count duration for subsequent sample counts. If this blank analysis generates a result that is below the minimum detectable concentration (MDC) for the analysis in question, it may be assumed that no significant contamination of the detector has occurred and samples may be counted on that detector. If the results of the blank analysis are above the calculated MDC, contamination of the detector should be suspected. A Supervisor must then be notified so that proper corrective action procedures may be implemented. The detector in question must be shown to be free of contamination before any sample analysis may proceed.

5. APPARATUS AND MATERIALS

5.1 Gas Flow Proportional Counter; LB5100-W, LB4100-W, or equivalent

5.2 Forceps, stainless steel -- keep separate set for background and source/sample handling

5.3 Stainless steel planchets, 47mm diameter, for background calibration and daily performance checks

5.4 Desiccator

5.5 Kimwipes™

6. REAGENTS

6.1 Methanol, reagent grade

6.2 Color-indicating Dri-Rite™

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 All planchets must be stored in a desiccator to prevent hygroscopicity. The residual mass of planchets that are stored outside a desiccator, awaiting disposal, must be re-verified prior to any requested re-analysis.

7.2 Always handle the sample planchets with forceps or tweezers to minimize sample exposure to the operator and contamination in the laboratory.

8. PROCEDURES

Instructions given below are for the Oxford Systems Unit Manager (OSUM) Version 1.10. Throughout the text of this document, < > defines a computer keystroke, and [ ] defines a menu option in the OSUM software.

8.1 OPERATING CONDITIONS

Each alpha/beta counting system shall be operating with detector bias as determined during the installation and calibration of the system. The proper setting is determined by the generation of a voltage plateau, as described below. The amplifier settings for the instrument shall be determined during instrument installation and calibration to maximize detector efficiency and minimize alpha/beta crosstalk. The operating conditions shall be verified daily by performance of the daily instrument performance checks as described below.

8.2 SAMPLE PREPARATION

Samples to be analyzed by this method will have been prepared by radiochemical procedures applicable to the radionuclide(s) being evaluated. Sample preparation may be limited to quantitative distribution onto a planchet or may be as complex as a complete digestion and chemical separation. See appropriate radiochemical procedure(s).

8.3 SAMPLE ANALYSIS PROCEDURE

The applications software for these instruments is a Windows™ product. It is assumed that the operator of the software is familiar with the basic operation of Windows™.

8.3.1 LOADING SAMPLES

8.3.1.1 To load the LB4100, open one of the four sample drawers in the front of the instrument. Place the sample planchet in one of the four planchet holders. Note the position of the sample on the sample benchsheet and in the instrument run log (Form 780). Close and lock the drawer.

8.3.1.2 To load the LB5100, planchets are placed in individual, numbered carriers in the sample rack. Samples to be counted are identified by one of several group markers, labeled A through L, which must be placed in front of the first numbered planchet holder in a count batch. The count batch is properly ended by placing another group marker or the "END" marker behind the last sample in the count batch. Note the carrier number of the sample on the sample benchsheet and in the instrument run log (Form 780).

8.3.2 SETTING COUNT PARAMETERS

8.3.2.1 Prior to starting the sample analysis, the count parameters must be set properly for each batch. The count parameters may include the α and β counting efficiency files and the required count duration.

8.3.2.2 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Edit Parameters]. Select the [LIMS Data] application. At this point, enter the desired count duration and select the efficiency files that correspond to the analysis to be run. Close this screen when the proper information is entered.

8.3.2.3 The LB5100 uses a typical pull down menu in the main screen. Select [Edit Parameters], choose the appropriate application, and continue as described in the preceding paragraph.

8.3.3 STARTING THE SAMPLE COUNT

8.3.3.1 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Create Batch]. Select the detectors to be started. Type in the proposed file name in the format XXImmdd where XX is the analysis type, I is the instrument used, mm is the month and dd is the day. The following Table specifies the appropriate XX designation:

Analysis Type	XX Designation
Gross α/β	AB
Radiostrontium	SR
Radium-228	RA
Radium-226	RD
Total Radium	TR
Chlorine-36	CL
Iodine-129	IO

Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc.

Type in the batch ID as shown on the laboratory benchsheet. Select [Run]. The instrument will proceed to prompt for sample IDs for each detector. Enter the sample IDs as they appear on the benchsheet. Select [Done]. For each sample entered, the instrument will now prompt for analysis volume (in grams or liters) and residual mass (in milligrams). Leave the analysis volume blank and enter the residual mass, where appropriate, when it appears on the benchsheet. Select [Next] to proceed to the next sample. Select [Done] when all sample masses have been entered. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log (Form 780) and on the LIMS benchsheet.

8.3.3.2 On the LB5100, select [Start Count] from the pull down menu. Select the application to be run. Enter the filename in the format listed above and select the group letter that corresponds to the group marker that was placed in front of the samples to be counted. Select [Done]. At this time the instrument will prompt for carrier ID, sample ID, analysis volume, and residual mass. After entering this information for all the samples to be analyzed, select [Done]. Enter the file name, group and carrier ID, date and time, type of analysis, etc. as indicated in the instrument run log (Form 780) and on the LIMS benchsheet.

8.3.4 UNLOADING SAMPLES

8.3.4.1 After the analysis is complete, the samples will be unloaded. In all cases the operator will check the positions of the samples and verify that the position matches the entries in

the run log and on the benchsheet.

8.3.4.2 On the LB4100, the sample analysis must be "freed" before the samples are unloaded. The detector icons on the screen will flash alternately green and yellow to indicate that the desired count time has elapsed and that data acquisition has been completed. Select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Unit Status]. Select the batch ID or file name corresponding to the completed count batch. Select [Free]. At this point the detector icons will stay green. Unlock and open the drawer. Remove the sample planchets, verifying the position against the run log and benchsheet entries. Close and lock the drawer. Initial the "Position Checked" column on the benchsheet.

8.3.4.3 On the LB5100, the sample batch is automatically completed and the carriers are restacked upon completion of the data acquisition. All that remains is to remove the samples, verifying the positions as described in the preceding paragraph.

8.4 DATA OUTPUT

8.4.1 Some tests require a file modification to properly use laboratory-determined base and progeny efficiencies, as well as crosstalk and attenuation factors.

8.4.1.1 Select [File] and [Run Excel].

8.4.1.2 Select [File], [Open…] to open the correct file located in C:\osum\lb4100\aqua\data*.xld, where * is the filename.

8.4.1.3 The library of efficiencies and calibration factors is found starting at cell Q110.

8.4.1.4 Select the appropriate box, including the header line, containing the necessary calibration information.

8.4.1.5 Depress <Ctrl> and <C> to copy the data range.

8.4.1.6 For base efficiencies, paste (<Ctrl> and <V>) the range in the appropriate cells beginning in column A.

8.4.1.7 For progeny efficiency, crosstalk, and attenuation factors, paste the range in the appropriate cells, beginning in column I.

8.4.1.8 Select [File], [Save], then [File], [Exit] to return to the OSUM program.

8.4.2 On both instruments, select [Data Output] from the main instrument menu. Select the correct filename from the displayed list. Data will be output in two forms -- a hard copy will be output from the printer, and a comma-delimited ASCII file will be created on the local drive. It is the ASCII file that will be used in the data reduction and reporting process.

Instrument A automatically creates the ASCII file during data output, but the ASCII file must be manually created on instrument B. To create the ASCII file manually on instrument B:

8.4.2.1 Select [File] and [Run Excel].

8.4.2.2 Select [File], [Open…] to open the correct file located in C:\osum\lb4100\aqua\data*.xld, where * is the filename.

8.4.2.3 Highlight the range from BU16 to CN16 and down to the bottom of the sample data.

8.4.2.4 Depress <Ctrl> and <C> to copy the data range.

8.4.2.5 Open a new Excel spreadsheet and paste the data into the sheet by selecting [Edit], [Paste Special], [Values].

8.4.2.6 Select [File], [Save as…].

8.4.2.7 Save new file under file type "CSV delimited" and name the file "*.ASC", where * is the same as the filename denoted above.

8.4.3 At this time, a preliminary review of the data should be performed to evaluate the quality of the data. Any analytical data quality problems should be identified. Calibration factors, achieved MDCs, Duplicate Error Ratios (DERs), spike recoveries, etc. should be evaluated. These items are formally checked in the data review process, but a preliminary review at this point will give any early warning of potential problems.

NOTE: Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

9. CALIBRATION

The operator is referred to the instrument-specific operation manuals, cited in Section 13,

for specific instructions on performing periodic calibrations. This Section contains those considerations that are specific to Paragon.

9.1 PLATEAU APPLICATION

Plateau measurements are performed to optimize detector operating voltage. A plateau will be run at least on a quarterly basis to verify that the slope at the operating voltage is less than 3.5 % / 100 volts. If the plateau shows a slope at the current operating voltage greater than 3.5%, all other parameters for the instrument will need to be recalibrated, as described below.

9.2 DISCRIMINATOR SETTINGS (CHANNEL CROSSTALK)

Discriminator will be set at the same level for each detector to consistently optimize beta to alpha crosstalk to a maximum of 1%.

Discriminator settings will be verified quarterly, during the plateau verification, by comparing the alpha source efficiency in both the alpha and beta Regions of Interest (ROIs) to those originally observed during the existing plateau calibration count. The observed verification values will be within 5% of the original value. Otherwise, the instrument may be recalibrated or other corrective action taken, with the radiochemistry Manager's approval.

9.3 EFFICIENCY CALIBRATIONS

9.3.1 Standards for calibration shall be traceable to the National Institute for Standards and Technology (NIST) and shall be an independent source from the current spiking standard. Standards for Gross Alpha/Beta analysis will normally be of ^{241}Am for alpha and ^{90}Sr for beta. EPA Drinking Water methodology requires a ^{230}Th alpha source. Project-specific instructions may require a ^{137}Cs beta source. Standards used for efficiency calibrations for analyses counted on the gas flow proportional counter will use standards specific for that analysis, unless other specific instructions are provided, as in the use of ^{89}Sr as a calibration source for ^{228}Ra analysis by EPA 904.0. The analysis systems shall be calibrated for each physical form of sample to be analyzed (e.g., sample evaporated on planchet, filter, etc.) at least annually. All calibration planchets have an expiration date of one year from last verification date.

9.3.2 OUTLIER TEST

9.3.2.1 Calibration standards are generally prepared in sets of at least five, to facilitate the efficient calibration of the instrument. Prior to using a set of calibration standards, a "gross outlier" test will be performed to eliminate the potential use of a calibration planchet that may have been improperly prepared, or suffer from non-uniform deposition of the standard.

9.3.2.2 Count the set of planchets sequentially on the same detector, either on the LB4100 or the LB5100, to achieve a maximum 2% counting uncertainty, at the 1σ confidence interval.

9.3.2.3 Calculate the mean and standard deviation of the set.

9.3.2.4 Any planchets that fall outside a ±2 standard-deviation acceptance limit and fall greater than 5% from the mean value, will be rejected and will not be used for calibrating the instrument.

9.3.3 To initiate efficiency calibrations, fill out a new line in the source table located at C:\OSUM\SOURCES.XLS in excel. Enter in the ID number, emission type (alpha or beta), the half-life (in days), DPM of source, reference date of standard used for source, and new archive filename.

9.3.3.1 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Edit Parameters]. Select the [Efficiency] application. At this point, enter the desired count duration that will ensure that 10,000 counts are acquired. Close this screen when the proper information is entered.

9.3.3.2 On the LB5100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Efficiency]. Select the detectors to be started. Type in the proposed file name in the format EXXmmddY, where XX is the test, mm is the month, dd is the day, and Y is the drawer. Type in the efficiency test name in place of a batch ID. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector. Enter the source ID number in place of the sample ID. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the benchsheet. Also make a notation in the instrument maintenance log book.

9.3.3.3 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Print]. Compare the detector's efficiency with the previously calibrated efficiency. New efficiency should be within 5% of the previous efficiency. If all efficiencies are acceptable, then [Archive] the efficiencies as "Official Values". If the

efficiencies are unacceptable, consult with the Department Manager for instructions.

9.4 MASS ATTENUATION CALIBRATION

9.4.1 Alpha and beta emitting samples that contain any measurable mass deposited on the planchet must be corrected for particle attenuation. This correction is then applied to the sample during the analysis phase. Multiple acquisitions of attenuation data are required. This data is obtained by creating multiple attenuation standards of the same activity and varying masses, normally 0 to 200mg. Each sample is counted in every detector, long enough to acquire approximately 10,000 counts. A fitted curve for the attenuation factor is then generated.

9.4.2 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Edit Parameters]. Select the [LIMS Data] application. At this point, enter the desired count duration that will ensure that 10,000 counts are acquired. Close this screen when the proper information is entered.

9.4.3 On the LB5100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [LIMS Data]. Select the detectors to be started. Type in the proposed file name in the format AXXmmdd where XX is the test, mm is the month, and dd is the day. Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc. Indicate the type of curve being preformed in place of a batch ID. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the benchsheet. Also make a notation in the instrument maintenance log book.

9.4.4 The detector icons on the screen will flash alternately green and yellow to indicate that the desired count time has elapsed and that data acquisition has been completed. Select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Free]. At this point, the detector icons will stay green.

9.4.5 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Close].

9.4.6 Repeat this process until all the attenuation planchets have been counted in every detector.

9.4.7 Use the data from the files to generate a curve, with the equation taking the general form bmx, where x is the residual mass of the sample planchet, in mg. The estimated target value for the m coefficient is 0.993 for an alpha attenuation curve, and 0.999 for a beta curve. The estimated target value for the b coefficient is 1.00. The template can be found at r:\inst\gfp\calibration\MassAtten_Template.xls.

9.5 INGROWTH CURVE FOR RADIUM-226

9.5.1 Assume that the total efficiency has two distinct components: (1) the base Ra-226 efficiency, that is always used at its full value, and (2) the aggregate efficiency of the three ingrown alpha-emitting daughter products, which is used in proportion to the degree of ingrowth.

9.5.2 Acquisitions of the efficiency at different stages of ingrowth are required in order to determine both the base efficiency and the progeny efficiency. Follow the steps outlined in Section 9.3 and count the efficiency planchets immediately after separation. Then count the planchets again after approximately 1 day, 1.5 days, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 9 days, 11 days, 14 days, 17 days, and 20 days.

9.5.3 Use the data from the files to generate a curve, as described below. The template can be found at r:\inst\gfp\calibration\Tot Ra Ingrowth Curve_Template.xls.

9.5.4 By adjusting the estimated base efficiency for Ra-226, the residual (progeny) efficiency for each calibration count is calculated as the arithmetic difference between the observed total efficiency and the estimated base efficiency. Theoretically, if the estimated base efficiency is correct, the residual (progeny) efficiency will be the same for all stages of ingrowth. In practice, set the base efficiency such that the variance in the individual residual efficiencies over the ingrowth period is minimized.

9.5.5 Since the base efficiencies are determined with planchets that have residual mass, it is necessary to adjust the mass attenuation correction curve accordingly. The mass attenuation curve is generated in the manner stated in Section 9.4 with the final mass attenuation equation in the form bmx-x°, where x° is the average residual mass of the base efficiency calibration planchets.

9.6 BACKGROUND CALIBRATIONS

9.6.1 1000-minute background determinations are performed weekly with a clean planchet.

9.6.2 Planchets, pucks, and inserts will be cleaned with RadiacWash™, rinsed with DI water, and dried thoroughly at least monthly. The drawer stage will be cleaned with methanol weekly.

9.6.3 Control limits for weekly background checks are based on historical control limits established from the first 10 data points in the population (+/- 3 sigma). Prior to establishing historical control limits, interim limits are set at <0.50cpm alpha and <3.00cpm beta.

9.6.4 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Background, Weekly]. Select the detectors to be started. Type in the proposed file name in the format BKXmmddW where X is the instrument used, mm is the month and dd is the day. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector -- leave as the detector IDs. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the benchsheet. Also complete the appropriate spots on the chart at the top of the instrument run log.

9.6.5 Upon completion, select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Archive] as "Official Values". Select [Yes] to replace the existing official values. Close this screen when completed. Open Excel, and print a hard copy of the calibration. If a detector is out of control, the background calibration should be repeated. If it is still out of control, the detector is tagged off-line for the week. If a detector continues to be off-line for the weeks to follow, consult with the Department Manager on how to proceed.

9.6.6 Finally, the weekly calibration values must be copied to the daily background check template to provide weekly control limits for the daily background checks that follow.

9.6.6.1 In the weekly calibration file, copy the range BI7..BJ27 to the clipboard.

9.6.6.2 Open the daily background check template file, BKGAB.XLP, and paste the contents of the clipboard into the same range, BI7..BJ27, by selecting the menu commands [Edit], [Paste Special], [Values], [OK]. See Step 10.2.2 for a more detailed explanation.

9.6.6.3 If weekly background calibrations are recounted on only

selected detectors, paste only those values into the existing BKGAB.XLP file, so as not to overwrite the previous, acceptable values for the other detectors.

9.6.7 On the LB5100, begin the count by selecting the following menu options; [LB5100], [Start Count], [Background_Weekly]. Enter the filename as described above, the group ID, and the analyst's initials. Upon completion of the count, select [LB5100], and [Data Output], enter the file name and print.

10. QUALITY CONTROL

10.1 DAILY INSTRUMENT PERFORMANCE CHECKS

10.1.1 Daily Instrument Performance Checks include both efficiency checks and background checks. Sample analyses must not only be preceeded by acceptable performance checks, but also must be followed by acceptable checks, usually the following day (i.e., all sample analyses will be bracketed with acceptable performance checks).

10.1.2 In the event that the performance checks <u>following</u> the sample analyses do not meet normal acceptance criteria, the impact on the data quality will be evaluated to determine whether the sample analyses should be redone. The sample analysis data may be used, with proper qualification, upon the Department Manager's approval.

10.2 DAILY BACKGROUND CHECKS

10.2.1 Daily background checks consist of a single 60 minute count of a clean planchet.

10.2.2 Control limits for the daily background check are derived from the weekly background calibration. The 1000 minute count rate is scaled to a 60 minute count rate and the Poisson uncertainty is calculated for that result. The final limits for the daily checks are calculated as the mean count rate for that detector ± three times the Poisson uncertainty.

10.2.3 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Background]. Select the detectors to be started. Type in the proposed file name in the format BKXmmdd where X is the instrument used, mm is the month and dd is the day. Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector -- leave as the detector IDs. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the

benchsheet. Also complete the appropriate spots on the chart at the top of the instrument run log.

10.2.4 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Archive] as "Daily Check". Close this screen when completed. Open Excel, and print a hard copy of the check. If a detector is out of control, the background check should be repeated. If it is still out of control, the detector is tagged off-line for the day and the effect on the samples that were counted on the previous day is evaluated. If a detector continues to be off-line for consecutive days, consult with a primary GFPC operator or the Department Manager on how to proceed.

10.2.5 On the LB5100, begin the count by selecting the following menu options: [LB5100], [Start Count], [Background_Daily]. Enter the filename as described above, the group ID, and the analyst's initials. Upon completion of the count, select [LB5100], and [Data Output], enter the file name and print

10.3 DAILY EFFICIENCY CHECKS

10.3.1 Standards for Daily Efficiency Checks shall be traceable to the National Institute for Standards and Technology (NIST).

10.3.2 Daily Efficiency checks are run for gross alpha and gross beta. Count durations may be automatically terminated after the acquisition of 10,000 counts, if desired. Control limits are established from the first 30 data points in the population (± 3 sigma). Prior to the collection of 30 data points, interim control limits of ±10% of the initial measurement are used.

10.3.3 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Efficiency]. Select the detectors to be started. Type in the proposed file name in the format EFXmmdd where X is the instrument used, mm is the month and dd is the day. Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector-enter in source ID. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the bench sheet. Also complete the appropriate spots on the chart at the top of the instrument run log.

10.3.4 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Archive] as "Daily

Check". Close this screen when completed. Open Excel, and print a hard copy of the check. If a detector result is outside of normal acceptance criteria, the check should be repeated. If it is still out of control, the detector is tagged off-line for the day and the effect on the samples that were counted on the previous day is evaluated. If a detector continues to be off-line for consecutive days, consult with the Department Manager for corrective action instructions.

10.3.5 On the LB5100, begin the count by selecting the following menu options: [LB5100], [Start Count], [Efficiency_Daily]. Enter the filename as described above, the group ID, and the analyst's initials. Upon completion of the count, select [LB5100], and [Data Output], enter the file name and print.

11. PERIODIC MAINTENANCE

11.1 CONTROL CHARTS

Control charts of the Daily Efficiency checks and the Backgrounds are printed out monthly using the [Control Chart] application from the main instrument menu. Control charts are to be used for trending analysis.

11.2 To facilitate the convenient management of sample data files, the following files can be relocated after the ASCII files are transferred to LIMS. Calibration files can be relocated anytime after the data is output.

11.2.1 Move sample files from:

C:\OSUM\LB4100\Orange (or Aqua)\DATA*.XLD and *.ASC

to

C:\OSUM\LB4100\Orange (or Aqua)\DATA\OLD*.XLD and *.ASC

11.2.2 Move calibration and performance check files from:

C:\OSUM\LB4100\Orange (or Aqua)\CAL*.XLD and *.ASC

to

C:\OSUM\LB4100\Orange (or Aqua)\CAL\OLD*.XLD and *.ASC

11.3 COMPUTER BACK-UP

The computer files are backed-up monthly using an external tape drive. Prior to performing the back-up, scandisk is run and the hard drive is defragmented. No samples can be counted during the back-up procedure, as OSUM needs to be closed.

After a successful backup of the instrument data, individual data files created since the last backup can be deleted from the following locations:

C:\OSUM\LB4100\Orange (or Aqua)\DATA\OLD*.XLD and *.ASC

C:\OSUM\LB4100\Orange (or Aqua)\CAL\OLD*.XLD and *.ASC

11.4 Specific instrument components will be cleaned periodically, as described in Section 9.

12. SAFETY, HAZARDS, AND WASTE DISPOSAL

12.1 SAFETY

Normal laboratory safety procedures must be complied with during the conduct of this procedure.

12.1.1 Laboratory gloves should be worn while handling the lead shielding; wash hands thoroughly afterward.

12.1.2 Laboratory gloves should be worn while using methanol and while cleaning instrument components.

12.2 HAZARDS

Bias applied to detectors is typically in the range of 1500 volts DC. This can result in electric shock if bias cables are disconnected while bias is applied. To minimize the possibility of electric shock, bias will be turned off to any detector before any cabling is disconnected.

12.3 WASTE DISPOSAL

Sample planchets are disposed of, after a minimum 90-day holding period, in a properly labeled steel drum, under the direction of the Waste Management Officer.

13. REFERENCES

13.1 LB4100 Instruction Manual, Oxford Instruments, Inc., Rev. 9/90.

13.2 LB5100-W Operation Manual, Oxford Instruments, Inc., Version 1.0 (1992).

DOCUMENT REVISION HISTORY

8/24/06: Discriminator checks and outlier tests for calibration sources incorporated. FoxPro and RadLims instructions removed. Other clerical changes made. Added DOCUMENT REVISION HISTORY section.

8/31/07: Added note (8.4.3) that acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification. Removed data reporting procedures. Added Form.

TABLE 1

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency and Background Checks	Daily	Within derived control limits.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Background Calibration	Weekly	Within derived control limits.	Tag method off-line. Determine and correct problem, re-establish limits; or document why condition is acceptable
Operating Voltage Plateau Check	Quarterly	Slope <= 3.5% per 100 volts	Recalibrate Plateau.
Discriminator Settings	Yearly, or when operating voltage is changed.	Beta to alpha crosstalk is <= 1%.	Adjust Discriminators.
Efficiency and Mass-Attenuation Calibrations	Yearly, or when operating voltage is changed.	For single point efficiency calibrations, the value will be within 5% of the previous calibration value. For mass attenuation curves, the fitted values shall be within 10% of the observed value for each point on the curve. Fitted values within 15% of the mass attenuation curve will be acceptable, with the department manager's approval. Initial Calibration Verifications (ICVs) will be within 10% of the expected value.	Tag method off-line. Determine and correct problem; verify source activity; recount and/or recalibrate or document why condition is acceptable.
Chemical Yield	Each sample, where method allows.	Each sample meets current control limits for analysis.	Re-prep; or Qualify or narrate why condition is acceptable

Note: This SOP and SOP 715 contain acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

Date _____ SOP 724r____

Paragon Analytics
Low Background Gas Flow Proportional Counter Log
Instrument: LB4100B

Instrument Daily Response and Background Checks

Det.	Daily Response Check Start 1	Status	Start 2	Status	Background Check Start 1	Status	Start 2	Status	Det. Status
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									

Det = Detector; α = Alpha; β = Beta; P = Pass; H = High; L = Low; OL = Offline; R = Recount; W = Weekly; NP = Not Processed

Weekly Background Calibration

	Current Calib. File ID	Weekly Calib. Started	Status	File ID
Dr A				
Dr B				
Dr C				
Dr D				

Dr = Drawer

Gas Supply

P-10 Supply		P-10 Flow	
Tank 1		Dr A	
		Dr B	
Tank 2		Dr C	
		Dr D	

Comments:

Date _____________ SOP 724r____

Paragon Analytics

Low Background Gas Flow Proportional Counter Log

Instrument: LB4100B

Det.	Sample ID	Batch	Test	Count Dur. (min)	Start Time	Analyst Initials	File ID	Output Initials

<u>Comments</u>:

Page No.: ______________ **B** Form 780r8.doc (6/23/06) Reviewed By / Date _______________

(cont. from page ___________ B)

Must Discard 30 Days from _____ (date printed)

PRAGON ANALYTICS
STANDARD OPERATING PROCEDURE 726 REVISION 6

TITLE: **DETERMINATION OF LEAD-210 IN SOILS, SEDIMENTS, AND WATERS**
Appendix A Amendment Added 11/30/07 DAS

FORMS: **302** **(use current iteration)**

APPROVALS:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/4/07

LABORATORY MANAGER _____ DATE 9/4/07

HISTORY: Rev0, 11/16/93; Rev1, 5/3/96; Rev2, 4/26/02; Rev3, 4/4/03; Rev4, 12/15/04; Rev5, 3/13/07; Rev6, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary for preparation of environmental soils, sediments, and waters for quantitative measurement of ^{210}Pb.

2. SUMMARY

2.1 Pb in soils and sediments is solubilized using nitric, hydrofluoric and hydrochloric acids.

2.2 Pb is pre-concentrated by passing the sample through a cation exchange column. A chromatographic resin with a high affinity for Pb is used to isolate ^{210}Pb from potentially interfering radionuclides. In nitric acid, Pb is retained on the resin while other unwanted sample constituents are not. Pb is stripped from the resin with hydrochloric acid (HCl). The purified solution containing Pb is mixed with liquid scintillation cocktail and counted in a liquid scintillation counter (LSC). Stable Pb, added into the samples at the beginning of the procedure to monitor the chemical recovery, is measured in the sample by ICP-AES before and after chemical separation.

2.3 Air filters may be analyzed by using the soil procedure.

2.4 This procedure may also be used for suspended solids deposited on filters. The dried filter may enter the procedure directly at the grinding stage of sample preparation. The sample aliquot weight, in this case, will have to be adjusted to account for the weight of the filter. The adjusted weight should be calculated on a Quality Assurance Summary Sheet (QASS, Form 302) and recorded on the benchsheet as the sample weight. The remainder of the preparation procedure is identical to that for a soil sample.

2.5 The resin also retains strontium (Sr), and with some slight modifications, this method can be utilized for a sequential preparation of both Pb and Sr. Pb and Sr are both loaded onto the column in nitric acid. Sr is stripped from the column in dilute nitric acid while Pb is retained. Once the Sr has been removed, Pb is stripped from the column with HCl. Refer to SOP 707 for the preparation of Sr samples.

2.6 Actinides are not retained in this procedure, and will pass through when Pb and Sr are loaded onto the column(s). Therefore, the column effluent from the load solutions and subsequent rinses, can be collected and saved for use in actinide separation and purification methods.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of the analyst to be familiar with the acceptance criteria for the quality control (QC) samples and other quality indicating parameters, as specified in SOP 715, and the LIMS program specifications related to the client, project, and test method being performed.

3.3 It is the responsibility of the analyst performing this method to notify the Instrument Lab of the expected delivery date of the prepared samples, and to coordinate the delivery with instrument capacity and production schedules. This method relies on the analysis of ^{210}Pb directly. The ingrowing ^{210}Bi progeny is a potential interferent, in sufficient amounts, and will cause a high bias in the analytical results. Consequently, the samples should be analyzed within four days of separation to minimize this interference. The laboratory control sample (LCS) results will provide accurate measure of any potential bias.

3.4 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file information, indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work, and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the handling, preparation or analysis of the samples. Any discrepancies must be noted, and corrective action taken and documented.

4. INTERFERENCES

4.1 This SOP is applicable to water and soil samples that do not contain significant concentrations of organically complexed Pb. Organically complexed Pb may not be retained by the cation exchange column. Consequently, samples that are suspected to contain organically complexed Pb should be muffled at 450 °C for at least four hours.

4.2 As described above, significant amounts of ingrowing ^{210}Bi can cause a high bias in the ^{210}Pb results. The samples should be counted within four days of separation (less than one progeny half-life) to minimize this potential interference. In any case, the LCS results provide a measure of any potential bias to the analytical results.

4.3 High concentrations of Group IIA Elements (especially Ca, Mg, Ba), may interfere with the acceptable chemical recovery of ^{210}Pb. If ICP analysis results indicate a low Pb carrier yield, and elevated concentrations of Ca, Mg, etc., it may be necessary to reduce the sample aliquot during reanalysis.

5. APPARATUS AND MATERIALS

5.1 Disposable ion exchange columns: 15mL resin volume with attachable funnel to receive 2 L bottle, Environmental Express #R1010 and #R1030, or equivalents.

5.2 Cation exchange column: Attach the funnel to the column (make certain that the column and funnel fit tightly). Precondition a disposable plastic column with 2-3 mL of methanol (the frit at the orifice of the column is hydrophobic). Transfer AG50x8 (or AG50x4) resin to the stem of the column as a slurry with DI water to the 7 cm mark.

5.3 Sr Resin™ column: Use a Bio-Rad® column (#731-1553) or equivalent, and transfer the Sr Resin to the column as a slurry with DI water. Add resin up to approximately the 1.6mL mark on the column. The Sr Resin is held in place by a layer of clean silica sand on top of the resin bed.

5.4 Eppendorf® pipets, or equivalent, and disposable pipet tips

5.5 Graduated cylinder, 1 L and 25mL sizes

5.6 Plastic bottles, disposable, 2 L

5.7 Specimen cups with lids, polypropylene, 250mL (8oz)

5.8 Analytical balance, 0.0001g sensitivity

5.9 Test tubes, disposable, 15mL

5.10 Graduated cylinder, plastic, 25mL

5.11 Glass cups, disposable

5.12 Liquid scintillation vials, plastic

5.13 Transfer pipets, polyethylene, disposable, 7mL, VWR #14670-103 or equivalent

5.14 Parafilm®

5.15 Hot Block, Environmental Express or equivalent

5.16 Steam bath

5.17 Vortex mixer

5.18 Whatman® filter paper pulp

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) below 50 ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 ^{210}Pb spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.2 Pb carrier, 1.0mg Pb/mL: Dissolve 1.60 g Pb $(NO_3)_2$ in 1000 mL of DI water. TLV = 0.05 mg/m^3 = 0.006 ppm (TWA).

The Pb carrier reagent must be analyzed by ICP to accurately determine the Pb concentration. This is accomplished by diluting the Pb carrier reagent 1000-fold with ICP diluting solution. Prepare in triplicate and submit to the Metals Lab for analysis. The preparation and standardization of this reagent must be documented in the Reagent Preparation Logbook.

6.3 Nitric acid 16N, concentrated, reagent grade. TLV = 2 ppm (TWA). Irritant, corrosive.

6.4 Hydrofluoric acid (HF), 48% reagent grade. TLV = 3 ppm.

6.5 Hydrochloric acid 12N, concentrated, reagent grade. TLV = 5 ppm (ceiling). Irritant, corrosive.

6.6 Nitric acid, 8N : Cautiously add 500 mL of conc. HNO_3 to approximately 400mL of DI water and dilute to 1 L. See 6.3 for TLV.

6.7 Nitric acid, 0.1N: Add 6.3 mL conc. HNO_3 to approximately 900mL DI water and dilute to 1 L. See 6.3 for TLV.

6.8 Nitric acid, 0.05N: Add 3.1 mL conc. HNO_3 to approximately 900mL DI water and dilute to 1 L. See 6.3 for TLV.

6.9 Nitric acid, 1N: Add 63 mL conc. HNO_3 to approximately 900mL DI water and dilute to 1 L. See 6.3 for TLV.

6.10 Hydrochloric acid, 6N: Add 500mL of conc. HCL to 400mL of DI water and dilute to 1 L. See 6.5 for TLV.

6.11 Hydrochloric acid, 4N: Cautiously add 330mL conc. HCl to 500mL DI water and dilute to 1 L. See 6.5 for TLV.

6.12 Hydrogen Peroxide (H_2O_2), ACS grade, 30%. TLV = 1 ppm (TWA).

6.13 ICP diluting solution: Carefully add 10 mL of conc. nitric acid and 50mL of hydrochloric acid to 940 mL of DI water. See 6.3 and 6.5 for TLVs.

6.14 Cation exchange resin, AG50x8 or AG50x4, Eichrom® or equivalent.

6.15 Sr Resin™ chromatographic resin (particle size 50-100 μm). Purchased from Eichrom Industries, Inc. (Darien, IL).

6.16 RadiacWash®.

6.17 Methanol, reagent grade. TLV = 200 ppm (TWA).

6.18 Nitromethane, reagent grade. Highly flammable. TLV = 20 ppm (TWA).

6.19 Ultima Gold LLT™ liquid scintillation cocktail.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 It is recommended that water samples be preserved at the time of collection by adding enough nitric acid (HNO_3) per liter of sample to bring the pH to 2 (2mL of conc. HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.2 The container choice should be plastic to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 SOIL PREPARATION

Soils/sediments must be prepared through the grinding stages of SOP 721.

NOTE: The acid dissolution procedure for ^{210}Pb in soil is identical to SOP 773 - Dissolution of Solids for Determination of Actinides, *except for the following*:

- Soils that require muffling will be muffled at a maximum temperature of 450 ^{0}C. Use paper pulp, rather than filter paper, for the method blank and LCS.
- Conc. HCl is added to the sample when re-dissolving the residual salts instead of conc. HNO_3.
- Boric acid is not added to the sample when redissolving the residual salts.

8.1.1 Weigh approximately 2g of soil (dried and finely ground) into a 250mL polypropylene cup. Record weight (W_s) on the benchsheet. Aliquot sizes may be adjusted to meet the client's requested detection limit.

8.1.2 Prepare a blank and blank spike, per Section 10. If other tests are being prepared sequentially with ^{210}Pb, the appropriate tracers, spikes and/or carriers should be added at this time.

8.1.3 Add 1.0mL of 1.0 mg/mL Pb carrier solution.

NOTE: A replicate 1.0mL aliquot (or similar known volume from a calibrated pipettor) of Pb carrier is diluted by adding 5mL of concentrated HCl and diluting to 1 L with DI water. After mixing thoroughly, a 10mL aliquot of this dilution is transferred to a test tube labeled "reference carrier" and submitted with the initial and final tubes for ICP analysis.

See Amendment for this Step, Appendix A. 11/30/07 DAS

8.1.4 Add 25mL conc. HNO_3 to each cup using a volumetric dispenser. Use caution when adding the acid, some soils, especially larger aliquot sizes, may be very reactive, initially.

8.1.5 Using a **plastic** graduated cylinder, add 25mL conc. HF to each cup (do not allow HF to come into contact with any type of laboratory ware made of glass since HF will dissolve glass).

8.1.6 Add 25mL of conc. HCl to each cup. Place a 100mL polypropylene cup as a cover onto the 250 mL cup containing the sample.

8.1.7 Allow the samples to pre-digest at least 1 hour at room temperature to allow any vigorous reaction to subside.

8.1.8 Place the cups on the steam bath and heat for at least 4 hours.

8.1.9 Uncover the cups and take to dryness on the steam bath.

8.1.10 For samples with low organic content, skip to Section 8.1.12. For samples with significant organic content proceed to Section 8.1.11.

8.1.11 Remove from the steam bath and add 10mL conc. HNO_3. An additional 5mL 30% H_2O_2 can be added to assist with dissolution of difficult matrices. Since the addition of H_2O_2 can result in a vigorous reaction, the samples should be allowed to stand at room temperature for a few minutes. After the reaction has subsided, return the cup to the steam bath and take to dryness.

8.1.12 Remove from the steam bath and add 10mL conc. HCL and about 140mL DI water to solubilize the solids. Mix well. Return cups to the steam bath for about 15 min. to warm solution and enhance dissolution of salts.

See Amendment, Appendix A. 11/30/07 DAS

8.1.13 Transfer the sample through a qualitative fluted filter paper into a 1 L graduated cylinder. Rinse the cup two or three times with DI water and transfer the rinsate to the filter.

8.1.14 Dilute to a final volume (V_s) of 1 L with DI water and transfer to a clean, labeled 2 L plastic bottle.

8.1.15 Mix each sample thoroughly by capping and shaking. Pipet a 10mL aliquot (R_i) from each sample into a disposable test tube. Cover with Parafilm® and label with the sample ID and “initial Pb”.

8.1.16 Prepare a cation exchange column per Section 5.2. Condition the column with ~30mL of 1N HNO_3.

8.1.17 Pass the sample through the column at a rate of about 1-2 mL/min. This is accomplished by inverting the 2 L bottle into the funnel that is attached to the top of the cation exchange column. The sample will feed automatically through the column.

8.1.18 After the sample has completely passed through the resin, rinse the column with 10 mL of 0.1N HNO_3.

8.1.19 Discard the feed and rinse solutions into the Paragon wastewater treatment facility.

8.1.20 Elute Pb and other cations with 50mL of 8N HNO_3. Collect the solution in a labeled 250mL cup.

8.1.21 Place on a steam bath and evaporate to dryness.

8.1.22 Extrude the resin from the column and collect in a wide mouth jar labeled "hazardous waste-used acidic resin" in the satellite accumulation area. When the satellite container is full, notify the site Waste Management Officer for further instructions. Soak the empty columns in RadiacWash®, rinse with tap water, and discard into the sanitary trash.

8.1.23 Once dry, dissolve the salts in 5mL of 8N HNO_3 solution. Add the acid to the specimen cup while the sample is still on the steam bath to facilitate complete dissolution of the salt residue.

8.1.24 Proceed to Section 8.3 of this SOP.

8.2 WATER PREPARATION

8.2.1 Using a graduated cylinder, measure the sample to the nearest graduation. Record the sample volume on the bench sheet (V_i). If the sample volume is not 1 L, dilute with deionized water to 1 L. Transfer into a 2 L disposable plastic bottle (usual sample volume = 1 L).

8.2.2 Prepare a blank and blank spike per Section 10. If sample is to be run sequentially for other tests, the appropriate tracers, spikes and/or carriers should be added at this time.

8.2.3 Add 1.00 mL of 1.0 mg Pb/mL carrier (1.0 mg Pb) (S).

NOTE: A replicate 1.0mL aliquot (or similar known volume from a calibrated pipettor) of Pb carrier is diluted by adding 5mL of concentrated HNO_3 and diluting to 1 L with DI water. After mixing thoroughly, a 10mL aliquot of this dilution is transferred to a test tube labeled "reference carrier" and submitted with the initial and final tubes for ICP analysis.

8.2.4 Mix sample thoroughly by inverting capped bottle several times and remove a 10mL aliquot (R_i) for ICP determination of Pb. Place aliquot

in 15mL test tube, seal with Parafilm and label with sample I.D. and "initial-Pb".

8.2.5 Prepare a cation exchange column per Section 5.2. Condition the column with ~30mL of 1N HNO_3. Pass the sample through the column at a rate of about 1-2 mL/min. This is accomplished by inverting the 2 L bottle into the funnel that is attached to the top of the cation exchange column. The sample will feed automatically through the column.

8.2.6 After the sample has completely passed through the resin, rinse the column with 10mL of 0.1N HNO_3.

8.2.7 Discard the feed and rinse solutions down the laboratory sink and into the Paragon wastewater treatment facility.

8.2.8 Elute Pb and other cations with 50mL of 8N HNO_3. Collect the solution in a labeled 250mL polypropylene cup. Place on a steam bath and evaporate to dryness.

8.2.9 See Section 8.1.22 above for column and resin disposal.

8.2.10 Dissolve the salts in 5mL of 8N HNO_3 solution. Add the acid to the specimen cup while the sample is still on the steam bath to facilitate complete dissolution of the salt residue.

8.2.11 Proceed to Section 8.3 of this SOP.

8.3 Pb PURIFICATION WITH Sr Resin™

8.3.1 Place a waste/effluent collection container under the columns.

8.3.2 Precondition a Sr Resin™ column (see Section 5.3 for preparation of Sr Resin™ columns) with 5mL of 8N HNO_3, collecting the rinsate for disposal.

8.3.3 Transfer the sample solution to the column using a disposable transfer pipet.

8.3.4 Using the disposable transfer pipet, rinse the cup with 2mL of 8N HNO_3 and add the rinsate to the column. Repeat twice, allowing the entire rinse volume to pass through the column each time.

8.3.5 Rinse the column with two 5mL aliquots of 0.05N HNO_3. Record the date and time to the nearest 10 minutes of the end of the last rinse on the benchsheet. This is the starting time of the ^{210}Bi ingrowth.

8.3.6 The contents of the waste container can be discarded into the Paragon wastewater treatment facility via the laboratory sink followed by plenty of cold tap water. The waste containers may be rinsed with RadiacWash® solution and tap water and re-used for collecting waste column effluent. If the waste containers are not needed they may be soaked in RadiacWash®, rinsed with tap water, and discarded into the sanitary trash.

8.3.7 Place a labeled disposable glass cup under each column.

8.3.8 Elute Pb from the column with six 5mL rinses of 6N HCl, allowing each rinse to pass through the column before adding the next rinse. Collect the eluate in the labeled disposable glass cups.

8.3.9 Add 5mL of 16N (conc.) nitric acid to the eluate in the glass cup. This will aid in breaking down organic constituents in the column effluent.

8.3.10 Take the samples to dryness by placing the glass cups on a Hot Block set at 100 ^{o}C.

8.3.11 Once dry, remove from Hot Block. While the glass cup is still warm, dissolve the residue by adding 1.0mL of 4N HCl. Immediately cap the glass cups to prevent evaporation and vortex to mix completely. Allow to stand 5 – 10 minutes. Warm the bottom of the capped glass cup briefly in a hot water bath and vortex to be sure all of the Pb is in solution. Allow glass cups to cool. Add 5.0mL of DI water. Record the final volume of 6 mL (V_{Pb}) on the benchsheet. Cap and vortex again.

8.3.12 Add 9.9mL of ICP diluting solution to a test tube that has been labeled with the sample ID and “final-Pb”. Pipet 0.1mL from the thoroughly mixed sample and transfer to the test tube. Cap the test tube and invert several times to mix thoroughly.

8.3.13 Submit the “initial and “final” aliquots to the Metals Lab for ICP determination of Pb concentrations in these solutions. The initial concentration (C_i) and the final concentration (C_f) will be used for the calculation of the chemical yield.

8.3.14 Upon the return of the ICP sample fractions to the lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the Paragon wastewater treatment facility (down the drain in the lab sinks with plenty of cold tap water). The test tubes may

be rinsed with RadiacWash® solution, followed with tap water, and discarded into the sanitary trash.

8.3.15 From the remaining sample in the glass cups, pipet 5.0mL into a plastic liquid scintillation vial. Add 15mL of Ultima Gold LLT™ cocktail to each vial. Cap and shake well to mix. Since the liquid scintillation vial is an optical surface, all labeling should be done on the cap, not on the vial itself. Wipe each vial down using a Kimwipe® moistened with methanol.

8.3.16 Relinquish the samples to the Instrument Lab for counting by liquid scintillation with all appropriate documentation. The LS vials will be analyzed and ultimately disposed of in the manner described in SOP 704.

8.3.17 AFTER THE ICP RESULTS HAVE BEEN REVIEWED AND DETERMINED TO BE ACCEPTABLE, the sample remaining in the glass cup may be disposed into the Pb waste carboy. The glass cups may be rinsed with RadiacWash® solution, followed with tap water, and discarded into the broken glass receptacle.

8.4 PREPARATION OF CALIBRATION STANDARDS

8.4.1 Provide the Instrument Lab with a total of twenty-four liquid scintillation vials consisting of twelve blanks and twelve calibration standards with approximately 1000-2500 dpm of NIST-traceable ^{210}Pb in each. The blanks and calibration sources should be progressively quenched with nitromethane in increments of 15 µL, beginning with 0 µL.

8.4.2 To accomplish this, label twenty-four 2 L disposable plastic bottles. Fill each with 1 L of acidified DI water. Add 1mL of Pb carrier to each. Spike the twelve calibration sources. Process like water samples, following this SOP (starting with Section 8.2.4). Once samples have been transferred to liquid scintillation vials and cocktail has been added, quench with a range of 0-165 µL of nitromethane in 15 µL increments for both the blanks and calibration sources. Shake to mix and wipe the vials with a Kimwipe® moistened with methanol. Relinquish to the Instrument Lab with appropriate documentation.

8.4.3 Each calibration must be verified with a calibration verification set that consists of three method blanks and three LCSs that are processed through the water method and variously quenched at the low, medium, and high ranges of the quench curve. The LCSs should be prepared with an independent second source of NIST-traceable ^{210}Pb, if possible.

The calibration verification set may be prepared either simultaneously with the calibration set or separately, as is most convenient. The verification samples must pass normal Paragon acceptance criteria for method blanks and LCSs.

9. CALCULATIONS

The following parameters must be recorded on the benchsheet. The parameters are necessary to calculate chemical recovery and also to provide the Instrument Lab with the sample aliquot size to be used in calculating the final results.

9.1 PARAMETERS

9.1.1 Soil Samples

W_s = dry weight of soil (g). Refer to Section 8.1.1.

V_s = final volume of digestate (mL). Refer to Section 8.1.14.

C_i = concentration of Pb determined in "initial-Pb" aliquot (µg/mL). Refer to Section 8.3.13.

C_F = concentration of Pb in eluate (µg/mL). Refer to Section 8.3.13.

V_{Pb} = final volume of redissolved sample (mL). Refer to Section 8.3.11.

9.1.2 Water Samples

V_i = initial sample volume (mL). Refer to Section 8.2.1.

S = volume of Pb carrier solution spiked into sample (mL). Refer to Section 8.2.3.

R_i = volume of solution removed for "initial - Pb" ICP analysis (mL). Refer to Section 8.2.4.

C_i = concentration of Pb determined in "initial - Pb" aliquot (µg/mL). Refer to Section 8.3.13.

V_{Pb} = final volume of redissolved sample (mL). Refer to Section 8.3.11.

C_F = concentration of Pb in Pb eluate (µg/mL). Refer to Section 8.3.13.

9.2 CHEMICAL RECOVERY CALCULATIONS

Calculate chemical recovery using the following calculations:

9.2.1 Soil Samples

$$Pb_i = \text{initial mass of Pb } (\mu g) = (C_i)\,(V_s - 10)$$

The factor of 10 accounts for the aliquot removed for ICP analysis. Refer to Section 8.1.15.

$Pb_F = (C_F)(V_{pb})(100)$

The factor of 100 accounts for the dilution made prior to ICP analysis. Refer to Section 8.3.12.

% Pb recovery $= (Pb_F / Pb_i)100$

Chemical recovery results must be submitted to the Instrument Lab.

9.2.2 Water Samples

Pb_i = initial mass of Pb (µg) $= (C_i)(V_i + S - R_i)$

Pb_F = final mass of Pb recovered (µg) $= (C_F)(V_{Pb})100$

% Pb recovery $= (Pb_F / Pb_i)(100)$

Chemical recovery results must be submitted to the Instrument Lab.

9.3 SAMPLE ALIQUOT SIZE TO BE USED IN FINAL RESULTS CALCULATION

9.3.1 For soils, the sample aliquot mass to be used in calculating the final results must be adjusted to account for aliquots that were removed to determine chemical recovery.

W_c = sample mass used in calculation of final results (g).

$= W_s \times [(V_s - R_i) / (V_s)] \times (5/V_{Pb})$

where 5 refers to the volume described in Step 8.3.15.

9.3.2 For waters, the sample aliquot volume to be used in calculating the final results must be adjusted to account for aliquots that were removed to determine chemical recovery.

V_c = sample volume used in calculation of final results (mL).

$= V_i [(V_i + S - R_i) / (V_i + S)]$

9.3.3 W_c and V_c must be submitted to the Instrument Lab in order to allow calculation of the final results.

9.4 TPU FACTORS

As defined in SOP 708, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty.

9.4.1 Water samples require a preparation uncertainty factor of 0.0972 (1σ). This is based on one gross aliquotting, one volumetric measurement, one ICP yield determination, and one pipetting.

$$0.0972 = \sqrt{.05^2 + .006^2 + .083^2 + .004^2}$$

9.4.2 Solid samples require a preparation uncertainty factor of 0.0974 (1σ). This is based on one gross aliquotting, one mass measurement, two volumetric measurements, one pipetting, and one ICP yield determination.

$$0.0974 = \sqrt{.05^2 + .003^2 + .006^2 + .006^2 + .004^2 + .083^2}$$

9.4.3 In practice, these two TPU factors are not significantly different. To facilitate the use of the radiochemistry reporting software, the greater of the two (0.0974) may be used for both matrices.

10. QUALITY CONTROL

Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.1 SOLID SAMPLES

10.1.1 As described above, Whatman® ashless paper pulp is used as the matrix for solid QC. Use enough to absorb the volume of carrier and spike solution added.

10.1.2 One blank is run per batch of 20 samples, or at a 5% frequency.

10.1.3 One sample duplicate is run per 10 samples, or at a 10 % frequency.

10.1.4 One laboratory control sample is run for each batch of 20 samples (5% frequency) with approximately 10-30 pCi ^{210}Pb/gram.

10.2 WATER SAMPLES

10.2.1 One blank using 1 L containing 5mL of concentrated HNO_3 and 995 mL of DI water is run per batch of 20 samples or at a 5% frequency.

10.2.2 One sample duplicate is run per 10 samples or at a 10% frequency.

10.2.3 One laboratory control sample (spiked blank, 1 L, containing 5mL of concentrated HNO_3 and 995mL of DI water) is run for each batch of 20 samples (5% frequency) with approximately 10 to 30 pCi ^{210}Pb/liter.

11. SAFETY, HAZARDS, AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

Care should be taken when diluting acids. Always add acids to water, not water to acid.

11.2 WASTE DISPOSAL

Specific waste disposal instructions are given in the body of the Procedure section.

12. REFERENCES

E.P. Horwitz, R. Chiarizia, and M. Dietz, "A Novel Strontium- Selective Extraction Chromatographic Resin", Solvent Extraction and Ion Exchange, 10 (2), 313-336 (1992).

NOTE: This reference presents data that shows the strong retention of Pb by the Sr•Spec chromatographic resin. Pb retention exceeds Sr retention by more than two orders of magnitude at certain activities.

DOCUMENT REVISION HISTORY

3/13/07: Rev5. Added Form and DOCUMENT REVISION HISTORY. Added scheduling comment and reference to LIMS program specifications to RESPONSIBILITIES. Changed minimum muffling time from 1hr to 4hrs. Added additional comment to INTERFERENCES section. Added Nitromethane to REAGENTS. Revised the calculations. Updated TPU calculations, and changed the preservative used in the QC samples from HCl to HNO_3.

8/31/07: For spiking solution Section 6, added second source statement. Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Section 7.1. Removed activity calculation from Section 9 and referenced SOP 708 instead. Added statement to Section 10 that acceptance limits for quality control parameters may vary per client specifications, consult applicable LIMS program specification.

11/30/07: Appendix A amendment added.

Appendix A

^{210}Pb Soil Modifications

Two modifications have been evaluated to improve the current ^{210}Pb soil procedure. These modifications reduce the required preparation time and remove potassium, which is a potential source of interference for chemical separation on the Sr-Spec column.

Procedures:

Modification to Step 8.1.3:

- A replicate 1.0 mL aliquot (or similar known volume from a calibrated pipet) of Pb carrier is diluted by adding 5mL of concentrated HCl and diluting to 200mL with DI water. After mixing thoroughly, a 1.0mL aliquot of this dilution is transferred to a test tube labeled "reference carrier" with 9.0mL of ICP diluting solution. This is submitted with the initial and final tubes for ICP analysis.

Beginning at Step 8.1.13:

- Transfer the digestate to a labeled 250mL centrifuge bottle. Rinse the cup three times with DI water and dilute to a final volume of 200mL.

- After mixing thoroughly, a 1.0mL aliquot of this solution is transferred to a test tube labeled with the sample ID and "initial Pb" with 9.0mL of ICP diluting solution. Cap and mix thoroughly.

- Add 100 mg of Ca (1.0mL of 100 mg/mL Ca solution)

  Note: Addition of Ca is unnecessary if the sample contains more than 100mg of native Ca. Samples containing high levels of Ca usually can be identified by the effervescence which occurs when the digestion acids are added. If high native Ca is suspected, the "initial Pb" solutions may be analyzed to determine the level of native Ca.

- Add 2g of oxalic acid and dissolve by shaking or vortexing.

- Add 20mL of concentrated NH_4OH. Mix well and allow precipitate to form.

- Centrifuge at approximately 3500 RPM for 10 minutes.

- Decant the supernatant and discard into the Paragon wastewater treatment facility.

- Dissolve the precipitate in 15mL of concentrated HNO_3 by vortexing.

- Bring the solution to 30 mL using DI water. Mix well. This is the 8N HNO_3 load solution to be used in the Pb purification with Sr-Spec resin.

- Centrifuge to separate any undissolved residue which may clog the Sr-Spec resin column.

- Decant the supernatant into a labeled 50mL centrifuge tube.

  Note: If any solids do not centrifuge down it may be necessary to filter the supernatant using a 0.7µm glass fiber syringe filter. If the supertanted is filtered, all rinses from the next Steps are to be filtered through the filter as well.

- Rinse the 250mL centrifuge tube with 5mL of 8N HNO_3 and shake well to rinse the entire tube. Centrifuge and add the rinsate to the 50mL centrifuge tube. Repeat this Step 2 more times.

- Perform Pb purification with Sr-Spec resin (Steps 8.3.1 through 8.3.6)

- Place a labeled 50mL centrifuge tube under each column.

- Elute Pb from the column with six 5mL rinses of 6N HCl, allowing each rinse to pass through the column before adding the next rinse. Collect the eluate in the labeled 50mL centrifuge tube.

- Add 20mg of Ca (0.2mL of 100 mg/ml Ca solution). Mix well.

- Add 15mL of concentrated NH_4OH. This must be done slowly and carefully. Add 5mL, cap and mix tube. Repeat two more times.

- Add 1g of Na_2CO_3. Mix well to dissolve the Na_2CO_3 and allow the Ca(Pb) carbonate to precipitate.

- Centrifuge and discard the supernatant into the Paragon wastewater treatment facility.

- Rinse the precipitate with 10mL of concentrated NH_4OH. Vortex to mix and centrifuge. Discard supernatant into the Paragon wastewater treatment facility.

- Dry the tube and precipitate by placing the uncapped centrifuge tube in a Hot Block set at 100 °C.

- Dissolve the residue by adding 1.0mL of 4N HCl. Add 5.0mL of DI water. Record the final volume of 6 mL (V_{Pb}) on the benchsheet. Cap and mix by vortexing.

- After mixing thoroughly, a 0.05mL aliquot of this solution is transferred to a test tube labeled with the sample ID and “initial Pb” with 10.0mL of ICP diluting solution. Cap and mix thoroughly.

- Continue per SOP 726R6 beginning at Step 8.3.13.

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 733 REVISION 7

TITLE: **CHECKING THE pH OF AQUEOUS SAMPLES IN THE RADIOCHEMISTRY DEPARTMENT**

FORMS: **631 (use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 10/3/07
QUALITY ASSURANCE MANAGER _____ DATE 10/3/07
LABORATORY MANAGER _____ DATE 10/4/07

HISTORY: Rev0, 5/06/93; Rev1, PCN #152, 3/4/94; Rev2, 2/14/00; Rev3, 4/10/02; Rev4, 3/28/03; Rev5, 5/17/04; Rev6, 2/27/06; Rev7, 9/28/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used to check and document the pH of aqueous samples being handled by the Radiochemistry Preparation Groups. Only the samples and/or containers actually being analyzed for radionuclides will be checked. Lab personnel will conduct the pH measurement prior to the use of the sample. The pH of the sample will be documented on the Sample Condition Form (Form 631) or on the electronic benchsheet, as applicable. This SOP does not apply to soil, sludge, organic, bioassay or any other non-aqueous samples.

The pH check is important for verifying the preservation status of the sample being analyzed. Presence or absence of acid preservatives can be crucial to analyses such as Tritium and Carbon-14, samples for such analyses should not contain any acid preservative. If the pH measurement on any sample scheduled for these analyses falls below 2, verify that there is no alternate sample container that is unpreserved. If all containers for such a sample were preserved, consult the Department and Project Managers for resolution.

2. SUMMARY

2.1 Aqueous samples that must be preserved by acidification are checked for pH using narrow range indicator paper (pH 0–2.5) at the beginning of any analysis. The sample is applied to the indicator paper using a disposable pipette. The result may be recorded on Sample Condition Form (631).

2.2 If the pH is not less than 2, the analyst may acidify the sample in its original container by adding the proper concentrated acid (generally HNO_3) in increments of 2mL per liter of sample until a pH less than 2 is achieved. At this time the date, time, volume of acid added, pH, and the analyst's initials are recorded on the sample container. The sample should then be stored for at least 24 hours prior to re-checking the pH and removing an aliquot for analysis. Any necessary deviations from this procedure should be reported to the Group Supervisor and the

Project Manager (PM) immediately. Also, samples that are highly basic (>pH 8-9) should be brought to the attention of the Group Supervisor and PM.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Strongly basic samples are not readily amenable to preservation by addition of acid. In addition to potential safety concerns surrounding vigorous reactions upon mixing acid and base, significant dilution may occur. Additionally, acid preservation may alter the chemical makeup of the sample and potentially compromise sample results. Samples that are highly basic (>pH 8-9) should be brought to the attention of the Group Supervisor and PM before proceeding.

4.2 Highly sedimented samples may not be amenable to this method. If significant visible sediments are present, the Group Supervisor and PM should be notified.

4.3 Indicator papers should be read while still wet. Your Supervisor will instruct you on how to read the indicators using the color chart on the box of test strips. Record (Form 631) the pH to the nearest tenth place (e.g., “8.5”).

4.4 Color-blind individuals should ask for assistance if their color blindness may interfere with visual distinction of the color changes in any pH range.

5. APPARATUS AND MATERIALS

5.1 Wide range indicating pH test strips (pH 0-14)

5.2 Narrow range indicating pH test strips (pH 0-2.5)

5.3 Disposable transfer pipets

5.4 Lab marker (e.g., Sharpie or equivalent)

6. REAGENTS

HNO_3, concentrated, Reagent grade. TLV = 2ppm (TWA). Irritant, corrosive.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Although the client is responsible for conducting the sampling process, it is emphasized that water samples should be collected in a manner that addresses the considerations discussed in EPA 900.0, Section Three, or Chapter Nine of EPA SW-846, as appropriate.

7.2 The container should generally be plastic rather than glass to prevent loss due to breakage during transportation and handling, unless specific analytical methods require glass containers.

8. PROCEDURE

8.1 Check out aqueous samples to be analyzed observing internal COC practices (SOP 318).

8.2 Even if the pH of the sample has already been written on the container, indicating that it has been checked by another analyst in an earlier analysis, the pH should still be re-verified prior to aliquotting. Various constituents of the sample may act as buffering agents, allowing the sample pH to increase over time.

8.3 Unless otherwise instructed, the sample should be homogenized or shaken immediately prior to the next step.

8.4 Using a transfer pipette, remove enough sample to wet the indicating area of the pH test strip.

8.5 Transfer the sample to the end of the narrow range (0–2.5) pH paper, being sure to completely wet the indicating area completely. Sample residuals remaining in the pipet shall <u>not</u> be returned to their original containers.

8.5.1 Compare the wet strip to the color chart on the box. Determine the pH to the nearest tenth (e.g., pH = 1.8).

8.5.2 So as not to confuse the pH readings, the individual pH for each sample should be recorded on the Sample Condition Form (631) before proceeding to the next sample. Alternately, the notation “pH<2” may be used.

8.5.3 If the pH reading falls at or above the maximum range of the test strip, repeat the test with a wide range strip (0–14). Refer to Section 2.2 for further instructions.

8.5.4 If the pH is not less than 2, the analyst may acidify the sample in it’s original container by adding the proper concentrated acid (generally

8.5.5 HNO_3) in increments of 2mL per liter of sample until a pH less than 2 is achieved. Mark date, time, volume of acid added, pH, and initials on the sample container. Sample should be held for a minimum of 24hrs before proceeding with analysis.

8.6 Once all markings have been made, the pH strips are set aside to dry then are disposed of in the trashcan. See Section 11.2.2 for disposal of sample residuals.

9. QUALITY ASSURANCE AND CONTROL

None required.

10. DEVIATIONS FROM METHOD

This is a proprietary method developed by Paragon. Therefore, there are no deviations to be noted.

11. SAFETY HAZARDS AND WASTE

11.1 SAFETY AND HAZARDS

11.1.1 Safety glasses, lab coats and gloves should be worn in the laboratory at all times.

11.1.2 Use care when handling strong acids (e.g., HNO_3, HCl, etc.). Work only in a fume hood with adequate ventilation and wear appropriate eye, face, and body protection.

11.2 WASTE DISPOSAL

11.2.1 The process waste from this procedure has been determined not to be hazardous other than the characteristic hazard of corrosivity. After pH determinations, strips are set aside to dry, then disposed of in the sanitary trash.

11.2.2 Sample residuals should be disposed of in the appropriate SAA.

12. REFERENCES

None.

DOCUMENT REVISION HISTORY

9/28/07 Minor editorial corrections throughout. In Summary and Section 8.5.4, updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57). Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 739 REVISION 9

TITLE: **PREPARATION OF SAMPLES FOR ANALYSIS BY GAMMA SPECTROSCOPY**

FORMS: **302** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/15/07

QUALITY ASSURANCE MANAGER _____ DATE 8/12/07

LABORATORY MANAGER _____ DATE 8-16-07

HISTORY: Rev0, 9/20/93; Rev1, PCN #104, 1/24/94; Rev2, PCN #412, 3/21/95; Rev4, 10/12/00; Rev5, 3/11/02; Rev6, 4/07/03; Rev7, 8/27/03; Rev8, 10/3/03 and 1/31/05 (no revisions); Rev9, 8/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps used to prepare soil, water and sludge samples for gamma spectroscopy analysis. Vegetation, air filter and bioassay samples are not addressed in this SOP, and must be handled on a case-by-case basis.

2. SUMMARY

Soils and sludges are prepared (i.e., dried and sieved) per SOP 721, prior to beginning the procedure outlined in this SOP. Some soils and sludges may omit such preparations if approval is given by the Radiochemistry or Project Manager. Waters are either filtered or left unfiltered prior to preparation as per work order or Radiochemistry Manager instructions. Waters are measured volumetrically into an appropriately sized Marinelli beaker. Soils are measured gravimetrically into a Lermer jar or a steel can, as appropriate for the sample size and the analyte. The gamma spec containers are sealed with their lids, and wiped with a damp paper towel to remove potential contamination.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 These procedures are to be performed only by personnel who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specification related to the client, project, and test method being performed.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Gamma spec samples must be produced only in the specific geometry for which the Instrumentation Group has calibrated their spectrometers.

4.2 New containers ordered for gamma spec must be equivalent to those currently in use. The Radiochemistry Manager or designee must approve the use of alternate containers or supplies in advance.

4.3 Gamma spec containers are not reusable due to the possibility of carry-over in the next analysis. Once the analysis is complete, the container is returned to the sample storage area.

4.4 The prep and instrumentation technicians maintain the internal Chain of Custody (COC). When the original client sample container is taken by a prep technician from the sample storage area, he/she logs the sample out as normal. Because gamma spec is a non-destructive test, samples that are designated for other (non-volatile) tests may be used. Check with Group Leaders if there are questions concerning sample availability or if samples are turn-around-time sensitive.

4.5 The prep technician is responsible for creating a gamma fraction for chain of custody. The prep analyst logs out the gamma container on behalf of the counting room analyst and relinquishes the sample along with the benchsheet. After counting, the gamma spec analyst will return the samples to the sample storage area and check them in. If the aliquot taken for gamma spec is needed for other analyses, log in/log out activities are managed by barcode scanning (COC SOP 318).

4.6 The standard filter geometry is a 47mm diameter filter mounted in a 2" stainless steel planchet. For Ra-226 analysis of a solid/soil sample, the packing must be done in a can as a geometry (GEO) 17. Usually the can packing will be done on an “As Received” basis, and the % moisture data will be provided to report on a dry weight basis. If the sample volume is limited, regular Gamma can be packed as a GEO 11 and the “Ra-can” could be packed with the available sample. If the can is not filled to the top, the technician should mark a line on the outside of the container indicating the height of the actual sample and write a Quality Assurance Summary Sheet (QASS), Form 302. This documentation will be included in the final report.

4.7 Filter samples can be digested using SOP 773 or SOP 767, then the digestate is diluted to 1000mL with DI water and packed for Gamma as GEO 1. Samples like vegetation, debris, gloves, wipes, iron bar, lead blocks, ashes, fruits, fish, cloth,

wood chips etc., will be treated with different methods based on the nature of the samples and conditions. The samples may be leached using different acids or digested and packed with different GEO. However, all geometry preparations will be documented on a QASS and a copy will be attached to the benchsheet.

5. APPARATUS AND MATERIALS

5.1 Balance, top loading, 0.01g sensitivity

5.2 Scoops, spatulas, tongue depressors

5.3 Graduated cylinders, type TD (to deliver), 1L

5.4 Marinelli beakers with lids, Ga-ma # 138G, or equivalent *, 2L

5.5 Lermer Jars with 89mm screw lid, plastic, or equivalent *, 16oz

5.6 Large funnel, glass/plastic

5.7 Vinyl tape

5.8 Parafilm™

5.9 Qualitative filter paper, fluted, VWR brand #313 or equivalent

5.10 Cans for Geo 17, House of Cans #3104 or equivalent *

* ***Equivalent containers require approval by the Radiochemistry Manager or designee.***

6. REAGENTS

Deionized (DI) water, obtained from the laboratory's DI water system

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Samples may be collected in any type of glass or plastic container.

7.2 Aqueous samples should be preserved to pH<2 with nitric acid.

7.3 If samples are to be stored for an extended period of time, refrigeration is recommended to prevent biological growth in the sample.

7.4 At the current time, there is no regulatory holding time established for gamma analysis. Many sampling and analysis plans, however, apply a default holding time of 180 days from date of collection. If samples are analyzed more than 180 days after collection, this fact should be noted in the laboratory data package case narrative.

8. PROCEDURE

8.1 PROCEDURE FOR WATER SAMPLES

8.1.1 Samples must be properly preserved before aliquotting. Verify that the pH is less than 2, per SOP 733. If the sample contains visible sediment or other conditions exist that make preservation impractical, notify the

Project Manager (PM) of the lab's intent to proceed with analysis of the unpreserved sample and document the situation on a Quality Assurance Summary Sheet (Form 302).

8.1.2 Do not prepare water samples in the same workspace where soil samples are being prepared. This avoids cross-contamination by dust.

8.1.3 If the sample contains sediment or suspended solids, check the work order for specific instructions as to whether or not the sample should be filtered. If it is not specified, filter per SOP 721. If the project instructions specify "Dissolved" or "Filtered", filter the sample through a fluted filter into a clean 1L graduated cylinder. Pre-filtering may be required for especially turbid samples. If the project instructions specify "Total" or "As Received," shake the sample container to mix thoroughly and aliquot as received.

8.1.4 Liquid samples are prepared in 2L Marinelli beakers. Measure the appropriate volume of water sample in a clean 1L type TD graduated cylinder to the nearest 0.01L (i.e., 10mL). Empty the sample into a clean, labeled Marinelli beaker.

8.1.5 The gravimetric method is adapted for liquid samples other than water. Place an empty Marinelli beaker on the top loading balance and tare the balance to zero. Add the sample slowly into the Marinelli beaker until the final weight is 1000 + 0.01g.

NOTE: If the sample volume provided falls short of the desired geometry, dilute to the appropriate geometry with DI water (e.g., dilute 600mL to 1L). *Make sure to record the original volume on the container and on the benchsheet.*

8.1.6 A method blank is made by adding a representative volume of DI water to an empty, labeled Marinelli beaker. The aliquot size used for the blank is the average volume of the sample volumes involved in the batch. The collection date for the blank is the date the samples are packed.

8.1.7 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made, independent second source LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size. For waters, indicate the following:

GEO NUMBER	LCS ALIQ.SIZE
1	1000 mL

8.1.8 Attach the lid of the Marinelli beaker and seal the lid using vinyl tape. Wipe the exterior of the container with a damp paper towel to remove potential contamination. Make sure the container is labeled with the sample ID, aliquot size, date of prep and initials.

8.1.9 Submit the prepared samples to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the gamma spec analyst will check the sample back in to the storage area per COC SOP 318 procedures.

8.2 PROCEDURE FOR SOIL AND SLUDGE SAMPLES

8.2.1 Unless approval to the contrary is given, all soil samples must be dried and sieved through a number 4 sieve prior to preparation for gamma spec analysis. Consult SOP 721 for drying and sieving procedures.

Containers for gamma spec soils are usually prepared when the soil is being prepared for other analyses under SOP 721. The gamma spec prep worksheet for soils should be filled out manually by the prep technician at the time of packing gamma, and the electronic benchsheet will be created later on. The prep worksheet will be attached to the benchsheet when the sample is relinquished to the counting room.

The benchsheet provides information about the prep date, technician, balance number, report basis, etc., as well as all the information about how the sample was packed. Any unusual situation will be documented on a QASS (Form 302).

8.2.2 When using Lermer jars, fill the container to the appropriate level according to the desired geometry. If enough sample is provided, use Geometry 13 (500g). If not, reduce the sample volume to Geometry 11 (100g).

8.2.2.1 Sample volumes should be maintained to within ½ cm of the correct geometry height in the container.

8.2.2.2 Zero out the container weight on the balance prior to weighing out a sample..

8.2.2.3 Soil samples should be well settled into their containers by gentle shaking with the lid on. Do not pack or compress soils into the containers.

8.2.2.4 Consult the Radiochemistry Manager or Group Leader if the sample volume provided is less than a Geometry 11. The analysis will usually still be conducted, but the Project Manager will need to be informed because of the effects on the efficiency calibration and detection limits.

8.2.3 For Ra-226 analysis by gamma spec, the samples will be packed as a GEO 17. Generally, the samples will be packed on a "Dry" basis, however, due to rush turn around times, the sample can be packed "As Received". To accomplish this, transfer the sample to a steel can (appropriate for GEO 17), until it is filled to the top. Tap the can to remove air pockets and to settle the sample. Do not press or "pack" the sample into the can. Add more sample to fill the can to the top. To ensure a tight seal, place a piece of Parafilm over the top of the can then cap the can with the metal lid and seal with the can sealer. Remove any excess Parafilm^{TM} from the outside of the can.

8.2.4 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size as follows:

GEO NUMBER	LCS ALIQ.SIZE
11	100g
13	500g
17	215g
26	215g
7	1s
8	1s
9	1s

8.2.5 After the preparation worksheet and the benchsheet are completed, fill out the LIMS tracking sheet. Submit the packet for a peer review.

8.2.6 Submit the samples prepared as above to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the instrument analyst

will check the sample back in to the storage area and fill out the internal COC.

8.3 CALCULATIONS

TPU FACTORS. As defined in SOP 708, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU):

8.3.1 Water samples require a preparation uncertainty factor of 0.0504 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one volumetric measurement. See the following equation:

$$0.0504 = \sqrt{0.05^2 + 0.006^2}$$

8.3.2 Solid samples require a preparation uncertainty factor of 0.0501 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one mass measurement. See the following equation:

$$0.0501 = \sqrt{0.05^2 + 0.003^2}$$

8.3.3 In practice, these two TPU factors are substantially equivalent. To simplify the data reporting procedure, the greater of the two (0.0504) may be used for both matrices.

9. QUALITY CONTROL

9.1 Method blanks will be run at a frequency of five-percent (i.e., one per 20 field samples) with a minimum of one per batch. Method blanks for water consist of deionized (DI) water. Method blanks for solid samples consist of an empty container, appropriate for the geometry (i.e., 13, 11, 17).

9.2 Laboratory Control Samples (LCS) will be run at a frequency of five-percent with a minimum of one per batch. The LCS consists of a pre-made source from an outside vendor.

9.3 Duplicate samples will be run at a frequency of ten-percent with a minimum of one per batch. If insufficient volume is available for a duplicate, a count duplicate may be used.

NOTE:

10. METHOD DEVIATIONS

SOP 739 is a Paragon Analytics procedure and there are therefore no deviations from a reference method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or when handling materials or equipment potentially contaminated with chemicals.

11.1.3 Soil samples should be handled in a hood as much as possible to avoid inhalation and cross contamination with dust. Workspaces should be wiped down with damp paper towels whenever dust is evident and always at the end of the shift.

11.1.4 Any non-original containers that are used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at minimum with: 1) the compound name, 2) NFPA Health, Flammability, and Reactivity ratings, and 3) date.

11.2 WASTE DISPOSAL

11.2.1 All waste materials (e.g., filter papers, paper towels, etc.) shall be surveyed for radioactivity and disposed of accordingly.

11.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

SOP 708, "Calculations for Radioanalytical Results."

DOCUMENT REVISION HISTORY

8/12/07: Updated references and added LIMS program specification language, Section 3.3. Updated COC language to barcode scanning throughout. Correction of Ra226 soil/sludge sample containers from aluminum to steel. Revamped Quality Control requirements, other format, clerical and typographical changes. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

Ammended 9/27/07 (Section 7.1): Hold for 24hrs (not 16) after pH adjustment (consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57) DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 746 REVISION 8

TITLE: **DETERMINATION OF RADIUM-228 ACCORDING TO EPA METHOD 904.0 OR SW846 METHOD 9320, WITH MODIFICATIONS.**

FORMS: 631 **(use most current iteration)**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 6/27/06
QUALITY ASSURANCE MANAGER _____ DATE 6/24/06
LABORATORY MANAGER _____ DATE 6-27-06

HISTORY: Rev0, 2/1/99; Rev1, 2/8/99; Rev2, 10/7/99; Rev3, 1/26/00; Rev4, 10/19/00; Rev5, 3/13/02; Rev6, 4/7/03; Rev7, 8/27/03; Rev8, 6/26/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- EPA Method 904.0 and SW-846 Method 9320 -- describe the measurement of radium-228 in waters, ground waters, and waste samples. This technique is devised so that the beta activity from actinium-228, which is produced by decay of radium-228, can be determined and related to the activity concentration of radium-228 present in the sample.

This SOP includes instruction for the digestion and separation of soil matrices. However, due to significant potential matrix interference issues, it is STRONGLY recommended that radium-228 analysis in soil and solid matrices be performed by gamma spectrometry, as described in PAR SOP 713. Where the use of this method is required for solid matrices, the default sample size is 0.5 grams, to achieve an MDC of approximately 5pCi/g. This allows for commonly encountered matrix interference issues, including low chemical recoveries.

To quantify actinium-228 and thereby determine radium-228, the efficiency of the beta counter for measuring the very short half-lived actinium-228 (avg. beta energy of 0.404MeV), is to be calibrated with a beta source of comparable average beta energy such as Sr-89 (avg. beta energy of 0.589MeV).

If desired, the determination of radium-226 may be conducted on the purified radium solution prior to barium sulfate precipitation determination of the chemical yield. Methods 903.1, 903.0 or their equivalent methods in SW846, HASL, or Standard Methods, are compatible with this approach.

2. SUMMARY

2.1 The radium isotopes in a water sample are collected by co-precipitation of barium and lead sulfate and purified by re-precipitation out of a basic EDTA solution.

After a 36-hour period to allow for the ingrowth of actinium-228, lead is removed as PbS, actinium is carried on yttrium (Y) as the hydroxide and mounted as the oxalate, and quickly beta counted to minimize decay of the short-lived Ac-228 (~6 hours).

2.2 In solids, radium-228 is liberated from the solid matrix by a total digestion of the solid. The sample is muffled, transferred to a polypropylene specimen cup and digested in the presence of strong acids. After digestion, the sample is brought up to volume with DI water and prepared as a water sample.

2.3 If radium-226 according to EPA Method 903.0 or 903.1 is requested, the supernatant containing radium following separation of the Y/Ac is taken into SOP 712 or 783, as appropriate.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst performing the method to notify the Instrument Lab Gas-Flow Proportional Counter analyst in advance of the number of samples arriving and the expected delivery date and time. This allows the analyst to schedule adequate instrument time to analyze the short-lived Ac-228 analyte.

3.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.3 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specifications related to the client, project, and test method being performed.

3.4 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action

taken and documented.

4. INTERFERENCES

4.1 As indicated in EPA method 904.0, performance studies show that the presence of strontium / yttrium-90 in a water sample will lend a positive bias to the measured radium-228 activity.

4.2 Excess barium in the sample may interfere with an accurate chemical yield determination.

4.3 The presence of significant quantities of dissolved constituents that may form insoluble sulfate precipitates interferes with the proper separation of radium and the subsequent quantification of Ra-228. In this case, reduced sample volumes may be required to minimize the matrix interference effects.

4.4 The presence of sediments in the preserved sample is a significant interference to this method. The client should field-filter the samples prior to preserving with HNO_3 and prior to sending them to Paragon. Concerns arise since the 'preservation' recommended by the EPA (adding acid to samples which may also contain barium and or sulfates), will potentially lead to analyte loss due to precipitation. If sediments are removed following 'preservation', significant analyte loss is possible. Likewise, if sediments are left in a sample, which is subsequently nitric acid preserved, radium leaching from the sediments may lead to a very significant high bias in measured radium concentrations.

4.4.1 The presence of significant quantities (>500mg) of suspended solids in a sample will interfere with collection of the barium sulfate precipitate. Any sample having visible sediments will be filtered prior to sample preparation.

5. APPARATUS AND MATERIALS

5.1 Stirring hot plate

5.2 Magnetic stir bars

5.3 Centrifuge

5.4 Polypropylene centrifuge tubes, Falcon 50mL, do not substitute

5.5 Stainless steel counting planchets, 2", flat

NOTE: Prior to use, the planchets are soaked in diluted Radiacwash™ for approximately three hours, drained, rinsed with deionized water, transferred to a metal pan, and placed in the drying oven until dry.

5.6 Plastic funnels

5.7 Graduated cylinders, 100mL and 1 or 2L

5.8 Pyrex™ beakers, or equivalent, 2L

5.9 Forceps

5.10 Polypropylene specimen cups, with lids, 150mL

5.11 Polypropylene specimen cups, 250mL

5.12 Eppendorf™ pipettors, or equivalent

5.13 Test tubes, 15mL polypropylene, disposable

5.14 Polyethylene test tube caps

5.15 Re-pipettor, Eppendorf™, Model 4780 or equivalent

5.16 Parafilm

5.17 Desiccator

5.18 Vortex mixer

5.19 Hot water bath

5.20 Transfer pipets

5.21 Whatman™ #42 filter papers, ashless, 90mm diameter

5.22 Qualitative fluted filter paper

5.23 Beakers, 100mL, Pyrex™, or equivalent

5.24 Analytical balance, Mettler™ AE 200, or equivalent

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) of less than 50ppm, shall be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Deionized (DI) water

6.2 Acetic acid, 17.4M, Glacial CH_3COOH, reagent grade, concentrated
TLV = 10ppm (TWA); Irritant

6.3 Ammonium hydroxide, 15M, NH_4OH, reagent grade, concentrated
TLV = 25ppm (TWA for NH_3)

6.4 Ammonium oxalate, 5%: Dissolve 25g $(NH_4)_2C_2O_4 \cdot H_2O$ in about 400mL of hot DI water. When cool, dilute to 500mL with DI water.

6.5 Ammonium sulfate, 200mg/mL: Dissolve 200g $(NH_4)_2SO_4$ in DI water and dilute to 1000mL.

6.6 Ammonium sulfide, 2%: Dilute 10mL $(NH_4)_2S$ (20-24%) to 100mL with DI water.

6.7 Standardized Barium Carrier, 16mg/mL (27mg/mL $BaSO_4$ yield)

6.8 Place a 1000mL Class A volumetric flask on a stir plate, add a stir bar and ~500mL of DI water. Add 28.5g $BaCl_2 \cdot 2H_2O$ and stir until completely dissolved, then add 5mL 16M HNO_3. Remove stir bar, rinsing with DI water, and dilute to 1000mL with DI water. Transfer to a clean, labeled 1L poly container. Document the preparation of this carrier in the Reagent Prep Logbook and Paragon's Standards and Solutions Database.
TLV = 0.5mg Ba/m^3 = 0.06ppm (TWA). Irritant

STANDARDIZATION OF Ba CARRIER BY ICP ANALYSIS
Prepare in triplicate a 1000-fold dilution of the Ba carrier using the ICP solution described in Section 6.11 below. Submit to the Metals Lab for analysis. Average the results and record in the reagent prep logbook.

6.9 Citric acid, 1M: Dissolve 210.14g of $C_6H_8O_7 \cdot H_2O$ in DI water and dilute to 1000mL.

6.10 EDTA basic reagent, 0.25M: Dissolve 80g NaOH in ~3L of DI water. Slowly add 372g of (ethylenedinitrilo)tetraacetic acid, disodium salt, dihydrate - EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$), while stirring. After the salt is in solution dilute to 4L. If necessary, adjust the pH to ≥10 using a minimal volume of 10M NaOH.

6.11 ICP diluting solution (1% HNO_3 / 5% HCl). Carefully add 10mL of concentrated HNO_3 and 50mL of concentrated HCl to 940mL of DI water. Mix thoroughly.
TLV = 2ppm for conc. HNO_3 (TWA), and 5ppm for conc. HCl (ceiling). Both irritants, corrosive

6.12 Lead carrier, 15mg/mL: Dissolve 23.98g $Pb(NO_3)_2$ in DI water. Add 5mL 16M HNO_3 and dilute to 1000mL with DI water.
TLV = 0.05mg/m^3 (=0.004ppm)

6.13 Lead carrier, 1.5mg/mL: Dilute 10mL lead carrier (15mg/mL) to 100mL with DI water.
TLV = 0.05mg/m^3 (=0.004ppm)

6.14 Methyl red indicator solution: Dissolve 0.100g methyl red sodium salt powder in 100mL of DI water.

6.15 Nitric acid reagent concentrated (16M HNO_3)
TLV = 2ppm (TWA). Irritant, corrosive

6.16 Nitric acid, 6M: Slowly and carefully add 375mL of concentrated nitric acid (reagent 6.15) while stirring to 625mL of DI water.
TLV=2ppm (TWA). Irritant, corrosive

6.17 Nitric acid, 1M: Add 63mL of concentrated nitric acid while stirring to 937mL DI water.
TLV = 2ppm (TWA). Irritant, corrosive

6.18 Sodium hydroxide, 18M: Place about 500mL of DI water in a beaker in a cold water bath. Very slowly and carefully dissolve 720g of NaOH; work in the hood. The solution will boil if the NaOH is added to quickly. After the solution is cool, dilute to 1L with DI water. Store in a plastic container.
TLV = 2mg/m^3 = 1.2ppm (ceiling). Irritant

6.19 Sodium hydroxide, 10M: Follow the same procedure as above, but use 400g of NaOH instead. Store in a plastic container.
TLV = 2mg/m^3 = 1.2ppm (ceiling). Irritant

6.20 Strontium Carrier, 20mg/mL: Dissolve 48.3g $Sr(NO_3)_2$ in DI water. Add 1mL 16M HNO_3, then dilute to 1000mL with DI water.

6.21 Sulfuric acid, 18N, H_2SO_4: Very carefully and gradually, add 500mL of reagent grade concentrated sulfuric acid, while stirring, to 500mL DI water.

CAUTION: The solution will boil if the reagent is added too quickly.
TLV = 1mg/m^3 (=0.25ppm) (TWA). Irritant

6.22 Sulfuric acid, 0.1N H_2SO_4: Add 5.6mL of 18N H_2SO_4 to ~900mL of DI water. Mix well and dilute to 1L with DI water. Alternately, add 120mL of 18N H_2SO_4

to ~2L of DI water, mix well and dilute to 22L.
TLV = 1mg/m^3 (=0.25ppm) (TWA). Irritant

6.23 Yttrium carrier, 9mg /mL: Add 1.143g Y_2O_3 to a Class A volumetric flask (100mL), and add 10mL DI water. Heat to boiling and, while stirring with a magnetic stirring hot plate, add small portions of conc. HNO_3. (About 6mL is necessary to dissolve the Y_2O_3. Small additions of deionized water also may be needed to replace the water lost by evaporation). After total dissolution, add 4mL conc. HNO_3 and dilute to 100mL with DI water (1mL = 9mg/mLY^{+3}).

Standardization: In triplicate, take 0.5mL of the Yttrium carrier solution and dilute 20-fold with DI water. Determine the concentration by ICP analysis.

6.24 Strontium-yttrium mixed carrier, 0.9mg Sr and 0.9mg Y / mL

6.24.1 Prepare Solutions A and B as indicated below:

Solution A: Dilute 20 mL of yttrium carrier to 100mL, using DI water.

Solution B: Dissolve 0.4384g. $Sr(NO_3)_2$ in DI water and dilute to 100mL.

6.24.2 Combine equal volumes of Solutions A and B; 1mL = 0.9mg Sr and 0.9mg Y.

6.25 Hydrofluoric acid (HF), 48.0-51.0%, conc.
TLV = 3ppm (ceiling). Irritant, burns, bone, teeth, fluorosis

6.26 Hydrochloric acid (HCl) 12M, reagent grade
TLV = 5ppm (ceiling). Irritant, corrosive

6.27 Triton X-100™ non-ionic surfactant solution, VWR #3929-2, or equivalent

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough 1M HNO_3 per liter of sample to bring the pH to 2 (15mL 1M HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of ~~16~~ 24 hours before analysis or transfer of the sample.

7.2 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 AQUEOUS SAMPLE PREPARATION

8.1.1 Verify and record (on Form 631) the pH of the sample according to SOP 733.

8.1.2 1.5L is a typical sample aliquot size for this method. However, this volume may need to be reduced if matrix interference is suspected. Use a graduated cylinder to measure the sample and pour into a clean, labeled 2L beaker. If less than 1.5L is used, record volume, then dilute to 1.5L with DI water.

8.1.3 Prepare quality control (QC) samples per Section 9.

8.1.4 Place the beakers on stirring hot plates. Add a stir bar to each.

8.1.5 To each sample, add 8mL of 1M citric acid, 8-10 drops of methyl red indicator, and 2 drops of non-ionic surfactant. The solution should be pink.

8.1.6 For all sample matrices, add 10mL of lead carrier (15mg/mL), 1mL of strontium carrier, 2mL of non-standardized yttrium carrier.

8.1.7 For solid samples that have undergone the digestion procedure described in Section 8.2.1, skip to Section 8.1.8. For aqueous samples, add 2.0mL of standardized barium carrier. Prepare a reference carrier solution by adding 2.0mL of standardized barium carrier to 1.5L of DI water. Add the appropriate amount of ^{228}Ra spiking solution to samples that require it per Section 9.

8.1.8 Add 15M NH_4OH drop-wise until a definite yellow color is obtained; then add a few drops in excess.

8.1.9 Heat to incipient boiling and maintain at this temperature for 30 min. while stirring.

8.1.10 Precipitate lead and barium sulfates by adding 18N H_2SO_4 drop-wise until the pink color reappears; then add 0.25mL excess (~5 drops). Add 8mL $(NH_4)_2SO_4$. Stir constantly and maintain temperature for 30 minutes. If the indicator has been destroyed during digestion, add a few drops of methyl red indicator.

8.1.11 Remove stir bars, rinsing with 0.1N sulfuric acid, and allow the solution to cool. Let precipitate settle for at least 4 hours or preferably overnight.

8.1.12 Aspirate supernatant. Transfer precipitate to a 50mL poly centrifuge tube, rinsing the last particles out of the beaker with 0.1N H_2SO_4. Centrifuge at 3,500 rpm for 10 minutes and discard the supernatant into the laboratory sink followed by plenty of cold tap water. **NOTE – For the remainder of this procedure any reference to centrifuging means centrifuge at 3,500 rpm for 10 minutes.**

8.1.13 Wash the precipitate with 15mL 16N HNO_3, vortex, centrifuge, and discard the supernatant into the laboratory sink or into the back of a fume hood, followed with plenty of cold tap water. Repeat this washing a second time. At the analyst's discretion, additional washes may be performed to thoroughly remove interfering constituents.

8.1.14 Add 25mL EDTA basic reagent and vortex well. Heat in a hot-water bath for about 10 min., stirring occasionally to aid in dissolution. If the precipitate does not dissolve after heating on the hot-water bath, add up to four 5.0mL increments of EDTA reagent until the precipitate dissolves completely. If the precipitate persists, an additional 5.0mL of 10M NaOH may be added. Document the total volume of EDTA reagent used to dissolve the precipitate on the benchsheet. If the sample re-precipitates while cooling, add a few drops of 10M NaOH to dissolve. Vortex to mix the solution and take the aliquot for the initial ICP analysis. If solids persist, consult your Supervisor prior to filtering per SOP 712.

8.1.15 How to take initial ICP aliquot

8.1.15.1 Vortex the sample to mix thoroughly. Using a calibrated pipette, aliquot 0.1mL of sample into a clean, labeled test tube containing 9.9 or 10mL of DI water (record the volume of water used). Cover with Parafilm, and invert several times or vortex to mix completely. With a calibrated pipette, aliquot 1.0mL of the diluted sample into another clean test tube labeled with the sample ID and "i" and containing 9.0mL of ICP diluting solution. Cover with a test tube cap and mix well. Set aside until final ICP aliquot has been taken.

8.1.15.2 At this time prepare an ICP "reference carrier" (RC) sample. Thoroughly mix the reference carrier solution, prepared in Section 8.1.6, on a stir plate. Add 1.0mL of the reference carrier solution to 9.0mL of ICP diluting solution, as stated above for samples. This RC sample will be submitted with the batch samples for ICP analysis to provide a reference

concentration for the yield calculations.

8.1.16 Add 1mL of strontium-yttrium mixed carrier, and mix thoroughly. Add a few drops of 10M NaOH if any precipitate forms.

8.1.17 Add 1mL $(NH_4)_2SO_4$ and stir thoroughly. Add 17.4M acetic acid drop-wise until barium sulfate precipitates; then add 2mL excess. **Do not vortex.** Heat in a hot water bath (about 10 min.) until precipitate settles. Centrifuge and discard supernatant into the Ba/Pb waste carboy, per Section 12.2 of this SOP.

8.1.18 Add 25mL EDTA basic reagent, vortex and heat in a hot-water bath until precipitate dissolves, (additional volume of EDTA reagent may be needed if the precipitate does not dissolve completely) then repeat Step 8.1.17. *Note the time of last barium sulfate precipitation on the benchsheet; this is T1, the beginning of the actinium-228 ingrowth time.*

8.1.19 Dissolve the precipitate with 25mL EDTA basic reagent. As before (i.e., Step 8.1.18), additional EDTA reagent may be required if the precipitate does not dissolve completely. Then add 1mL of lead carrier (1.5mg/mL) and 1.0mL of standardized yttrium carrier. If $BaSO_4$ precipitates (a cloudy white solid), dissolve with a few drops of 10N NaOH. If $Y(OH)_3$ forms (a stringy, floating precipitate), dissolve with a few drops of 16M HNO_3.

NOTE: Prepare a reference carrier solution by adding 1.0mL of standardized yttrium carrier to a 50mL centrifuge tube. To this, add 25mL of 8M HNO_3 and dilute to 50mL with DI water. Cap the polypropylene tubes and routinely store for **36 hours for ingrowth of Ac-228**.

8.1.20 After the 36-hour ingrowth period, vortex the samples. Add 0.3mL (about 6 drops) $(NH_4)_2S$ and 0.5mL (about 10 drops) 10M NaOH. Cap and shake vigorously until lead sulfide precipitates. Centrifuge and decant supernatant into a clean tube. Rinse the centrifuge tubes into the Ba/Pb waste carboy. Used centrifuge tubes may be soaked in Radiacwash, rinsed in tap water and discarded in the sanitary trash.

8.1.21 In preparation to perform Step 8.1.24, place a bottle of 18M NaOH on a stir plate and mix thoroughly.

8.1.22 Add 1mL lead carrier (1.5mg/mL), 2 drops $(NH_4)_2S$, and 2 drops of 10M NaOH to repeat precipitation of lead sulfide as before. Centrifuge and filter supernatant through Whatman™ #42 filter paper, ashless, 90mm diameter, and into a clean tube. Precondition the filters

with ~1mL of DI water. After the sample has passed through the filter, rinse twice with 1mL of DI water. Discard the filters into the filter lead waste. Rinse the funnels with 1mL of DI water, collecting the filtrate into the centrifuge tube.

8.1.23 **Due to the short half-life of actinium-228, the remainder of the prep should be completed in less than 4 hours. The Counting Lab should be notified in advance of incoming samples.**

8.1.24 Add 16mL of thoroughly mixed 18M NaOH to each sample. Cap and shake well and digest in a hot water bath for about 30min. until yttrium hydroxide coagulates.

NOTE: Document time of yttrium hydroxide precipitation as T2 (time when samples come off steam bath); *this is the end of the actinium-228 ingrowth time and the beginning of actinium-228 decay time*.

8.1.25 Centrifuge and decant the supernatant into a 150mL poly specimen cup. *Save for barium yield determination (Section 8.1.27).*

8.1.26 Dissolve the precipitate with 2mL 6M HNO_3. Vortex and heat in a hot water bath for about 5min. Add 3mL DI water and re-precipitate yttrium hydroxide with 6mL 10M NaOH. Vortex and heat in a hot water bath for about 10min. until precipitate coagulates. Centrifuge and add this supernatant to the supernatant produced in the previous Step in order to determine barium yield. Using a 100mL graduated cylinder, measure this combined supernatant and record the volume on the benchsheet.

8.1.27 FINAL ICP ANALYSIS. The aliquot for final ICP analysis must be taken from the combined supernatant collected. Follow the steps outlined in Section 8.1.15 to obtain the final ICP aliquot.

Upon the return of ICP sample fractions to the prep lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the PAR wastewater treatment facility (i.e., down the laboratory sink with plenty of cold tap water). The remaining Ba supernatant from above can be disposed of into the Ba/Pb waste carboy. The test tubes and centrifuge tubes may be soaked in Radiacwash™ and rinsed with tap water. Dispose of the centrifuge tubes and test tubes in the sanitary trash.

8.1.28 Dissolve the precipitate with 2mL 1M HNO_3, vortex, and heat in a hot water bath for 5min. Additional 1M HNO_3 may be added drop wise to achieve dissolution of the precipitate. If additional 1M HNO_3 is used,

add proportionally increased volumes of DI water and 5% $(NH_4)_2C_2O_4 \cdot H_2O$ (Ammonium Oxalate) in the following Step.

8.1.29 Add 3mL of DI water and 2mL 5% $(NH_4)_2C_2O_4 \cdot H_2O$; heat about 10min. to coagulate, centrifuge, and discard supernatant into the laboratory sink followed by plenty of cold tap water.

8.1.30 Rinse precipitate with 10mL of DI water. Centrifuge and discard supernatant into the laboratory sink.

8.1.31 Add 10mL of DI water, 6 drops 1M HNO_3 and 6 drops 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat and stir in a hot water bath for 5-6 min. The time on the water bath should be monitored carefully, as this may significantly affect the chemical yields for the samples. Centrifuge and discard supernatant into the laboratory sink.

8.1.32 Label a stainless steel planchet, per sample, and place planchets on a hot plate.

8.1.33 Add approximately 4mL of DI water to the centrifuge tubes and vortex until all of the precipitate is suspended. Working quickly to avoid the precipitate settling, remove the cap and rinse once with DI water; pour rinse into a planchet. Empty the contents of the centrifuge tube onto the planchet, rinse tube with DI water, add rinse to the planchet. The sample should be evenly distributed on the planchet. Allow solid to settle. Dry on a hot plate at setting 2 or 3. Submit planchets to the Counting Lab immediately for analysis. Used centrifuge tubes may be soaked in Radiacwash™, rinsed in tap water, and discarded in the sanitary trash.

8.1.34 After counting, place each planchet in a labeled 150mL poly cup and add approximately 10mL of 8M HNO_3 to dissolve the yttrium oxalate precipitate.

8.1.35 Thoroughly rinse the planchets with 8M HNO_3 into the poly cups. After rinsing, the planchets can be disposed of in the sanitary trash.

8.1.36 The dissolved sample and rinse is brought up to 50mL with DI water.

8.1.37 Remove a 0.5mL aliquot from each sample, including the reference carrier from the note after Step 8.1.19, into a 15mL test tube containing 9.5mL of ICP diluting solution, to bring the total volume to 10mL. The samples are then capped, shaken, and brought to the Metals Lab for yttrium analysis by ICP.

Upon the return of ICP sample fractions to the prep lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the PA wastewater treatment facility (i.e., down the laboratory sink with plenty of cold tap water). The test tubes may be soaked in Radiacwash™, rinsed with tap water, and disposed of in the sanitary trash.

8.2 SOLID SAMPLE PREPARATION

8.2.1 Verify and record (on Form 631) the condition of the sample.

8.2.2 Weigh 0.5g of dried, pulverized soil into a permanently labeled glass beaker. Record the sample weight and beaker number on the bench sheet.

8.2.3 Prepare QC samples according to Section 9.

8.2.4 Dry the beakers on a hotplate set at 2 (Samples must be completely dry prior to muffling.). Cover the beakers with a watch glass and muffle at 600°C for at least 4 hours.

8.2.5 Transfer the sample to a 250mL polypropylene cup, using at least 25mL 16N HNO_3 to rinse the beaker. Scraping with a plastic spatula may be necessary to remove all of the soil from the beaker.

8.2.6 Add 25mL HF, 25 mL 12N HCl, cover with a 100mL polypropylene cup, and heat for 4 hours on a steam bath.

8.2.7 Remove the 100mL beaker and evaporate to dryness. The 100mL beakers may be rinsed thoroughly with tap water and discarded into the sanitary trash.

8.2.8 Add 10mL 8N HNO_3, and approximately 100mL DI water to the samples while they are on the steam bath to facilitate dissolution.

8.2.9 Once the samples are fully dissolved, transfer the samples to 2L graduated cylinders using DI water to completely rinse the cups. Bring the samples to a final volume of 1500mL with DI water.

8.2.10 Transfer the samples to 2000mL beakers and proceed with aqueous sample preparation at Step 8.1.4.

8.3 PREPARATION OF CALIBRATION STANDARDS

8.3.1 Label and tare weigh 5 stainless steel 2-inch diameter flat planchets.

8.3.2 Spike between 1,000 and 10,000 dpm of NIST-traceable Sr-89 directly

onto each planchet.

NOTE: If the standard matrix is HCl, the standard must be converted to a nitric matrix during planchetting to avoid corroding the planchet. This can be accomplished by adding ~5mL 16N HNO_3 to the planchet along with the spiking solution.

8.3.3 Add 0.5mL of Sr carrier (approximately 10mg).

8.3.4 Dry on a hot plate set at "2".

8.3.5 Weigh on an analytical balance. Record the mass on the benchsheet.

8.3.6 Submit to the Counting Lab with all necessary documentation.

8.3.7 The calibration should be verified with the preparation and analysis of four method blanks and four ^{228}Ra LCSs, spiked at approximately 500dpm, performed per this SOP.

9. QUALITY CONTROL

NOTE: For solid matrices, the blank and LCS are prepared using a qualitative filter paper, instead of the 1500mL DI water used for aqueous QC.

9.1 One method blank, prepared with 1500mL of DI water, is prepared for each batch of twenty or fewer samples. To be acceptable, the method blank activity shall be less than the MDA (or, if higher, less than the contract required MDC). Samples associated with an elevated method blank are acceptable if the sample activity is greater than five times the blank activity.

9.2 One LCS, prepared with 1500mL of DI water for aqueous samples is prepared for each batch of twenty or fewer samples. The LCS activity should fall within the general range of 5-10 times the requested detection limit (default = 1pCi/L). The LCS sample accuracy (measured activity/added activity) will fall within currently established control limits, as described in the LIMS program specifications.

9.3 A duplicate is prepared at a frequency of one per ten or fewer samples. The duplicate sample DER will be within the established control limits, as described in the LIMS program specifications. Some clients may require use of RPD as a measure of precision. The duplicate sample RPD will be within specified control limits. Duplicate samples with activity levels less than 5 times the MDC will not be assessed using RPD.

9.4 Method 9320 requires that a matrix spike be prepared at a frequency of one per twenty or fewer samples. The matrix spike should fall within the general range of

5-50 times the expected sample activity. For samples that are not expected to be significantly above the default detection limit, the LCS spiking levels are appropriate for the MS as well. The MS sample recovery will fall within currently established control limits. Also, see note in Section 11.4 below.

9.5 The overall chemical yield, calculated as the product of the barium and yttrium yields, shall be 40-110%. The individual barium and yttrium yield should also fall within these limits.

9.6 Batches for which the associated QC samples do not meet established criteria may need to be rerun. A non-conformance report (NCR, SOP 928) should be filled out, the Radiochemistry Technical Manager notified and appropriate corrective action implemented and documented.

10. CALCULATIONS

10.1 Calculate the radium-228 concentration, Act, in pCi/L or pCi/g as follows:

$$Act = \frac{(SCPM - BKGCPM)(Ac * T_3/60)}{F * E * V * Y_T * D * (1 - e^{(-AcT_1)}) * (e^{(-AcT_2)}) * (1 - e^{(-AcT_3/60)})}$$

Where:

Act = sample activity (pCi/L, pCi/g)

SCPM = gross sample beta count rate (cpm)

BKGCPM = background beta count rate (cpm)

Ac = decay constant for actinium-228 = ln2 / 6.15 hours = 0.113075 h^{-1}

F = activity conversion factor from dpm (for pCi = 2.22, for Bq = 60)

E = actinium-228 detection efficiency (cpm/dpm)

V = sample aliquot (L, g)

Y_T = total chemical yield, see Section 10.8

D = decay correction for radium-228 = $e^{(-RaT4)}$

T_4 = time elapsed between sample collection (or reference date) and actinium separation T_1 (days)

Ra = decay constant for radium-228 = ln2 / 2100 days = 0.00033004 d^{-1}

T_1 = elapsed time (hours) between the start of the actinium ingrowth (T_0) and the start of actinium decay (T_1) = (T_1 - T_0)

T_2 = elapsed time (hours) between the start of the actinium decay (T_1) and the start of the sample count (T_2) = (T_2 - T_1)

T_3 = duration of sample count (min)

10.2 Calculate the one sigma associated counting uncertainty, CU, in pCi/L or pCi/g as follows:

$$Unc = \frac{\sqrt{(SCPM/T_3) + (BKGCPM/BT)}(Ac * T_3/60)}{F * E * V * Y_T * D * (1 - e^{(-AcT_1)}) * (e^{(-AcT_2)}) * (1 - e^{(-AcT_3/60)})}$$

Where:

BT = background count time

10.3 Calculate the one-sigma total propagated uncertainty (TPU), in pCi/L or pCi/g as follows:

$$TPU = \sqrt{CU^2 + (IU^2 * Act) + (PU^2 * Act)}$$

The instrument uncertainty, IU, can be found in SOP 743.

The prep uncertainty, PU, is 0.1374. This is based on SOP 743 guidelines for one gross aliquotting, four quantitative transfers, three volumetric measurements, and two ICP determinations:

$$0.1374 = \sqrt{0.05^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2 + 0.006^2 + 0.006^2 + 0.083^2 + 0.083^2}$$

10.4 Calculate the one sigma minimum detectable concentration, MDC, in pCi/L or pCi/g as follows:

$$MDC = \frac{(4.65 * \sqrt{(BKGCPM/T_3)} + 2.71)(Ac * T_3/60)}{F * E * V * Y_T * D * (1 - e^{(-AcT_1)}) * (e^{(-AcT_2)}) * (1 - e^{(-AcT_3/60)})}$$

10.5 The detection efficiency, E, is calculated as follows:

$$E = \frac{(StCPM - BKGCPM)}{StDPM}$$

10.6 Calculate the barium chemical recovery for aqueous samples, Ba, as a percentage, as follows:

$$Ba_i = V_i * ICP_i * DF$$

$$Ba_f = V_f * ICP_f * DF$$

$$Ba_{RC} = V_{RC} * ICP_{RC} * DF$$

$$Ba = \frac{Ba_f}{X} * 100$$

Where:

Ba_i = barium recovery from initial ICP aliquot (µg)

V_i = final dilution volume when taking initial ICP (mL)

ICP_i = initial barium concentration measured by ICP (µg/mL)

DF = dilution factor

Ba_f = barium recovery from final ICP aliquot (µg)

V_f = final dilution volume when taking final ICP (mL)

ICP_f = final barium concentration measured by ICP (µg/ml)

Ba_{RC} = barium recovery from RC aliquot (µg)

V_{RC} = RC final volume (mL)

ICP_{RC} = RC barium concentration measured by ICP (µg/mL)

X = either Ba_i or Ba_{RC}, whichever is greater

10.7 Calculate the yttrium chemical recovery for aqueous samples, Y, as a percentage, as follows:

$$Y_f = V_f * ICP_y * DF$$

$$Y_{RC} = V_{RC} * ICP_{yRC} * DF$$

$$Y = \frac{Y_f}{Y_{RC}} * 100$$

Where:

Y_f = yttrium recovery from final ICP aliquot (µg)

ICP_y = final yttrium concentration measured by ICP (µg/mL)

Y_{RC} = yttrium recovery from RC aliquot (µg)

ICP_{yRC} = RC yttrium concentration measured by ICP (µg/mL)

10.8 Calculate the total chemical yield, Y_T, as a percentage, as follows:

$$Y_T = Ba * Y * 100$$

For chemical yields above 100%, assume a quantitative recovery and use 100% in the yield calculation. This avoids a low bias in the final analytical results.

10.9 Calculate the actual volume, V_A, of sample analyzed (accounting for volumes of sample removed) as follows:

$$V_A = V * \frac{V_i - V_{ICP}}{V_i}$$

Where:

V_{ICP} = initial aliquot taken for ICP (mL)

11. DEVIATIONS FROM METHOD

11.1 EPA Method 904.0 addresses drinking water samples. There is no official holding time for analyses in the 900 series. This procedure is substantially compliant with Method 904.0.

11.2 Method SW846 9320 addresses ground water and waste water samples. There is a holding time of six months for SW846 9320. This procedure is substantially compliant with Method SW846 9320.

11.3 In addition to describing a procedure for aqueous samples, this SOP describes a procedure for determining Ra-228 in soil, which the laboratory employs at a client's request. Also, this SOP provides procedures for determining the chemical yield as an addition to EPA Method 904.0. This measurement increases the accuracy of the method.

11.4 Paragon routinely monitors Ba yields by ICP analysis, in which case, a matrix spike is not necessary. The client Statement of Work (SOW) should be checked for method and QC requirement specifications.

11.5 25mL of EDTA is used to dissolve the $Ba(Ra)SO_4$ precipitate. This volume ensures a complete dissolution of the precipitate in a normal sample.

11.6 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of Paragon's internally derived acceptance criteria.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.2 Safety glasses, and lab coats must be worn in the radiochemistry prep labs at all times.

12.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.7 below.

12.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.1.6 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

12.2 WASTE DISPOSAL

The analytical process effluent has been determined to not be hazardous in other than corrosivity except the Ba and Pb containing supernatants. These supernatants must be segregated into the Ba and Pb waste containers supplied by the Waste Disposal Coordinator.

13. REFERENCES

13.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, Method 904.0, Radium-228 Drinking Water Method, Page. 49.

13.2 SW-846, Method 9320, Radium-228, Rev. 0, September 1986.

13.3 Radiochemical Analytical Procedures for the Analysis of Environmental Samples, EMSL-LV-0539-17, Determination of Radium-226 and Radium-228 in Water, Soil, Air and Biological Tissue, Page 19.

13.4 Greenberg, A.E., J.J. Connors, and D.J. Jenkens, eds., Standard Methods for the Examination of Water and Wastewater, 15th ed., American Public Health Assoc., Washington, D.C., Method 707, Page 600, 1980.

13.5 Cable, Peter and Bill Burnett, Florida State University, “Radium-228 in Natural Waters via Extraction Chromatography”, Paper at 38th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, November, 1992, Santa Fe, NM.

13.6 Burnett, Bill, Peter Cable, Reide Corbett and Michael Schultz, Florida State University, "Update on Extraction Chromatographic Procedure for Radium-228 in Natural Waters", Paper at the 39th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, October 1993, Colorado Springs, CO.

13.7 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.8 PAR SOP 743 "Estimating Total Propagated Uncertainties for Radiometric Analyses".

14. DOCUMENT REVISION HISTORY

Revision 8 provides instruction for the analysis of soil matrices, and changes the default MDC from 1pCi/g to 5pCi/g. Other changes are clerical and typographical in nature; 'DOCUMENT REVISION HISTORY' Section added; Form 631 incorporated into SOP as attachment.

SAMPLE CONDITION FORM

METHOD: _____ MATRIX: _____ EXTRACTION DATE: _____ TECHNICIAN: _____		
WORK ORDER #	SAMPLE CONDITION	SAMPLE ODOR

Form 631fc3.frm (01/20/99)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 748 REVISION 4

TITLE: PREPARATION OF WATER AND SOLID SAMPLES FOR THE ANALYSIS OF Fe-55 BY EICHROM METHOD FEW01

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07
QUALITY ASSURANCE MANAGER _____ DATE 9/3/07
LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 3/2/02; Rev1, 4/7/03; Rev2, 8/27/03; Rev3, 11/29/04; Rev4, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the method for the preparation of water and solid samples for the analysis of Fe-55 using TRU® resin.

2. SUMMARY

Iron (Fe), including Fe-55, is isolated from a sample matrix using Eichrom TRU® resin, according to Eichrom Method FEW01. Fe is retained on the TRU® resin in 8N HNO_3 and is eluted from the resin with 2N HNO_3. The purified sample is mixed with liquid scintillation cocktail and analyzed on a liquid scintillation counter. An aliquot of the sample is analyzed for Fe by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) before and after purification on the column, to provide a measure of chemical yield.

Fe-55 is analyzed directly by liquid scintillation counting. No other parent nuclides or progeny are involved in this analysis. Under normal conditions, default MDCs are 50 pCi/g in solids and 50 pCi/L in waters.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 It is the responsibility of the analyst to perform the calibration for this method using recently prepared calibration standards to prevent excessive quenching. In the assessment of the instrument calibration, the quench curves should encompass the expected quench factor of freshly prepared batch QC samples.

3.3 The analyst must be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specifications related to the client, project, and test method being performed.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder information indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 The sensitivity of this procedure is limited by the fact that stable Fe is abundant in many types of samples and that a maximum of 3 mg Fe can be retained by a 2mL TRU® resin column.

4.2 Fe-59 is a beta-emitting isotope of iron that may interfere with the analysis of Fe-55. Quality assurance against this type of interference is done at the liquid scintillation counter by monitoring the higher energy beta region of the spectra, as described in SOP 704.

4.3 The presence of visible sediments in water samples may interfere with the TRU column performance. At the analyst's discretion, samples with visible sediment may be filtered with a qualitative paper filter prior to removing any sample aliquant.

5. APPARATUS AND MATERIALS

5.1 analytical balance, 0.0001g sensitivity

5.2 specimen cups, polypropylene, disposable, 110mL (Falcon 35-4014 or equivalent) and 220mL (Falcon 35-4020 or equivalent) with lids (Falcon 35-4017 or equivalent)

5.3 centrifuge tubes, 50mL, VWR brand or equivalent

5.4 centrifuge

5.5 plastic fitted funnel

5.6 glass scintillation vials, 20mL

5.7 disposable, BIO-Rad® Ion exchange columns or equivalent

5.8 test tubes, plastic

5.9 pipettes, Eppendorf® or equivalent and disposable pipet tips

5.10 graduated cylinder, plastic, 25mL

5.11 steam bath

5.12 hot plate or Environmental Express HotBlock®, or equivalent.

6. REAGENTS

NOTE: Threshold Limit Value (TLV) and other hazard information may also be given here. As stated in Section 12.1.4 below, any chemical with a TLV below 50 ppm must be worked with in a laboratory fume hood. The absence of this information does not mean that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Fe-55 spiking solution. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.2 Concentrated nitric acid, HNO_3, reagent grade. TLV = 2 ppm (TWA). Irritant, corrosive.

6.3 Concentrated hydrochloric acid, HCl, reagent grade. TLV = 5 ppm (ceiling). Irritant, corrosive.

6.4 Concentrated phosphoric acid, H_3PO_4, reagent grade. TLV = 1 mg/m^3 (= 0.25 ppm). Irritant.

6.5 Nitric acid, HNO_3, 8N: Cautiously add 500mL conc. reagent grade HNO_3 to 400mL DI water. Dilute to 1 L with DI water. TLV = 2 ppm (TWA, conc. HNO_3). Irritant, corrosive.

6.6 HNO_3, 2N: Carefully add 130mL of conc. HNO_3 to 700 mL of DI water. Dilute to 1L with DI water. TLV = 2 ppm (TWA, conc. HNO_3). Irritant, corrosive.

6.7 ICP diluting solution: Carefully add 10mL of conc. Nitric acid and 50mL of conc. Hydrochloric acid to 940mL of DI water. TLV = 5 ppm (ceiling) for HCl. Irritant, corrosive. TLV = 2 ppm (TWA) for Nitric Acid. Irritant, corrosive.

6.8 TRU® resin, 100-150µm, either pre-packed columns or bulk resin, for packing columns in the lab.

6.9 Fe carrier: 20mg Fe^{3+}/mL (dissolve 96g of $FeC_{l3} \bullet 6H_2O$ in 1.0L of 0.5N HCl)

6.10 Ultima Gold® AB scintillation cocktail

6.11 Nitromethane, reagent grade. TLV = 20 ppm.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Water samples should be collected in plastic or glass containers and acidified with nitric acid to pH <2. If water samples are collected without preservation, they should be brought to the laboratory within 5 days, and then be preserved and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.2 Solid samples should be collected in plastic or glass containers.

8. PROCEDURE

8.1 INITIAL TREATMENT OF WATER SAMPLES

8.1.1 Ensure that the samples have been preserved, as described in Section 7.1.

8.1.2 If necessary, visibly sedimented samples may be filtered using a qualitative filter paper.

8.1.3 Aliquot approximately 110mL into a labeled 220mL specimen cup.

8.1.4 Pipet 1.0mL of the digestate from the specimen cup into a disposable test tube containing 9.0mL ICP solution, and labeled with the sample ID and "native Fe". Mix well and submit to the metals lab for ICP-AES analysis. The results of the ICP analysis will only be used to determine the appropriate sample aliquot for Fe-55 analysis.

8.1.5 Proceed directly to Step 8.3.

8.2 INITIAL TREATMENT OF SOLID SAMPLES

8.2.1 Weigh approximately 1g of sample into a 50mL centrifuge tube. Record the actual sample mass on the benchsheet.

8.2.2 Prepare QC samples for solid matrices per Section 10.

8.2.3 Add 15mL of DI water, 10mL of conc. HNO_3 and 10mL of conc. HCl to the sample.

8.2.4 Heat the sample for 1 hour on a steam bath.

8.2.5 Remove the sample from the steam bath and allow to cool.

8.2.6 Centrifuge at approximately 3,500 rpm for 10 minutes.

8.2.7 Decant the supernatant into a labeled 220mL specimen cup.

8.2.8 Add DI water to dilute the leachate solution to a final volume of 110mL. The graduations on the Falcon cups specified in Section 5.2 above have been demonstrated to be sufficiently accurate for performing this

dilution.

8.2.9 Cap the sample cup tightly and mix the contents thoroughly.

8.2.10 Pipet 1.0mL of the digestate from the specimen cup into a disposable test tube containing 9.0mL ICP solution, and labeled with the sample ID and "native Fe". Mix well and submit to the metals lab for ICP-AES analysis. The results of the ICP analysis will only be used to determine the appropriate sample aliquot for Fe-55 analysis.

8.2.11 Proceed directly to Step 8.3.

8.3 ALIQUANT DETERMINATION BASED ON NATIVE IRON CONTENT AS MEASURED BY ICP-AES

TRU® resin has the capacity to retain a maximum of 3mg Fe. The amount of sample solution that can be treated with TRU® resin is dependent on the concentration of dissolved Fe in the sample. Normally, most water samples are expected to be low in dissolved Fe. Acidic aqueous samples and leachates may be high in Fe. Sample solutions suspected to be high in Fe should be analyzed by ICP so that a reduced aliquant can be calculated that will not overload the TRU® resin column.

In this SOP, sample solutions are classified in three groups according to Fe content. Each type is treated accordingly:

Type	Fe conc. (mg/L)	Aliquot to Prepare	Stable Fe Carrier
Low	< 5	100 mL	0.1 mL of 20 mg/mL
Med.	≥ 5 and ≤ 30	100 mL	none
High	>30	determined by ICP	none

If the Fe conc. > 30 mg/L, calculate the aliquot volume to prepare for TRU® resin using the following equation:

$$A = 3\ mg * 1000\ mL / [Fe]$$

where:

A = the aliquot (mL) of sample to purify with TRU® resin

[Fe] = the Fe concentration (mg/L) in the sample measured by ICP.

In cases where non-standard aliquots are determined, based on the ICP-AES data, supporting notation should be provided on the original bench sheet and should include the sample-specific results and an example calculation. Other equivalent documentation may be acceptable, at the supervisor's discretion.

8.4 SAMPLE PREPARATION

8.4.1 Transfer the appropriate aliquot of sample solution into a disposable 220mL polypropylene cup. Record the aliquot volume (A) on the benchsheet.

8.4.2 Prepare QC samples for water samples per Section 10.

8.4.3 Spike the LCS with 100 - 500 dpm of Fe-55. The source should be a second source independent of the calibration source.

8.4.4 For samples low in Fe (< 5 mg/L), add 0.1mL of stable Fe carrier (20 mg Fe/mL) to the cup.

8.4.5 **After mixing the sample thoroughly**, pipet a 1.0mL aliquot of the solution into a test tube for "initial" ICP analysis. Dilute the 1.0mL aliquot to a final volume of 5.0 mL using ICP diluting solution (see Section 6). Mix well and label with the sample ID and "initial". The results of this ICP analysis will be used to determine the pre-separation mass of iron in the sample, and will be entered into the ICP worksheet in LIMS.

8.4.6 In addition, a replicate 0.1mL aliquot (or similar known volume from a calibrated pipettor) of stable Fe carrier is diluted with DI water to 100 mL. After mixing thoroughly, a 1.0mL aliquot of this dilution is transferred to a test tube labeled 'reference carrier', diluted up to 10.0mL using ICP diluting solution, and submitted with the "initial" ICP fractions to provide a reference concentration for the ICP calculations.

8.4.7 Any remaining sample digestate should be capped, properly labeled, returned to the sample storage area, and a new fraction should be created in the LIMS internal chain of custody, indicating that a new sample fraction was created.

8.4.8 Place the cup containing the sample on a steam bath and evaporate the sample to dryness.

8.4.9 After the sample solution has evaporated, dissolve the residue in 10mL of 8N HNO_3. Proceed to Section 8.5 for purification of Fe using TRU® resin.

8.5 ISOLATION OF Fe USING TRU® RESIN

8.5.1 Prepare a TRU® resin column for each sample in the batch. Pre-packed columns purchased from the vendor (Eichrom) can be used, or columns can be prepared in the lab.

8.5.2 To prepare the columns, attach a fitted funnel to each empty BIO-Rad® column, and add about 2 mL of bulk TRU® resin slurried in DI water. Add a 4-5 mm layer of clean silica sand over the resin bed and place a waste cup underneath each column.

8.5.3 Condition each column with 5mL of 8N HNO_3. Collect the effluent in the waste cup.

8.5.4 Transfer each sample solution from Section 8.4.9 to a prepared TRU® resin column. Collect the effluent in the waste cup.

8.5.5 Complete the transfer by rinsing each sample beaker with 5mL of 8N HNO_3. Apply the rinsate to the column. Collect the effluent in the waste cup.

8.5.6 Rinse each column with 10mL of 8N HNO_3. Collect the effluent in the waste cup. The contents may now be disposed of into the Paragon wastewater treatment facility (i.e., down the drain in the lab sinks with plenty of cold tap water).

8.5.7 Used disposable cups may be rinsed with Radiacwash® solution and tap water and re-used for collecting waste column effluent. If the cups are not needed, they may be soaked in Radiacwash®, rinsed with tap water and discarded into the sanitary trash.

8.5.8 Elute Fe by rinsing each column with 15mL of 2N HNO_3. Collect the eluate from each column in a clean, labeled 20 mL glass scintillation vial.

8.5.9 Cap each vial tightly and vortex to mix the eluate until the solution is homogeneous. Pipet a 0.10mL aliquot from each vial into a labeled test tube for "final" ICP determination of Fe. **NOTE: The solution in each vial must be well-mixed and completely homogeneous before an aliquot is removed with a pipet.** Dilute the 0.10 mL aliquot to a final volume of 10.0mL using ICP diluting solution. Mix the diluted ICP aliquot thoroughly to ensure homogeneity.

8.5.10 Submit both the "initial" and "final" ICP fractions to the metals lab for analysis.

8.5.11 Evaporate the solution in each scintillation vial from Step 8.5.9 by carefully heating on a hotplate or HotBlock®.

8.5.12 After cooling, add 0.25mL of conc. HCl, using a calibrated pipet, to each vial to dissolve the residue.

8.5.13 Once the residue has been dissolved, add 4.75mL of DI water, using a calibrated pipet. Add 2 drops of conc. H_3PO_4 and 15mL of Ultima Gold® AB scintillation cocktail to each vial. Mix thoroughly.

8.5.14 Submit the prepared samples to the Instrument Lab. The Instrument Lab will analyze and ultimately dispose of the scintillation vials in the manner described in SOP 704.

8.5.15 Upon the return of the ICP sample fractions to the lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the Paragon wastewater treatment facility (i.e., down the drain in the lab sinks with plenty of cold tap water). The test tubes may be rinsed with a Radiacwash® solution, followed with tap water, then discarded into the sanitary trash.

8.5.16 Submit the ICP results and the calculated chemical yields to the instrument lab.

8.5.17 Used TRU® resin columns are discarded by extruding the resin from the column and placing the resin in the established waste stream labeled "Hazardous Waste - Used Acidic Resin" in the Satellite Accumulation Area in the lab. When the satellite container is full, notify the Waste Disposal Coordinator for further instructions. Emptied columns may be soaked in a Radiacwash® solution, rinsed in tap water, then discarded into the sanitary trash.

8.6 PREPARATION OF CALIBRATION STANDARDS

Calibration standards for this method are prepared upon request from the primary operator of the liquid scintillation counter system. A series of increasingly quenched blanks and Fe-55 spiked efficiency standards are prepared in order to establish background and efficiency "quench curves".

8.6.1 EFFICIENCY QUENCH CURVE CALIBRATION

8.6.1.1. To create the efficiency quench curve standards, add approximately 300-1000 dpm Fe-55 spiking solution to each of twelve scintillation vials. The spiking solution should be traceable to NIST and should be a "second source", independent of the solution used for spiking batch QC samples.

8.6.1.2. To each scintillation vial, add 0.1mL of the same stable Fe carrier used in the normal preparation of samples and batch QC.

8.6.1.3. Take the vials to dryness on a hotplate. After drying, remove

from heat and allow to cool.

8.6.1.4. To each vial, add 0.25mL concentrated HCl, 4.75mL DI water, two drops concentrated H_3PO_4, and 15 mL Ultima Gold®AB cocktail.

8.6.1.5. Nitromethane is used as the quenching agent. Nitromethane is not added to the first vial. To the remaining vials, add nitromethane in increasing 15µL increments.

8.6.1.6. Cap the vials tightly, mix thoroughly, and submit to the Counting Lab. The Counting Lab will analyze and ultimately dispose of the scintillation vials in the manner described in SOP 704.

8.6.2 BACKGROUND QUENCH CURVE samples are created using the same number of scintillation vials and the same procedure used in Sections 8.6.1.1 through 8.6.1.6, omitting the addition of Fe-55 spiking solution.

8.6.3 BATCH CALIBRATION BLANKS are created, in triplicate, with each batch of samples, by following the same procedure described in 8.6.2, with the exception that the three blanks should be quenched to approximately the low, middle, and high regions of the quench curve. The results from these batch calibration blanks will be used to adjust the background quench curve, as discussed in SOP 704.

9. CALCULATIONS

9.1 Calculate the actual volume (V_A) of sample analyzed , accounting for volumes of sample removed for ICP analysis, as follows:

$$V_A = V * \frac{V_i - icp_i}{V_i} * \frac{V_f - icp_f}{V_f}$$

where:

V = initial sample aliquot (L, g)

V_i = sample dilution/digestate volume prior to taking the initial ICP aliquot (mL)

icp_i = initial aliquot taken for ICP (mL)

V_f = post-separation sample volume (mL)

icp_f = final aliquot taken for ICP (mL)

9.2 Calculate the chemical recovery (Y) as follows:

9.2.1 Calculate the initial mass of Fe present in the actual sample volume analyzed:

$$M_i = C_i * DF_i * (V_i - icp_i)$$

where:

M_i = initial pre-separation mass of Fe present in the actual sample volume analyzed (ug)
C_i = concentration of Fe in the initial aliquot taken for ICP (ug/mL)
DF_i = dilution factor for icp_i, prior to ICP analysis

9.2.2 In cases where Fe carrier was added to the sample, calculate the minimum amount of Fe that can be present after the addition of Fe carrier:

$$M_r = C_r * DF_r * Vr * (V_i - icp_i) / V_i$$

where:

Mr = reference mass of Fe present in the carrier added (ug)
Cr = concentration of Fe in the aliquot of the reference carrier taken for ICP (ug/mL)
DFr = dilution factor for the reference carrier solution, prior to ICP analysis
Vr = total volume of the reference carrier solution, prior to taking ICP aliquot

NOTE: The initial mass of Fe may be underestimated due to matrix interference in the ICP measurement of the pre-separation concentration of Fe. This is the case when the calculated initial mass of Fe (M_i) is less than the 'reference carrier' mass (M_r). In this case, the reference carrier concentration is substituted for M_i below. If the discrepancy is greater than 15%, a note about the matrix interference is made in the case narrative.

9.2.3 Calculate the final mass of Fe present in the actual sample volume analyzed:

$$M_f = C_F * DF_f * (V_f)$$

where:

M_F = final post-separation mass of Fe present in the actual sample volume analyzed (ug)
C_i = concentration of Fe in the final aliquot taken for ICP (ug/mL)
DF_i = dilution factor for icp_f prior to ICP analysis

9.2.4 Calculate the chemical yield for Fe:

$$Y = M_f / M_i$$

9.3 The activity concentration, counting uncertainty, total propagated uncertainty, and minimum detectable concentration calculations are provided in SOP 708. Per SOP 708, however, the following preparation uncertainty factor is specific to this method:

9.3.1 Preparation Uncertainty- Aqueous Samples:
The Preparation Uncertainty factor for aqueous samples is 0.0973. This is based on one gross aliquotting, two volumetric measurements, and one ICP yield determination:

$$0.0973 = \sqrt{0.05^2 + 2 * \left(0.006^2\right) + 0.083^2}$$

9.3.2 Preparation Uncertainty- Solid Samples:
The Preparation Uncertainty for solid samples is 0.1007. This is based on one gross aliquotting, one mass measurement, one quantitative transfer, three volumetric measurements, and one ICP yield determination:

$$0.1007 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 3 * \left(0.006^2\right) + 0.083^2}$$

9.3.3 In practice, these two values are substantially equivalent and the larger of the two, 0.1007, may be used for both matrices.

10. QUALITY CONTROL

Required frequency and acceptance criteria for batch QC sample is discussed in SOP 715.

10.1 One method blank sample is prepared and analyzed with every batch of up to 20 field samples. The method blank consists of an empty polypropylene cup for soils (basically a reagent blank) and 100mL DI water for aqueous samples.

10.2 One sample duplicate is prepared and analyzed with every group of up to 10 field samples. A batch of 11 – 20 samples will have two duplicates.

10.3 One blank spike (LCS) is prepared and analyzed with every batch of up to 20 field samples. An appropriate amount of Fe-55 spiking solution is spiked into an empty polypropylene cup (soils LCS) or 100mL DI water (water LCS). The spike is added before the QC sample receives any chemical treatment.

11. DEVIATIONS FROM METHOD

Modification has been made to this method to support the preparation and analysis of solid matrices.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.2 Safety glasses and lab coats must be worn in the radiochemistry prep

labs at all times.

12.1.3 Gloves, safety glasses and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or samples or when handling potentially contaminated materials.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.2 below.

12.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.1.6 Care should be taken when diluting acids. Always add acid to water, ***NOT*** water to acid.

12.2 WASTE DISPOSAL

12.2.1 Wastes that are "corrosive only", such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the Paragon wastewater treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity), may be neutralized in the waste treatment facility.

12.2.2 All acid wastes not containing HF that are generated in ion exchange operations, are disposed of to the waste tanks (i.e., down the drain in the lab sinks with plenty of cold tap water) unless otherwise specified due to hazardous constituents.

13. REFERENCES

13.1 Eichrom Technologies, Inc., Analytical Procedure FEW01, "Iron-55 in Water". April 30, 2001, pp 1-4.

13.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

8/31/07: Changed default MDC to 50 pCi/g,L (SUMMARY). Added INTERFERENCES Section 4. Clarified use of second independent source for spiking (SECTION 6). Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Sections 7.1. In PROCEDURES Section, provided for filtering sedimented waters; changed soil digestion technique to use a centrifuge tube and changed default soil aliquot to 1g; clarified initial ICP determination; reduced LCS spiking level. Removed activity, MDC, and TPU calculations from Section 9

and referenced SOP 708 instead. Included note in Section 10.3 that the LCS spike is added before the QC sample receives any chemical treatment. Added DOCUMENT REVISION HISTORY Section.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 751 REVISION 2

TITLE: **ACTINIDES – AMERICIUM / CURIUM SEPARATION – PURIFICATION BY TRU™ AND TEVA™ SPEC COLUMN**

FORMS: **NONE**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 8/15/07
QUALITY ASSURANCE MANAGER _____ DATE 8/14/07
LABORATORY MANAGER _____ DATE 8-16-07

HISTORY: Rev0, 11/08/02; Rev1, 5/17/04 and 1/31/05 (no revisions); Rev2, 8/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the isolation of Americium (Am) and Curium (Cm) in water samples, filter leachates, vegetation, and soil digestate solutions using TRU™ resin followed by purification using TEVA™ resin. Also described is the mounting of Am for quantitation by alpha spectroscopy. Before using this procedure, an aqueous or solid sample must be prepared as described in the appropriate aqueous (SOP 776) or solid (SOP 773) preparation SOP, followed by ion exchange separation per SOP 778. The Am/Cm fraction separated from the previous procedure is dissolved in 3N HNO_3 prior to separation with TRU™ resin.

2. SUMMARY

The Am/Cm fraction (from previous dissolution and ion-exchange SOPs) is dissolved in 3N HNO_3. The sample solution is passed through a TRU™ resin column containing resin that is equilibrated in 2N HNO_3. The resin is washed with 2N and 0.5N HNO_3 to complete the isolation of Am/Cm from the sample matrix. Am/Cm is stripped from the column by washing with 9N and 4N HCl. The Am/Cm is further purified from interfering rare earth elements using TEVA™ resin. Finally, the Am/Cm is co-precipitated with lanthanum fluoride and mounted on a filter membrane for quantitation by alpha spectroscopy.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specification related to the client, project, and test method being performed.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

The presence of Thorium in the sample may cause interference with the Am spectrum. When the aliquot size for analysis is larger than normal and if the sample is a sequential analysis for Pu, U, and Am, care must be taken to remove Th from the sample. If the Th is not separated from the sample, Th-228 may appear in the Am-241 Region Of Interest (ROI) and produce a false positive result. A nitrate column may be run in addition to the routine sample prep to ensure all Th is removed from the sample as needed.

5. APPARATUS AND MATERIALS

5.1 Disposable BIO-Rad™ Ion exchange columns

5.2 Plastic funnel, fitted

5.3 Repeater pipet and tips

5.4 Steambath, stainless steel

5.5 Graduated cylinder, plastic, 25mL

5.6 Suction filter apparatus for 25mm membrane

5.7 Filter membrane, 25mm, 0.1µm porosity

5.8 Stainless steel cupped planchet, 1.25 inch diameter

5.9 Hot block

5.10 Pipets, Eppendorf™ or equivalent and tips

5.11 Polypropylene beaker, disposable, 220mL

5.12 Centrifuge bottle, 250mL capacity

5.13 Glass cup, disposable, Environmental Express #SC432, or equivalent

5.14 Double-sided tape

5.15 Transfer pipets, disposable

5.16 Wash bottles

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) of less than 50ppm, shall be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Reagent water. Obtained from the laboratory's deionized (DI) water system.

6.2 Nitric acid (HNO_3), conc., reagent grade. TLV = 2ppm (TWA). Irritant, corrosive.

6.3 3N HNO_3: Cautiously add 190mL of conc. HNO_3 to approximately 600mL DI water and dilute to 1L. See above for TLV.

6.4 2N HNO_3: Cautiously add 130mL conc. HNO_3 to approximately 600mL DI water and dilute to 1L. See above for TLV.

6.5 0.5N HNO_3: Cautiously add 31mL conc. HNO_3 to 800mL DI water and dilute to 1L. See above for TLV.

6.6 Hydrochloric acid (HCl), conc., reagent grade. TLV = 5ppm (ceiling). Irritant, corrosive.

6.7 9N HCl: Cautiously add 750mL conc. HCl to 200mL DI water and dilute to 1L. See above for TLV.

6.8 4N HCl: Cautiously add 330mL conc. HCl to 500mL DI water and dilute to 1L. See above for TLV.

6.9 2N HCl: Cautiously add 170mL conc. HCl to approximately 600mL DI water and dilute to 1L. See above for TLV.

6.10 Hydrofluoric acid, HF, conc. (48%-51%), reagent grade. TLV = 3ppm.

6.11 Hydrofluoric acid (HF), 3N: Dilute 104mL conc. HF to 1L with DI water. Use a plastic graduated cylinder and store in a plastic bottle. TLV = 3ppm.

6.12 Ascorbic Acid, reagent grade.

6.13 Ascorbic acid solution: Dissolve 200mg ascorbic acid /mL DI water. Prepare fresh daily before use.

6.14 Formic acid (HCOOH), 98%, reagent grade. TLV = 5ppm.

6.15 Ammonium thiocyanate (NH_4SCN), reagent grade.

6.16 2M ammonium thiocyanate/0.1M formic acid: For every 100mL of solution, dissolve 15.2g NH_4SCN and 0.35mL 98% formic acid in 100mL DI water.

6.17 1M ammonium thiocyanate/0.1M formic acid: For every 100mL of solution, dissolve 7.6g NH_4SCN and 0.35mL 98% formic acid in 100mL DI water.

6.18 Lanthanum carrier, 0.1mg La^{+3}/mL: Dissolve 0.312g high purity $La(NO_3)2•6H_2O$ in 1000 mL of 1N HCl.

6.19 Methanol, reagent grade. TLV = 200ppm.

6.20 Silica sand.

6.21 TRU™ resin and TEVA™ resin, 100-150µ size. Purchase from Eichrom Industries, Inc.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

SOPs 773 and 776 address Sample Collection, Preservation and Handling for samples in association with this procedure.

8. PROCEDURE

8.1 PREPARATION OF SAMPLE SOLUTION FOR TRU™ RESIN

8.1.1 The acidic effluent from the preceding separation procedure should be collected in a disposable plastic beaker. Place the beaker on a steam bath and take to dryness. *Note that the sample may not completely dry.*

8.1.2 Dissolve the sample residue in 25mL of 3N HNO_3. To aid in dissolution of the residue, place the sample on the steambath for a few minutes.

8.1.3 After the sample residue is completely dissolved, add 1.0mL of 200mg ascorbic acid / mL DI water (the ascorbic acid solution must be prepared fresh daily) to each sample. Proceed to Section 8.2.

8.2 ISOLATION OF AM/CM USING TRU™ RESIN COLUMN

8.2.1 Prepare a TRU™ resin column by filling a BIO-Rad™ column to the 1.6mL mark with a slurry of TRU™ resin and DI water. Add a 4-5mm layer of clean sand to the top of the resin bed. Attach an

Environmental Express funnel to the column. Place waste cups underneath the columns.

8.2.2 Condition the column with 5mL of 2N HNO_3, discard column effluent down the drain in the lab sinks with large amounts of water.

8.2.3 Apply sample solution to the prepared TRU™ resin column, discard column effluent. The effluent may be discharged into the Paragon wastewater treatment facility (i.e., down the drain in the lab sinks with large amounts of water).

8.2.4 Rinse the sample cup with 5mL of 2N HNO_3 and add to the column, discard column effluent (down the drain in the lab sinks with large amounts of water).

8.2.5 Rinse column with 5mL of 0.5N HNO_3, discard column effluent down the drain in the lab sinks with large amounts of water.

8.2.6 Rinse column with 3mL of 9N HCl, collect column effluent in a clean disposable glass cup labeled with the sample ID and "Am/Cm-TEVA".

8.2.7 Rinse column with 20mL of 4N HCl, collect column effluent in the same labeled glass cup as above.

8.2.8 Place the glass cup containing the Am/Cm fraction on a hot block set at approximately 100˚C and heat the solution to dryness.

8.2.9 Used TRU™ resin columns are discarded by extruding the resin from the column and placing the resin in the established waste stream labeled "Hazardous Waste – Used Acidic Resin" in the Satellite Accumulation Area in the lab. When the satellite container is full, notify the Waste Management Officer for further instructions. Emptied columns may be soaked in a RadiacWash™ solution, rinsed in tap water and discarded into the sanitary trash.

8.3 PURIFICATION OF AM/CM USING TEVA™ RESIN

8.3.1 Re-dissolve the sample from Step 8.2.8 in 5mL of 2M NH_4SCN / 0.1M formic acid solution. Place the sample on the hot block for 5 minutes to ensure dissolution.

8.3.2 Prepare a TEVA™ resin column by filling a BIO-Rad™ column to the 1.6mL mark with a slurry of TEVA™ resin and DI water. Add a 4-5mm layer of clean sand to the top of the resin bed. Place waste cups beneath the columns.

8.3.3 Condition a TEVA™ resin column by passing 5mL of 2M NH_4SCN / 0.1M formic acid solution through it. Collect the effluent in a waste cup.

8.3.4 Transfer the sample solution onto the TEVA™ column using a disposable polyethylene transfer pipette. Rinse the sample container with 5mL of 2M NH_4SCN / 0.1M formic acid solution and place the sample on the hot block for 5 minutes. Apply the rinsate to the column.

8.3.5 Rinse the sample cup with two 5mL volumes of 1M NH_4SCN / 0.1M formic acid solution. Apply the rinsate to the TEVA™ column. Allow the first 5mL to pass through the column completely before applying the second 5mL. The purpose of this Step is to wash lanthanides from the column. Discard waste from Steps 8.3.3 - 8.3.5 in the ammonium thiocyanate carboy.

8.3.6 Strip Am/Cm from the column with three 5mL volumes of 2N HCl. Collect the effluent from the column in a clean polypropylene beaker labeled with the sample ID and "micro ppt for Am/Cm". Allow each portion of 2N HCl to drain completely before applying the next.

8.3.7 To decompose thiocyanate, add 2.5mL conc. HNO_3 and 7.5mL concentrated HCl to the Am strip solution. Swirl gently to mix. Place the container on a steam bath and heat until about one drop of solution remains.

8.3.8 Add 5mL conc. HNO_3 to the sample from the previous Step only if any black colored and brown colored solution is noticed and heat on the steambath until the volume is reduced to about one drop.

8.3.9 Used TEVA™ resin columns are discarded by extruding the resin from the column and placing the resin in the established waste stream labeled "Hazardous Waste – Used Acidic Resin" in the Satellite Accumulation Area in the lab. When the satellite container is full, notify the Waste Management Officer for further instructions. Emptied columns may be soaked in a RadiacWash™ solution, rinsed in tap water and discarded into the sanitary trash.

8.4 AMERICIUM/CURIUM MICRO-PRECIPITATION

8.4.1 Add 1mL conc. HCl to the dried sample residue in the cup from Section 7.3.8. Wait 15 minutes to resolubilize the residue. Add 14mL DI water to the cup and mix.

8.4.2 Add 1.0mL lanthanum carrier. Mix well. Add 5mL 3N HF. Mix well.

8.4.3 Allow sample to stand for a minimum of 15 minutes.

8.4.4 Label taped planchets with sample ID, Batch ID, and analyte.

8.4.5 Place a 25mm filter membrane on a filter funnel assembly and turn the vacuum on. Rinse with 1-2mL of methanol (this will make the filter less hydrophobic). When the methanol is almost passed through, add approximately 5mL of DI water.

8.4.6 When the water is almost passed through the filter, pass the co-precipitated sample through the filter membrane.

8.4.7 Rinse the sample cup with 10mL DI water and add to the filter funnel, once the load solution has passed through. After the rinse has passed through, rinse the filter with an additional 10mL of DI water.

8.4.8 After filtration, keep vacuum on and remove the funnel. Use a "Sharpie" marker to place a dot on the outside edge of the filter. This helps identify the right side of the filter in case the filter flips during transaction. Carefully remove the filter membrane with a pair of forceps and fix it face up on the double-sided tape that was placed on the prepared planchet. Dry the filter membrane with the planchet under the fluorescence light bulb for a minute. DO NOT KEEP THE PLANCHET FOR A LONG TIME UNDERNEATH THE LAMP AS IT MIGHT MELT THE DOUBLE SIDED TAPE.

8.4.9 The sample is analyzed by Alpha Spectroscopy and reported according to Paragon SOP 714. Submit the prepared samples and the updated benchsheet to the counting lab. The counting lab will analyze and ultimately dispose of the planchet and filter in the manner described in SOP 714.

9. QUALITY CONTROL

9.1 Method blanks, LCSs, sample duplicates and sample spikes are prepared as specified in the previous associated procedure. Refer to SOP 776 for aqueous samples (SOP 773) for solid samples.

9.2 Calibration standards are not prepared for this method, however electroplated sources are purchased from an outside vendor, Isotope Products Laboratories, and used for instrument calibration. Refer to SOP 714 for calibration standards.

10. CALCULATIONS

TPU FACTORS. As defined in SOP 708, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU). The following TPUs come from the sample prep

previously completed in SOP 778, "Actinides -- Uranium, Plutonium, and Americium/Curium (partial) Sequential Separation by Ion Exchange".

10.1 Solid samples (that require initial prep using SOP 773) require a preparation uncertainty factor of 0.0665 at the one-sigma level. This factor is based on one gross aliquoting (sample homogeneity), one mass measurement, one tracer addition, two quantitative transfers and one reagent addition. See the following equation:

$$0.0665 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2}$$

10.2 Water samples (that require initial prep using SOP 776) require a preparation uncertainty factor of 0.0667 at the one-sigma level. This factor is based on one gross aliquoting (sample homogeneity), one volumetric measurement, one tracer addition, two quantitative transfers and one reagent addition. See the following equation:

$$0.0667 = \sqrt{0.05^2 + 0.006^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2}$$

10.3 Water and solid samples prepared by TRU™ resin column require a preparation uncertainty factor of 0.0264 at the one-sigma level. This TPU is estimated from one quantitative transfer and two reagent additions. See the following equation:

$$0.0264 = \sqrt{0.025^2 + 0.006^2 + 0.006^2}$$

10.4 Water and solid samples prepared by TEVA™ columns require a preparation uncertainty factor of 0.0257 at the one-sigma level. This is based on one quantitative transfer and one reagent addition. See the following equation:

$$0.0257 = \sqrt{0.025^2 + 0.006^2}$$

10.5 Water and solid samples prepared by microprecipitation require a preparation uncertainty factor of 0.025 at the one-sigma level. This TPU is estimated from one quantitative transfer. See the following equation:

$$0.025 = \sqrt{0.025^2}$$

11. DEVIATIONS FROM METHOD

This method was developed by Paragon Analytics, using the references cited in Section 13, and contains no deviations from applicable standardized methods.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.2 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

12.1.3 Gloves, safety glasses and lab coats must be worn when working with any chemicals (e.g., standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

12.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.1.6 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation and personnel safety features. Never inhale or allow skin or clothing to be exposed to HF fumes.

12.1.7 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

12.2 WASTE DISPOSAL

12.2.1 Wastes that are "corrosive only", such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the Paragon wastewater treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

12.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Management Officer for disposal.

12.2.3 The ammonium thiocyanate effluent that is generated using TEVA™ resin (Section 7.3) is collected in a labeled waste carboy. Notify the Waste Management Officer for disposal.

12.2.4 All acid wastes not containing HF or NH_4SCN that are generated in separation operations are disposed of to the waste tanks (i.e., down the drain) unless otherwise specified due to hazardous constituents.

13. REFERENCES

13.1 Eichrom Technologies, Inc. Americium, Plutonium and Uranium in Soil (2 gram sample). Draft Procedure 0.3. August 6, 2001.

13.2 Yamato, A. An Anion Exchange Method for the Determination of ^{241}Am and Plutonium in Environmental and Biological Samples, Journal of Radioanalytical Chemistry, Vol. 75, Nos 1-2 (1982), pages 265- 273.

13.3 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.4 Paragon SOP 708 "Calculations for Radioanalytical Results".

13.5 Campagnola, G.; Procedure Modification for Am-241 Analysis 3, Paragon Analytics trial, R:\Meth_Dev\Actinides\Am Procedure Modification, 2/5/04.

DOCUMENT REVISION HISTORY

8/12/07: DEVIATIONS and DOCUMENT REVISION HISTORY Sections added. Text references updated to SOP 708 -- Calculations for Radioanalytical Results.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 753 REVISION 3

TITLE: **DETERMINATION OF RADIOACTIVE IODINE AND CHLORINE IN ENVIRONMENTAL SAMPLES -- EPA METHOD 902.0**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7/6/06

QUALITY ASSURANCE MANAGER _____ DATE 7/6/06

LABORATORY MANAGER _____ for KDC DATE 7/6/06

HISTORY: NEW, Rev0, 4/5/94; PCN # 195, Rev1, 4/10/02; Rev2, 4/4/03; Rev3, 7/5/06.

re-released w/o revision 3/13/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary for preparation of water and solid samples for quantitative measurement of ^{129}I and other isotopes of iodine, as well as, ^{36}Cl and other isotopes of chlorine. In the separation of iodine in water samples, this method is substantially equivalent to EPA Method 902.0, except where noted. Specifically, the EPA method does not address chemical yield determinations, and this procedure estimates chemical yields by the analysis of a spiked split of the sample. Neither does the EPA method address the preparation of solid matrices. In addition, the EPA method does not address the chemical separation or analysis of radioactive isotopes of chlorine.

2. SUMMARY

2.1 Stable iodate carrier is spiked into an acidified water or the leachate of a solid sample. The iodate is reduced to the iodide state with Na_2SO_3 and all radioactive iodine and chlorine are precipitated as AgI and AgCl. The precipitate is dissolved with zinc powder and sulfuric acid. The iodine is re-precipitated as PdI_2 and filtered. Palladium will precipitate iodide in the presence of Cl^- and Br^-, separating iodide from these halides. The filter is mounted on a planchet for beta counting. The filtrate from the PdI_2 is collected and excess SO_4 is removed by adding $BaNO_3$. The chlorine is reprecipitated as AgCl and mounted onto a planchet for beta counting.

2.2 A composite measure of the chemical yield and counting efficiency (i.e., the 'total efficiency') is determined by parallel processing of a replicate aliquot of each sample spiked with a known quantity of ^{129}I and/or ^{36}Cl. The spiked sample is referred to as the "yield spike". (Note: this spike is NOT a 'matrix spike'; a matrix spike is a QC sample and is NOT used to generate data for chemical yield corrections, but rather to provide quality control information about analyte

recovery).

2.3 Reproducibility of the process is critical in generating accurate chemical yield information. The analyst should treat all samples identically and must note any anomaly, which could cause a significant variation in yield between a sample and its associated yield spike.

2.4 If elevated sample activity is expected, the initial sample aliquot size may be reduced, or additional spike added so that the expected tracer count uncertainty does not exceed 10% of the tracer activity. Consult with a Supervisor to determine proper spiking levels for samples.

2.5 For each sample prepared, an associated yield spike is also prepared. This yield-spiked sample should be a replicate aliquot of leachate or water of the original sample and should be spiked high enough to minimize uncertainty in the total efficiency calculation (i.e., at least 10 times the expected sample activity). A typical batch of samples is named and would be spiked as follows:

02-01-123-01	
02-01-123-01DUP	
02-01-123-01SYS	1000-2000dpm ^{129}I spike and/or 1000-2000dpm ^{36}Cl
02-01-123-02	
02-01-123-02SYS	1000-2000dpm ^{129}I spike and/or 1000-2000dpm ^{36}Cl
02-01-123-03	
02-01-123-03SYS	1000-2000dpm ^{129}I spike and/or 1000-2000dpm ^{36}Cl
02-01-123-04	
02-01-123-04SYS	1000-2000dpm ^{129}I spike and/or 1000-2000dpm ^{36}Cl
CL020101-1MB	
CL020101-1LCS	**100-200**dpm ^{129}I spike and/or **100-200**dpm ^{36}Cl
CL020101-1SYS	1000-2000dpm ^{129}I spike and/or 1000dpm ^{36}Cl

(Note: for purposes of calculations, the total efficiency for the batch QC Yield Spike is applied to the blank and the LCS.)

2.6 The sample and the associated spike should be counted on the same detector. (Although calculations account for variation in detector efficiency and background, uncertainty in these corrections are eliminated when the sample and associated spike are counted on the same detector.)

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method.

This demonstration may come in the form of Supervisory/ training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 Solid samples should not be muffled due to the potential volatility of iodine and chlorine.

4.2 Glass fiber filters exhibit beta activity due to naturally occurring radionuclides, potentially including actinides and potassium-40. For iodine, three filter blanks are processed with the samples and used to determine the contribution to background and in determining background correction to be applied to samples.

5. APPARATUS AND MATERIALS

5.1 hotplates

5.2 top-loading balance, resolution to 0.01g

5.3 centrifuge

5.4 centrifuge tubes, polypropylene, 50mL

5.5 mechanical shaker

5.6 stir plates

5.7 stir bars, PTFE™-coated, magnetic

5.8 Whatman™, #41 filter paper, or equivalent

5.9 vacuum filtration apparatus, 47mm

5.10 fritted support base, 47mm

5.11 glass fiber filters, 47mm

5.12 filtering flask with side-arm, 1000mL

5.13 funnel, 300mL

5.14 clamps

5.15 Pyrex™ beakers, 1500mL or 2000mL

5.16 flat planchets, stainless steel, 2-inch diameter

5.17 Polypropylene cups, disposable, with snap-tight lid, 220mL

5.18 double-sided adhesive tape

5.19 vortex mixer

6. REAGENTS - Only reagent grade or better chemicals shall be used.

NOTE: Threshold Limit Value (TLV) and other hazard information may be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding

6.1 Deionized (DI) water, ASTM Type II

6.2 Iodate carrier (IO_3^-), 10mg/mL (as I^-): Dissolve 1.68g KIO_3 in DI water and dilute to 100mL. Store in an amber container.

6.3 Hydrochloric acid (HCl), 12M (concentrated). TLV = 5ppm (ceiling). Irritant, corrosive.

6.4 Nitric acid (HNO_3), 16M (concentrated). TLV = 2ppm, (TWA). Irritant, corrosive.

6.5 Nitric acid, 1M: Cautiously add 63mL of concentrated nitric acid to 800mL of DI water. Dilute to 1 liter. TLV = 2ppm, (TWA). Irritant, corrosive.

6.6 Hydrochloric acid, 6M: Mix 1 volume 12M HCl (conc.) with 1 volume DI water. TLV = 5ppm (ceiling). Irritant, corrosive

6.7 Palladium chloride ($PdCl_2$), anhydrous.

6.8 Palladium chloride, 0.2M: Dissolve 3.542g $PdCl_2$ in 100mL 1M HCl. TLV = 5ppm (ceiling). Irritant, corrosive.

6.9 Silver nitrate, 1.0M: Dissolve 17g $AgNO_3$ in DI water and dilute to 100mL. Store in an amber glass bottle. TLV = 0.0014ppm

6.10 Sodium sulfite, 1M: Dissolve 5g Na_2SO_3 in 40mL DI water. Prepare fresh reagent weekly.

6.11 Sulfuric acid (H_2SO_4), (concentrated). TLV = 0.25ppm (TWA). Irritant.

6.12 Sulfuric acid, 2N: Mix 1 volume conc. H_2SO_4 with 17 volumes of DI water. TLV = 0.25ppm (TWA). Irritant.

6.13 Methanol (MeOH). TLV = 200ppm. Neuropathy, vision, central nervous system effects.

6.14 Barium nitrate, $Ba(NO_3)_2$.

6.15 Zinc powder. TLV = 1.9ppm

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Although the client is responsible for conducting the sampling process, it is emphasized that water samples be collected in a manner that addresses the considerations discussed in EPA 900.0 Section Three, except that the sample should <u>not</u> be preserved by acidification with HNO_3.

7.2 The container should be amber glass to minimize exposure to light.

8. PROCEDURE

8.1 SOLIDS

8.1.1 As the samples are to be split following leaching, twice the volume of sample is leached. Weigh the appropriate mass of sample into a 220mL polypropylene cup. (The default aliquot mass is 2 grams, therefore weigh out 4 grams). Add 100mL of 1M nitric acid.

8.1.2 Allow any vigorous reaction to subside then cap each sample tightly.

8.1.3 Place the capped samples on the "Big Bill" mechanical rotator/shaker at approximately 100rpm. Shake/leach the samples overnight.

8.1.4 After leaching, filter each sample into a second, clean, labeled polypropylene cup, or other suitable container, using Whatman™ #41 filter paper. Rinse the cup and filter paper with 5mL of 1M nitric acid.

8.1.5 Gravimetrically split the samples into two equal halves. Label the first cup with the sample ID and the second cup with the replicate sample work order ID to denote the spiked sample.

8.1.6 Add 1.0mL of stable iodate carrier to each sample.

8.1.7 Add the appropriate amount of ^{129}I and/or ^{36}Cl spiking solution to the yield spike samples and the LCS.

8.1.8 Dilute each solid sample leachate to 1.0L with DI water and continue with the waters procedure in Section 8.2.3, eliminating the addition of iodate carrier.

8.2 WATERS

8.2.1 Using a graduated cylinder, measure a 1000mL aliquot of water sample and transfer to a 2000mL Pyrex™ beaker. Prepare two beakers for each sample. Label the first beaker with the sample ID and the second beaker with the replicate sample work order ID to denote the spiked sample.

8.2.2 Spike the yield spike samples and the LCS with the appropriate activity of ^{129}I and/or ^{36}Cl at this time.

8.2.3 Add 7.5mL conc. HNO_3 and 1.0mL of iodate carrier to the beaker. Place a magnetic stir bar in the beaker and mix the sample on a magnetic stir plate.

8.2.4 Add 4mL 1M Na_2SO_3 and stir for 30 minutes.

8.2.5 Add 2mL 1M $AgNO_3$ and stir for 1 hour. Allow the precipitate to settle for another hour.

8.2.6 Using a vacuum, filter the suspension through a glass fiber filter. Collect the filtrate in a waste container, provided by the Waste Disposal Coordinator, labeled "Aqueous Lab Waste". Refer to the Waste Disposal Coordinator for ultimate disposal of this waste stream when the container is full.

To minimize the potential for cross-contamination of spiked and unspiked samples, a separate filtration apparatus should be used for each sample.

8.2.7 Transfer the filter with the precipitate to a plastic specimen cup. Add 1g zinc powder, 10mL DI water and 2mL of 2N H_2SO_4. Shake on a mechanical shaker at 300rpm for at least one hour. This is a good place to stop for the day if necessary.

8.2.8 Using vacuum, filter the slurry through a glass fiber filter. Collect the filtrate in a 50mL polypropylene centrifuge tube, which is stacked on top of another centrifuge tube inside the 1000mL filtering flask. Rinse the specimen cup with a few mL of DI water to complete the transfer of the slurry to the filter.

8.2.9 Collect the filter and residue in a pan and air dry in a fume hood. otherwise scan the dried material for radioactivity with an NE Electra hand probe, per Paragon's Radiation Protection Plan (RPP). If the material is considered radioactive waste it should be transferred directly to the Waste Disposal Coordinator for ultimate disposal as "Mixed Waste", otherwise it may be disposed of in the "Contaminated Soils and Solids" waste container. Refer to SOP 003 and 315 or the Waste Disposal Coordinator for disposal when this container is full.

8.2.10 If analyzing for Chlorine skip to Step 8.2.12

8.2.11 Add 2mL of 6M HCl to the filtrate.

8.2.12 Add 1mL of 0.2M $PdCl_2$ to the filtrate.

8.2.13 Rinsing with methanol, filter the sample and collect the precipitate on a glass fiber filter. Wash alternately with 5mL portions of DI water and methanol. If analyzing for Chlorine collect the filtrate in a 50mL polypropylene centrifuge tube, which is stacked on top of another centrifuge tube inside the 1000mL filtering flask and proceed to Step 8.2.17 for the chlorine procedure. If only analyzing for Iodine, collect the filtrate in an "Aqueous Lab Waste" container provided by the Waste Disposal Coordinator. Refer to the Waste Disposal Coordinator for ultimate disposal of this waste stream when the container is full.

8.2.14 Place each sample filter in a clearly labeled 2" planchet and allow air-drying overnight. A convenient way to air-dry the samples are to place the planchets in the desiccator overnight. After the sample filter has dried, mount the filter on the planchet with double-sided adhesive tape.

8.2.15 Submit sample planchets and three blank filters mounted on planchets to the Instrumentation Lab for counting.

8.2.16 The Instrument Lab will analyze the samples and ultimately dispose of the filter and planchet in the manner described in SOP 724.

8.2.17 To the filtrate from Step 8.2.13, add approximately 0.5 grams of $Ba(NO_3)_2$ to each sample to remove any excess sulfate.

8.2.18 Centrifuge the sample at 3500rpm for 15 minutes.

8.2.19 Decant the supernatant into a clean 50mL centrifuge tube and add 2mL of $AgNO_3$ to precipitate AgCl.

8.2.20 Centrifuge the sample at 3500rpm for 15 minutes.

8.2.21 Decant the supernatant into the ^{129}I waste carboy.

8.2.22 Add 10mL of 1M HNO_3 to each sample, then vortex to wash the precipitate.

8.2.23 Centrifuge the sample at 3500rpm for 15 minutes.

8.2.24 Decant the supernatant into the ^{129}I waste carboy.

8.2.25 Add 4mL of 1M HNO_3 to each sample and vortex.

8.2.26 Working quickly to avoid settling of the precipitate, transfer each sample, rinsing with 1M HNO_3 in a wash-bottle, to a labeled stainless steel flat planchet.

8.2.27 Take the sample to dryness on a hotplate.

8.2.28 Submit to the Instrument Lab, with the appropriate documentation, for counting by gas flow proportional counter (GFPC).

9. PREPARATION OF CALIBRATION STANDARDS

9.1 IODINE CALIBRATION

9.1.1 Spike 3000-5000dpm ^{129}I into one liter of DI water (prepare 5 calibration sources).

9.1.2 Proceed to Step 8.2.3.

9.2 CHLORINE CALIBRATION

9.2.1 Spike approximately 10000dpm of ^{36}Cl into each labeled 50mL centrifuge tube (prepare 5 calibration sources).

9.2.2 Add 5mL of 1M $AgNO_3$ to each sample and mix well.

9.2.3 Centrifuge the samples at 3500rpm for 15 minutes. Decant the supernatant into the appropriate waste carboy.

9.2.4 Add 4mL of 1M HNO_3 to each sample.

9.2.5 Transfer each sample, rinsing with 1M HNO_3, to a labeled stainless steel flat planchet.

9.2.6 Take the sample to dryness on a hotplate.

9.2.7 Submit to the Instrument Lab, with the appropriate documentation, for counting by gas flow proportional counter.

10. CALCULATIONS

10.1 The **CHEMICAL YIELD** for this procedure is estimated by the analysis of a spiked split of the sample.

$$Yield = \frac{\left(\left(SSGrCPM - SSBkgCPM\right)/SSDetEff\right) - \left(\left(SmplGrCPM - BkgCPM\right)/DetEff\right)}{SpkDPM}$$

10.2 The sample **ACTIVITY** is calculated as follows:

$$\text{Activity} = \frac{\left(\text{SmplGrCPM}\right) - \left(\text{BkgCPM}\right) - \left(FiltCPM\right)}{\text{Denom}}$$

The activity calculation **DENOMINATOR** is calculated as follows:

$$\text{Denom} = \text{FinAli} * \text{Dec} * \text{ActCnv} * \text{DetEff} * \text{Yield}$$

10.3 Calculate the **ONE-SIGMA COUNTING UNCERTAINTY** as follows:

$$\text{CountingUnc.} = \frac{\sqrt{\left(\text{SmplGrCPM}/\text{SmplTime}\right) + \left(\text{BkgCPM}/\text{BkgTime}\right) + \left(FiltCPM / FiltTime\right)}}{\text{Denom}}$$

10.4 **TPU FACTORS**. As defined in SOP 743, the following 1σ preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty.

10.4.1 FOR IODINE SAMPLES:
Water samples require a preparation uncertainty factor of 0.172. This is based on one gross aliquoting (sample homogeneity), one volumetric measurement, one tracer addition and three quantitative transfers. The estimated TPU related to the spiked split method is 15.63%. See the following equation:

$$0.172 = \sqrt{0.05^2 + 0.006^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.1563^2}$$

Solid samples require a preparation uncertainty factor of 0.173. This is based on one gross aliquotting (sample homogeneity), one mass measurement, one tracer addition and four quantitative transfers. The estimated TPU related to the spiked split method is 15.63%. See the following equation:

$$0.173 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.1563^2}$$

In practice, these values are substantially equivalent. For simplification in reporting, the larger factor of 0.173 may be conservatively used for both matrices.

10.4.2 FOR CHLORINE SAMPLES:
Water samples require a preparation uncertainty factor of 0.172. This is based on one gross aliquoting (sample homogeneity), one volumetric measurement, one tracer addition and five quantitative transfers. The estimated TPU related to the spiked split method is 15.63%. See the following equation:

$$0.175 = \sqrt{0.05^2 + 0.006^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.1563^2}$$

Solid samples require a preparation uncertainty factor of 0.173. This is based on one gross aliquotting (sample homogeneity), one mass measurement, one tracer addition and six quantitative transfers. The estimated TPU related to the spiked split method is 15.63%. See the following equation:

$$0.177 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.1563^2}$$

In practice, these values are substantially equivalent. For simplification in

reporting, the larger factor of 0.177 may be conservatively used for both matrices.

10.5 Calculate the **ONE-SIGMA TOTAL PROPAGATED UNCERTAINTY (TPU)** as follows:

$$TPU(pCi/unit) = \sqrt{Counting\,Unc.^2 + (Activity * 0.173)^2 + (Activity * 0.056)^2}$$

This is based on SOP 743 guidelines for the TPU preparation factors described above and the in-house preparation of calibration standards.

10.6 The 2σ **MINIMUM DETECTABLE CONCENTRATION** (MDC) is calculated as follows:

$$MDC = \frac{4.65 * \sqrt{(BkgCPM + FiltCPM) * SmplTime} + 2.71}{SmplTime * Denom}$$

10.7 The 2σ **DECISION LEVEL** (DL) activity is calculated as follows:

$$DL = \frac{2.33 * \sqrt{((BkgCPM + FiltCPM) * SmplTime)}}{SmplTime * Denom}$$

where:

Activity = ^{129}I activity (default units pCi/L)
SmplGrCPM = analyte gross count rate (cpm)
SmplTime = sample count time (min)
BkgCPM = background count rate (cpm)
FiltCPM = net blank filter average count rate (cpm)
BkgTime = background count time (min)
FiltTime = blank filter count time (min)
Denom = activity calculation denominator
DetEff = sample counting efficiency
FinAli = final dilution/preparation adjusted aliquot (Note: dilution factor is included in this number to reflect the quantity of original sample taken for analysis (L)
ActCnv = activity conversion factor from DPM to desired units (2.22 for pCi, 60 for Bq)
Dec = decay factor $e^{(-\lambda t)}$ (fractional)
$\lambda = \ln 2 / t_{1/2}$
$t_{1/2}$ = half-life for ^{129}I in same units as decay time

t = decay time in same units as half-life
BkgTime = background count time (min)
SSGrCPM = spiked sample gross (cpm)
SSBkgCPM = spiked sample background (cpm)
SSDetEff = spiked sample detector efficiency
SpkDPM = spike addition DPM decay corrected to count date
Yield = fractional chemical yield

11. QUALITY CONTROL

11.1 One blank is run per batch of twenty or fewer samples (5% frequency).

11.2 One duplicate is run per batch of 10 or fewer samples (10% frequency).

11.3 One spiked blank (LCS) is run per batch of 20 or fewer samples (5% frequency).

11.4 The five calibration standards should be counted on a single detector prior to use. The data should be reviewed by the primary instrument analyst to determine any outliers. These planchets should be marked "do not use" and removed from the calibration set.

12. DEVIATIONS FROM METHOD

This SOP is substantially compliant with EPA Method 902.0 for the analysis of drinking waters. Deviations from and distinctions between this and the reference method are described below:

12.1 A measure of chemical yield is determined by spike addition to splits of each sample to address potential bias from differences in detection efficiency resulting from sample self-absorption and to minimize potential bias resulting from the presence of iodide in the water sample.

12.2 This procedure has been modified to accommodate matrices other than drinking waters. The procedure treats solubilized radioactive constituents in digestate or leachate solutions as a water sample.

12.3 One PdI_2 precipitation is carried out in this procedure whereas Method 902.0 carries out the precipitation twice.

12.4 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the laboratory's internally-derived acceptance criteria.

12.5 This method also addresses the separation and analysis of Cl-36, where the EPA method only addresses the separation and analysis of I-129.

13. SAFETY, HAZARADS AND WASTE DISPOSAL

13.1 SAFETY AND HAZARDS

13.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

13.1.2 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

13.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

13.1.4 Any chemicals with a TLV of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents, acids). TLVs may be found in the reference cited in Section 13.2 below.

13.1.5 All non-original containers used to hold reagents (e.g. wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

13.1.6 Care should be taken when diluting acids. Always add acids to water, not water to acids.

13.2 WASTE DISPOSAL

13.2.1 Where indicated, waste solutions should be collected in a container provided by the Waste Disposal Coordinator. Consult the Waste Disposal Coordinator for disposal of this waste stream.

13.2.2 Wastes that are “corrosive only”, such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the PAR waste water treatment facility. These materials that are “corrosive only” (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

14. REFERENCES

14.1 USEPA. 1980. Prescribed Procedures for Measurement of Radioactivity in Drinking Water. “Method 902.0”. EPA/600 4-80-032.

14.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

14.3 PAR SOP 743R4 “Estimating Total Propagated Uncertainties for Radiometric

Analyses".

14.4 Paragon Analytics, Project ID 02-15-001, "Empirical Measurements for TPU Determinations", March 2002.

14.5 Wangeline, C.; Chlorine-36 in Water, Paragon Analytics trial, R:\Meth_Dev\Cl36\watermethod, 4/5/05.

14.6 Wangeline, C.; Chlorine-36 in Soil, Paragon Analytics trial, R:\Meth_Dev\Cl36\soilmethod, 5/24/05.

DOCUMENT REVISION HISTORY

7/5/06: Sequential separation of chlorine for ^{36}Cl analysis incorporated; added LIMS Program Specification language to Section 3; comments regarding sample containers were added to Section 7. Other minor editorial changes.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 754 REVISION 5

SOLID 5/5/07 (DAS)

TITLE: PREPARATION OF SAMPLES FOR TRITIUM ANALYSIS BY MICROWAVE OVEN

FORMS: 631, 1306 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 5/1/07

QUALITY ASSURANCE MANAGER _____ DATE 4/26/07

LABORATORY MANAGER _____ DATE 4-30-07

HISTORY: NEW, 3/23/95; Rev1, 10/08/99; Rev2, 4/26/02; Rev3, 4/04/03; Rev4, 3/15/05; Rev5, 4/27/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary for preparation of soil samples for measurement of water exchangeable tritium, utilizing distillation by microwave oven. This procedure is very efficient at extracting water from the solid matrix. Tritium that is bound to compounds other than water, will not be measured using this method. Oxidation of the solid to convert organic bound tritium to tritiated water may be required prior to distillation, if total tritium results are required.

2. SUMMARY

Tritium activity in the water content of a soil sample is radio assayed after separating the water from the sample by microwave heating, and the collection of the resulting vapor through condensation.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data

involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Volatile radionuclides that co-distill with the free water in a sample may lead to high bias in results. These would include, but are not limited to, low boiling organic compounds labeled with radiocarbon. The activity in the window above the region of interest (ROI) for tritium is monitored to identify samples where such interferences may be present.

4.2 Samples with very low moisture content may need to be equilibrated with tritium-free water prior to distillation. The addition of water will decrease sensitivity. The dilution affected by adding water must be accounted for in subsequent calculations of sample activity.

4.3 Avoid prolonged exposure of soil samples to air because of loss of moisture. Keep all sample containers tightly closed.

4.4 Rocky soils or those containing significant quantities of debris should be aliquotted, if possible, to exclude large rocks and other extraneous materials.

4.5 The scintillation vial is an optical surface. Any markings or material on the outside of the scintillation vial will interfere with the detection of scintillation. These should be removed prior to analysis by wiping the vial with a lint-free lab wipe and alcohol. All labeling must be done on the cap of the vial.

4.6 The presence of visible coloration in the distillate will act as an ‘inner filter’. This effect, known as ‘color quenching’ is an interference to the detection of the scintillation. The quench indicating parameter or (QIP, usually H-number) should be monitored and variations in quench that could correspond to greater than 10% relative bias in the efficiency, should be addressed by using standard additions to determine a sample-specific efficiency.

4.7 The presence of particulate contaminant in the final water distillate may interfere with the detection of the scintillation. This effect is known as ‘physical

quenching'. The symptoms, control limits, and corrective actions are identical to those mentioned in Section 4.6 above.

4.8 The presence of chemical contaminants in the final water distillate may inhibit scintillation. This effect is known as 'chemical quenching'. The symptoms, control limits, and corrective actions are identical to those mentioned in Section 4.6 above.

4.9 Due to the incompatibility of the matrix with microwave heating, samples containing metallic particles will need to be distilled by placing the sample in a 250mL round bottom flask, and distilled using the apparatus for water preparation.

4.10 The percent moisture value must be determined for all soil samples before starting the tritium analysis. One exception to this may be Performance Test (PT) samples. Consult with the Radiochemistry Technical Manager or designee prior to proceeding.

4.11 Sludge samples or those with an excessive amount of moisture may boil vigorously and "pop", contaminating the tubing and distillate. To avoid this, a piece of filter paper is cut to fit into the plastic jar over the sample. This will allow the moisture to pass while containing the sample. Filter paper should also be placed over the Blank and Blank Spike samples.

5. APPARATUS AND MATERIALS

5.1 pipettes, mechanical, previously calibrated per SOP 321, disposable pipette tips

5.2 dispenser, repipette, adjustable, 1-20mL

5.3 top loading balance, 0.1g sensitivity

5.4 graduated cylinder, 50mL

5.5 liquid scintillation vial, borosilicate glass, Teflon™-lined cap, 20mL

5.6 plastic jar, and cap with appropriate holes drilled for tubing in cap, also cap with no holes for storage purposes

5.7 glass beads

5.8 vacuum flask, with rubber stopper containing drilled hole for tubing

5.9 microwave, with appropriate holes drilled for tubing

5.10 1/4" outer-diameter Tygon™ tubing or equivalent

5.11 3/8" outer-diameter Tygon™ tubing or equivalent

5.12 forceps

5.13 ring stand, 3-prong clamps

5.14 desiccant tube, polyethylene. Fabricate by placing glass wool in one end of the tube, and filling with Drierite™, or equivalent desiccant. Place glass wool in the other end of the tube, to hold the desiccant in place.

5.15 glass pipette, 10mL, disposable, used as a moisture scrubber

5.16 Pyrex™ brand condenser #2400 or equivalent

5.17 spatula or disposable wooden tongue depressors

6. REAGENTS

NOTE: Threshold Limit Value (TLV) and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not mean that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding

6.1 Liquid scintillation cocktail, Ultima Gold™ LLT or equivalent

6.2 Tritium-free, laboratory deionized (DI) water

6.3 Drierite™ or equivalent desiccant. TLV = 24.45ppm (TWA)

6.4 Acetone. TLV = 500pm (TWA), irritant

6.5 Sand, quartz, Aldrich #27,473-9 (-50 to -70 mesh) or equivalent

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIME

7.1 Samples are collected and stored in tight-sealing glass jars so as to minimize the possible loss of water through evaporation

7.2 No preservation is necessary.

7.3 If elevated levels if tritium are expected, the Radiochemistry Technical Manager or designee should be contacted to ensure safe handling, and to take steps to minimize the risk of sample cross-contamination during storage and preparation.

7.4 At the current time, there is no regulatory holding time for tritium. Many sampling and analysis plans, however, apply a default holding time of 180 days for this analysis. If samples are analyzed more than 180 days after collection, this fact should be noted in the data package case narrative.

8. PROCEDURE

8.1 SAMPLE PREPARATION

8.1.1 Verify and record the sample condition on a solids sample condition form (Form 631).

8.1.2 Prior to sample preparation, a percent moisture analysis (SOP 642) should be performed on the samples to determine the appropriate aliquot size.

8.1.3 Label the caps of two sets of scintillation vials for each sample.

8.1.4 Label a clean plastic jar for each sample.

8.1.5 The amount of soil used is primarily dependent on how much soil is needed to produce 20mL of distilled water. Given the % moisture, calculate the amount of soil needed to produce this volume of distillate (assuming 100% recovery).

NOTE: Unless otherwise indicated, a maximum sample weight of 200 grams should be used regardless of the moisture content. If less than 200 grams is available, do not use the entire sample unless approved by the appropriate Project Manager. Additional deionized water may be added with a graduated cylinder or pipette in order to produce a total volume of 20mL of distilled water for testing. Any water added to a sample is noted on the benchsheet. If water is added to samples, the water should equilibrate with the solid sample overnight in the refrigerator.

8.1.6 Aliquot the calculated amount of sample into the labeled jars using a wooden tongue depressor or spatula.

8.1.7 Record the sample weight to the nearest 0.1g on the benchsheet. Keep the clean, labeled lid on the jar until ready for testing.

8.1.8 Prepare batch QC samples per Section 9.

8.1.9 Add laboratory deionized water to any samples that require it to produce 20mL of distillate.

8.1.10 Allow samples and QC to equilibrate overnight in cold storage. Be sure all jars are tightly capped to avoid tritium losses from evaporation.

8.1.11 Prior to using the microwave apparatus to distill samples, an equipment blank is prepared and analyzed per Section 8.2 to monitor potential sample contamination.

8.1.12 Replace lid with clean lid drilled with 1/4” holes. Put the jar in the microwave and connect to 1/4” tubing.

8.1.13 Connect tubing to condenser, connect tubing from moisture scrubber tube to jar, and connect desiccant tube to moisture scrubber.

8.1.14 Place a labeled scintillation vial in the vacuum flask ~half full of glass beads (to support vial) under the condenser outlet. Insert the rubber

stopper containing the condenser outlet into the vacuum flask to seal the flask.

8.1.15 Use the laboratory vacuum to apply a gentle vacuum to the flask, and turn on the water to the condenser.

8.1.16 Turn on the microwave, at 1-2 minute intervals, at full power, not allowing any condensation to form in the air intake tube.

8.1.17 As the sample heats, the vapor will condense in the condenser and drop into the scintillation vial.

NOTE: Do not dry the sample, overheat the jar, or heat too rapidly or melting of the plastic jar will occur. Be careful to keep an eye on the distillate flow through the condenser. If flow should decrease or stop, shut the microwave off

8.1.18 When sufficient distillate has been collected, turn off the microwave. 10.0mL of distillate is typically used for sample analysis, if less than 10.0mL is available, refer to Section 8.1.25 below.

8.1.19 Once distillation is complete, carefully remove the scintillation vial from the flask using a pair of forceps. Cap the vial and set it aside until ready to mix with cocktail.

8.1.20 Remove the jar containing the sample from the microwave. CAUTION: The jar will be hot. Replace the original lid and return this fraction to sample storage and document it as a tritium fraction on the chain of custody.

NOTE: Dried sample may be used for alpha spec or gamma spec.

8.1.21 Clean the setup thoroughly by flushing two or three times with DI water. Dry the apparatus with acetone prior to distilling the next sample. Collect the acetone in a flammable waste container.

8.1.22 Allow the distillate to cool completely prior to aliquotting. This will minimize tritium losses due to evaporation, and allow an accurate volumetric measurement by pipet.

8.1.23 Using a calibrated pipette (SOP 321), remove 10.0mL of the distillate collected in Step 8.1.18 above and dispense into a labeled borosilicate vial. Save the remainder of the distilled sample as a reserve.

8.1.24 Add 10mL of Ultima Gold^{TM} LLT cocktail to the vial and shake well to homogenize.

NOTE: The Ultima Gold™ dispenser is calibrated monthly to deliver 10mL using a Class A volumetric flask and recorded in the calibration logbook.

8.1.25 If there is less than 10mL of distillate available for analysis, conduct the transfer on the balance. Record the mass of the distillate added as the analytical aliquot (assuming 1g/mL). Then carefully add tritium-free water to bring the final mass of liquid in the vial to 10g. Make a note in the 'Comments' section on the benchsheet regarding dilution necessary to meet the calibration geometry.

8.1.26 Clean the surface of each vial by wiping with a lab wipe moistened with methanol or isopropyl alcohol, to remove smudges or other discolorations on the surface.

8.1.27 Without touching the surface of the glass, load the vials into the scintillation counting rack, beginning with the calibration blank.

8.1.28 Verify each vial ID and rack and position against that recorded on the benchsheet.

8.1.29 Submit the vials to the Counting Lab with all necessary documentation.

8.1.30 All samples should be dark-adapted for approximately two hours prior to counting.

8.1.31 The Counting Lab will analyze and ultimately dispose of the scintillation vials in the manner described in SOP 704.

8.2 EQUIPMENT BLANK

8.1.1 Between each prep batch of samples, an equipment blank is prepped and analyzed to confirm that the apparatus is not contaminated. This is accomplished by placing ~200g of sand into a sample container, adding 50mL of DI water, and processing as a sample per Section 8

8.1.2 The Counting Lab will analyze the equipment blank and return a report to the prep lab. This report is kept in the ^{3}H Equipment Blank History binder in the prep lab.

8.3 PREPARATION OF EFFICIENCY CALIBRATION STANDARDS

8.3.1 A one-point calibration source is conducted as follows: Prepare, in triplicate, a NIST-traceable tritiated water standard diluted to 50-500dpm/mL with deionized water, to a final volume of approximately 50mL. The solution is then distilled and aliquotted per SOP 700. The average efficiency is calculated as described in SOP 700.

8.3.2 A one-point efficiency is highly accurate and will be used for the calculations of all results showing a QIP result corresponding to the average observed for the calibration standard (within +/- 10% relative efficiency or, lacking this calibrated range, +/- 15 of mean H-numbers). Any sample falling outside this range will be calibrated by sample specific addition of minimum known volume (<200µL) of NIST-traceable tritiated water.

9. QUALITY CONTROL

9.1 CALIBRATION BLANK

For each batch of twenty or fewer samples, a calibration blank consisting of tritium-free water and liquid scintillation cocktail will be prepared in the same proportions as that in the samples. This sample is used to establish a population of blanks used for determining the instrumental background and shall not be distilled or subjected to any other processing. This sample is placed in the first position of the first rack of samples.

9.2 METHOD BLANK

Place 200g of clean, quartz sand into a sample container. Add 50mL of tritium-free deionized water. Process as a sample per Section 8.1. One blank is analyzed with each batch up to 20 samples, or at a minimum frequency of 5%.

9.3 LCS AND MATRIX SPIKES

9.3.1 For the LCS, place 200g of clean, quartz sand into a sample container. Add the appropriate spike volume to a graduated cylinder and bring the total volume up to 50mL with deionized water. Pour the spiking solution over the sand and shake the sand and water solution to mix. Process the LCS as a sample per Section 8.1. An LCS (i.e., blank spike) is run with each batch of samples up to 20, or at a minimum of 5% frequency.

9.3.2 Applicable acceptance limits for the LCS are 85-115%. Project-specific acceptance limits may apply and supersede default limits.

9.3.3 For matrix spike samples, evenly disperse the spiking solution over the sample. Cap the sample and shake thoroughly. Matrix spikes are prepared with each batch of samples up to 20, or at a minimum of 5% frequency. Applicable acceptance limits are 85-115%. Project-specific acceptance limits may apply and supersede default limits.

9.4 SAMPLE DUPLICATE

A duplicate sample analysis is run for each batch of up to ten samples or at a minimum frequency of 10%. If there is insufficient sample available to run a duplicate, an additional blank spike may be substituted for each duplicate.

10. DEVIATIONS FROM METHOD

This method extracts water from solid samples as described in the EPA EERF procedures manual (H-01-H-03). It is not an azeotropic distillation, and utilizes microwave radiation to generate the necessary heat to extract the water from the sample.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Microwaved samples reach high temperatures. Use appropriate thermal protective handling gear and/or allow samples to cool before handling.

11.1.2 Samples containing metallic particles will need to be distilled by the water method (SOP 700) due to the incompatibility of the matrix with microwave heating. The metal particles will superheat and lead to a breach in the distillation vessel.

11.1.3 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.4 Wear gloves, safety glasses and lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.5 Any chemicals with a TLV of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 Acetone used for equipment drying is collected in a plastic container and disposed as non-halogenated laboratory waste.

11.2.2 Dump the soil from the container into a two liter wide-mouth Nalgene bottle. The container shall be labeled Post Tritium Distillation Soil Residues. Please segregate any sample with non-environmental levels of activity into separate containers from the environmental level samples. The soil residue will be analyzed for radionuclide content to determine classification as non-radioactive or radioactive. The non-radioactive samples will be disposed of in the contaminated soils and solids waste. Radioactive soils will have further analyses performed to

determine status as LLRW or Mixed Waste.

11.2.3 RADIOCHEMISTRY ANALYTICAL EFFLUENT DISPOSAL
If the distillate from the tritium soil analytical process effluent has been determined to not be hazardous, this material may be discharged into the Paragon wastewater treatment facility. Here the activity will be monitored to ensure compliance with Colorado Rules and Regulations pertaining to Radiation Control Part 4 regarding discharges to sanitary sewers.

11.2.4 Distilled sample remnants may remain in the scintillation vial until the samples have been analyzed and the results reported. Once it is determined that this fraction is no longer needed, it can be disposed of in the proper carboy labeled "C-14 and Tritium Distillate Remainders".

11.2.5 The Counting Lab staff is currently handling disposal of samples and cocktail mix. These glass vials are accumulated (intact) in a container provided by the Waste Disposal Manager.

12. REFERENCES

USEPA Eastern Environmental Radiation Facility (EERF) Procedures Manual-78-1, 1978; EPA 520/5-84-006, 1984. Adapted for microwave use at Paragon by Steve Workman.

DOCUMENT REVISION HISTORY

4/27/06: Revision 5. Added LIMS program specification language (3.3). Added spatula or disposable wooden tongue depressors to equipment list (5.17). Added hold time comment (7.4) consistent with SOP 700. Changed Step 8.1.19 to a NOTE following Step 8.1.17. Reordered Section 9 (moved Method Blank to 9.2). Reordered WASTE DISPOSAL (moved Acetone to 11.2.1; moved RADIOCHEMISTRY ANALYTICAL EFFLUENT DISPOSAL to 11.2.3). Corrected EERF Manual reference (Section 12), both previous references were actually the same thing. Added DOCUMENT REVISION HISTORY. Attached Forms.

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Paragon Analytics

TRITIUM RUN LOG

_____ Logbook/Page No. **SOP 700 Rev ___** Form 1306r1.doc (3/30/2003)

Date	Workorder/ Sample Number	Column ID	Flask ID	Run No.	Comments	Technician's Initials

Reviewed by / Date _____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 755 REVISION 9

TITLE: DETERMINATION OF TECHNETIUM-99 IN SOLID AND WATER/AQUEOUS SAMPLES

FORMS: 302 (use current iteration)

APPROVED BY:
TECHNICAL MANAGER _____ DATE 7/21/08
QUALITY ASSURANCE MANAGER _____ DATE 7/20/08
LABORATORY MANAGER _____ DATE 7/21/08

HISTORY: Rev0, PCN 211, 4/8/94; Rev1, PCN #559, 11/9/95; Rev2, 10/6/99; Rev3, 1/26/00; Rev4, 4/26/02; Rev5, 11/08/02; Rev6, 4/04/03; Rev7, 5/17/04; Rev8, 5/3/06; Rev9, 7/17/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the preparation of environmental solid and water samples for quantitative measurement of Technetium-99 (^{99}Tc).

2. SUMMARY

2.1 ^{99}Tc in the form of the TcO_4^{-1} (pertechnate ion) is extracted from acidified water samples by passing the sample through a column containing Eichrom TEVA Resin™. ^{99}Tc in the form of the TcO_4^{-1} ion is extracted from a dried and ground solid sample by leaching in 1M HNO_3 and passing the leachate through a column containing Eichrom TEVA Resin™.

2.2 After the sample has been extracted, the resin is transferred from the column into a liquid scintillation (LS) vial. LS cocktail is added to the resin and ^{99}Tc is measured by liquid scintillation counting. A short-lived gamma emitter, Tc-99m, is used as a tracer for this procedure. Technicium-99m is spiked into the sample at the beginning of the procedure and is quantified in the final prepared vial by gamma counting.

2.3 Samples that are known or suspected to be high in Th-234 may require additional cleanup by hydroxide precipitation because Th-234 is a beta-emitting radioisotope that can interfere in the determination of ^{99}Tc by LSC. Samples that are high in natural uranium are likely to also be high in Th-234 because Th-234 is a daughter of U-238.

3. RESPONSIBILITIES

3.1 Technicium-99m is a short-lived isotope, with a 6.02 hour half-life, and must be ordered in advance, for delivery on each day that the method is performed. It is the responsibility of the analyst performing the method to place the order for Tc-99m, under the direction of the Radiation Safety Officer (RSO), or other licensed user of radioactive materials, and to inform the RSO upon receipt of the Tc-99m in the lab.

3.2 It is the responsibility of the analyst performing the method to notify the instrument lab gamma technician in advance of the number of samples arriving and the expected delivery date and time. This allows the gamma technician to schedule adequate instrument time to analyze the short-lived Tc-99m tracer.

3.3 It is the responsibility of the analyst performing the method to ensure that the Tc-99m solution and subsequent dilutions are stored inside the lead shield in the radioactive standards lab for at least four days prior to disposal. The standard and subsequent dilutions must be labeled with the receipt date prior to storage.

3.4 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.5 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specifications related to the client, project, and test method being performed.

3.6 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.7 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.8 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 All radionuclides that undergo beta emission (including ^{14}C, ^{32}P, ^{35}S, and ^{90}Sr) are effectively removed using Eichrom TEVA Resin™ unless they are present in the sample at exceptionally high levels.

4.2 Tritium can be extracted along with technetium due to the absorption of tritium-labeled compounds by the resin. Interference by tritium can be eliminated by setting the counting window for ^{99}Tc above the maximum beta emission energy for tritium.

4.3 Samples should be acidified with nitric acid prior to analysis. Acidification has been shown to reduce adsorption of Tc by polyethylene containers (see Reference 13.4). Pertechnate (TcO_4^{-1}) is readily soluble and is the predominant species of technetium under oxidizing conditions.

4.4 Samples that are high in natural uranium can contain significant Th-234. Since Th-234 undergoes beta decay with an emission energy similar to that of ^{99}Tc, additional separation steps may be required for samples high in natural uranium (and Th-234).

4.5 When a ^{99m}Tc tracer is used, the decay product is ^{99}Tc. Care should be taken to ensure that the amount of ^{99m}Tc used does not contribute measurable quantities of ^{99}Tc to the analytical fraction. See Section 8.1.1.1 for details.

4.6 The production of a ^{99m}Tc standard may occasionally result in the contamination of the standard with the ^{99}Mo parent. The reference vials used to calibrate the gamma spectrometer in this procedure should also be counted on the liquid scintillation counter, as described in Section 10.2, to ensure that ^{99}Mo or other interfering radionuclides are not present in the ^{99m}Tc standard.

4.7 Soluble organic constituents in the sample can interfere with the chemical separation process, causing low chemical yields, and can cause quenching during liquid scintillation counting. Organic constituents can be removed by muffling at 600° for four hours, or until complete removal of organic material is achieved. If the samples are to be muffled, organic material such as potting soil must be added to the QC samples to prevent volatilization of technetium. Alternately, organics can be removed by passing the sample solution through a column containing Eichrom Pre-Filter Resin™ prior to extraction with TEVA Resin™.

4.8 The scintillation vial is an optical surface. Any markings or material on the outside of the scintillation vial will interfere with the detection of scintillation. These should be removed prior to analysis by wiping the vial with a lint-free lab wipe and alcohol. All labeling must be done on the cap of the vial.

4.9 The presence of visible coloration will act as an ‘inner filter’. This effect, known as ‘color quenching’, is an interference to the detection of the scintillation. The presence of particulate contamination in the final sample may interfere with the detection of the scintillation. This effect is known as ‘physical quenching’. The presence of chemical contaminants in the sample may inhibit scintillation. This effect is known as ‘chemical quenching’.

4.10 The quench indicating parameter or (QIP) (H-number or SQPe number) should be monitored and variations in quench that could correspond to greater than 10% relative bias in the efficiency should be addressed by using standard additions to determine a sample specific efficiency.

5. APPARATUS AND MATERIALS

5.1 specimen cups, polypropylene, disposable, 100mL and 220mL

5.2 scintillation vials, glass, 20mL

5.3 graduated cylinder, 25 mL

5.4 tongue depressor

5.5 transfer pipet, 2mL

5.6 Eppendorf™ pipet, and disposable pipet tips

5.7 repeater pipet, and disposable pipet tips

5.8 column (BIO-RAD™ catalog no. 731-1553)

5.9 Whatman™ #41 filter paper, or equivalent

5.10 pipet bulb

5.11 analytical balance

5.12 steam bath

5.13 hot plate

5.14 syringe with hypodermic needle, 10mL

5.15 centrifuge tube, 250mL

5.16 centrifuge

5.17 funnels, both fitted and glass

5.18 vortex mixer

5.19 microliter syringe

6. REAGENTS - **Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids)**

6.1 Tc-99m (metastable Tc-99). Must be obtained "fresh" from the vendor on the day needed for use because the half-life is very short ($T_{½}$ = 6.02 hrs).

6.1.1 Open the lead shield (pig) and carefully withdraw a 1mL aliquot of the Tc-99m primary standard from the vial using a 10mL syringe fitted with a hypodermic needle.

6.1.2 Dispense the aliquot of Tc-99m into a disposable specimen cup containing approximately 100mL DI water. Cap and mix well. This creates approximately a 100X intermediate dilution.

6.1.3 Using a 10mL syringe, transfer approximately 10mL of the intermediate dilution into another disposable specimen cup that contains approximately 70mL of DI water. Cap and mix well. This creates approximately an 800X working dilution.

6.1.4 Remove the adhesive label from the Tc-99m delivery and attach it to a Quality Assurance Summary Sheet (QASS, Form 302), which should accompany the benchsheet.

6.2 ^{99}Tc spiking standard for LCS and matrix spike/matrix spike duplicate.

6.3 De-ionized (DI) water, ASTM Type II, or equivalent.

6.4 Hydrogen peroxide, H_2O_2, 30%.

6.5 Ferric chloride carrier, 20mg Fe^{3+}/mL. Dissolve 96g $FeCl_3 \cdot 6H_2O$ in one liter of 0.5M HCl.

6.6 Ammonium hydroxide, NH_4OH, conc., reagent grade.

6.7 Concentrated hydrofluoric acid, HF. TLV = 3ppm.

6.8 Concentrated nitric acid, HNO_3. TLV = 2ppm.

6.8.1 1.0M HNO_3: Carefully add 63mL of concentrated HNO_3 to 800mL of DI water and dilute to a final volume of 1000mL with DI water.

6.8.2 0.1M HNO_3: Carefully add 100mL of 1M HNO_3 to 800mL of DI water and dilute to a final volume of 1L with DI water.

6.8.3 0.01M HNO_3: Carefully add 10mL of 1M HNO_3 to 800mL of DI water and dilute to a final volume of 1L with DI water.

6.9 0.5M HF / 0.02M HNO_3: Carefully add 17.8mL of conc. HF and 20mL of 1M HNO_3 to 800mL of DI water and dilute to a final volume of 1L with DI water.

6.10 TEVA Resin™ chromatographic resin, 50-100um particle size, Eichrom Industries.

6.11 Pre Filter Resin™, 50-100um particle size, Eichrom Industries.

6.12 Ultima Gold AB™ liquid scintillation cocktail

6.13 Methanol, reagent grade. Used with laboratory wipes to clean outside surface of

liquid scintillation vials. Flammable. TLV = 200 ppm.

6.14 Nitromethane, reagent grade. Necessary only when a Quench curve (Section 9) is prepared. Flammable. TLV = 20 ppm..

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 It is recommended that water samples be preserved at the time of collection by adding enough conc. HNO_3 per liter of sample to bring the pH to less than 2 (2mL of conc. HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.3 Solid samples are dried (105°C) for a minimum of 4 hours and ground for homogenization according to SOP 721. An experiment to investigate the volatilization of ^{99}Tc from soil during drying was carried out under Paragon internal work order 03-13-020. Results demonstrated that Tc-99m spiked onto a soil sample was not volatilized after heating overnight at 105°C.

7.4 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

NOTES: For any samples where pre-screening activity or other knowledge is available and indicates alpha activity **in excess of 100dpm (45pCi)** a $Fe(OH)_3$ precipitation will be carried out in order to co-precipitate and remove Th-234.

For any samples where pre-screening activity is available and indicates alpha activity **in excess of 1000 dpm (450 pCi)** a $Fe(OH)_3$ precipitation and a 0.5M HF/0.02M HNO_3 rinse will be carried out for Th-234 decontamination.

8.1 WATER PREPARATION

8.1.1 Obtain “fresh” Tc-99m (metastable Tc-99) from the supplier, preferably at the beginning of the same day that the samples are to be prepared. Dilute the Tc-99m stock solution as necessary to a Tc-99m activity that is appropriate for spiking into samples.

8.1.1.1 The activity of Tc-99m added to each sample should not be such that the Tc-99m will decay to a ^{99}Tc activity which is greater than 1/3 the requested detection limit for liquid scintillation counting. Typically 600-1,000pCi (at the

reference time of standard dilution) is sufficient.

8.1.1.2 The activity of Tc-99m added to each sample should result in an activity that is approximately 10 times the detection limit on the gamma spectroscopy instrument (600-1,000 pCi/sample and 6,000–10,000pCi/reference vial). The three reference vials should be counted on the same gamma detector for a sufficient period of time to acquire a total of 10,000 counts which is approximately 1% (1σ) counting uncertainty. Samples should be counted for a sufficient period of time to acquire 5% (1σ) counting uncertainty. Results for all samples must be decay corrected to the same date and time.

8.1.2 Measure an appropriate aliquot of sample into a clean beaker of suitable size (the default aliquot for water is 250mL).

NOTE: If a water sample is observed to contain solid particles, filter the sample through qualitative filter paper and measure an aliquot of the filtrate for ^{99}Tc analysis. Unless specifically instructed otherwise by the client, only the aqueous portion of a water sample is prepared for ^{99}Tc analysis.

8.1.3 Using an Eppendorf™ pipet, trace each sample with 0.1mL of the Tc-99m solution prepared in Step 8.1.1. Trace each reference vial with 1.0mL of the same Tc-99m solution. Refer to Section 8.4 for the preparation of the standard reference vials. Also, spike the LCS with 1.0mL of ^{99}Tc standard spiking solution (approximately 500dpm/mL) as well as any MS/MSD samples that have been requested.

8.1.4 For routine water samples that are clear and colorless, go directly to Step 8.3 (separation by TEVA Resin™). Non-routine samples must be handled on a case-by-case basis.

8.1.5 If the sample has known or suspected alpha activity greater than 100dpm proceed to Step 8.2.10, otherwise go to Step 8.3.

8.1.6 Turbid samples may require more rigorous filtering. Unusual aqueous samples may contain dissolved organic constituents that can cause quenching in liquid scintillation counting. Dissolved organics can be destroyed by heating with H_2O_2 (Step 8.1.6.1.) or removed by passing the sample through a column containing pre-filter resin (Step 8.1.6.2.). The analyst must document in a QASS (Form 302) any procedures used to treat non-routine samples.

8.1.6.1 Peroxide digestion to destroy organics: Add 10mL of 30% H_2O_2 for every 1L of sample (if the sample aliquot is 250mL, add 2.5mL of H_2O_2 solution). Heat the sample on a hotplate for approximately 1 hour. Stir the sample occasionally. If bubbling due to decomposition of H_2O_2 has not stopped as the sample cools, continue heating until bubbling ceases.

8.1.6.2 Prepare a pre-filter column as follows: transfer Eichrom Pre-filter Resin™ as a slurry with DI water to an empty BIO-RAD™ column until the bottom stem section is filled (2.0mL). Attach a fitted funnel to the column. Place a regular funnel, with a Whatman™ 41 filter in it, on top of the fitted funnel and rinse the column with DI water. Place a clean, labeled beaker under the column. Pass the sample solution through the column, collecting the effluent in the beaker. Rinse the column with DI water and collect.

8.2 SOIL AND SOLID PREPARATION

8.2.1 Obtain and prepare "fresh" Tc-99m (metastable Tc-99) from the supplier, as described in 8.1.1.

8.2.2 Weigh an appropriate aliquot of dried and ground sample into a 220mL polypropylene specimen cup (the default aliquot is 2 grams).

8.2.3 Using an Eppendorf™ pipet, trace each sample with 0.1mL of the Tc-99m solution prepared in Step 8.1.1. Trace each reference vial with 1.0mL of the same Tc-99m solution. Refer to Section 8.4 for the preparation of the standard reference vials. Also, spike the LCS with 1.0mL of ^{99}Tc standard spiking solution (approximately 500dpm/mL) as well as any MS/MSD samples that have been requested.

8.2.4 To the sample in the specimen cup add 40mL of 1N HNO_3. Place a 100mL polypropylene beaker on top of 220mL beaker as a cap to cover the sample.

8.2.5 Place the sample on a steam bath to heat for about ½ hour.

8.2.6 Remove the samples from the steam bath and carefully add 5mL of 30% H_2O_2 solution to the sample, in 1mL increments. For dark samples add the 5mL of 30% H_2O_2 dropwise. **The addition of H_2O_2 can cause a vigorous reaction! Be cautious and alert. Always wear gloves and protective eyewear.**

8.2.7 Once foaming has subsided place the 100mL beaker back down on top

of the sample beaker. Resume heating for about 1½ hours. Carefully observe the sample for a few minutes and watch for evidence of foaming.

8.2.8 After the sample has been heated for a total of about 2hrs. remove the sample from the steambath and allow to cool.

8.2.9 If the sample is suspected or known to be high in Th-234, go to Step 8.2.10, otherwise go to Step 8.2.11.

8.2.10 Separate Th-234 from ^{99}Tc by co-precipitation with $Fe(OH)_3$. Quantitatively transfer the sample in the disposable beaker to a 250mL centrifuge bottle. To the sample add 1mL of 20mg/mL ferric iron carrier, then carefully add about 5mL of concentrated NH_4OH to precipitate $Fe(OH)_3$. Swirl to mix. After the $Fe(OH)_3$ has completely formed, centrifuge the sample for about 15 minutes @ 3500rpm. The supernatant will be used for further analysis below. The precipitate may be discarded.

8.2.11 If it is the analyst's judgment that the leachate from Step 8.2.9 or supernatant from Step 8.2.10 has significant color (yellow or brown), the sample should be passed through a column containing Eichrom Pre-Filter Resin™ (Step 8.2.12). If the analyst judges that the filtrate does not have significant color (the sample is clear), go directly to Step 8.3.

8.2.12 Prepare a pre-filter column as follows: transfer the pre-filter resin as a slurry with DI water to an empty BIO-RAD™ column until the bottom stem section is about half full (1.0mL). Attach a fitted funnel to the column. Place a regular funnel, with a Whatman™ 41 filter in it, on top of the fitted funnel and rinse the column with DI water. Transfer the sample leachate solution to the column, rinsing with DI water to complete the transfer. Collect the effluent from the column in a clean, labeled polypropylene specimen cup.

8.3 SEPARATION OF TC-99

8.3.1 For each sample prepare a TEVA resin™ column as follows: transfer the TEVA Resin™ as a slurry with DI water to an empty BIO-RAD column until the bottom stem section is filled (2.0mL). Attach a fitted funnel to the column. Place a regular funnel, with a Whatman™ 41 filter in it, on top of the fitted funnel and rinse the column with 5mL of 0.1M HNO_3.

8.3.2 Transfer each sample solution to a prepared TEVA resin™ column through the Whatman™ 41 filter. Complete the transfer by rinsing with DI water. Discard the effluent from the column down the lab sink with

plenty of cold water.

8.3.3 In cases where pre-screening activity is available and indicates alpha activity **in excess of 1000dpm,** the following rinse will be carried out: after the sample has completely passed through, rinse the column with 25mL of 0.5M HF/0.02M HNO_3. Discard the effluent from the column. The purpose of this step is to remove residual Th-234 from the column.

8.3.4 After the sample solution has completely passed through, rinse the column with 50mL of 0.01M HNO_3. Discard the effluent from the column.

8.3.5 Using a pipet bulb to apply pressure to the orifice of the column, carefully force the TEVA Resin™ out of the column into a clean LS vial. To complete the transfer, plug the column orifice with a small red cap and pipet 3.0mL of 0.1M HNO_3 into the column. After swirling transfer the 0.1M HNO_3 rinsate out of the column into the LS vial.

8.3.6 To the vial add 15mL of Ultima Gold AB™ LS cocktail. Cap the vial and mix thoroughly by inversion and vortexing. Wipe the outside of each vial with methanol to ensure a clean optical surface.

NOTE: The final volume of the samples, the reference for yield determination, and the calibration vials for calibration in the LS vial should always be kept constant (the standard volume used is 19mL as detailed below).

- 15mL Ultima Gold AB™ LS cocktail.
- Resin slurried with DI water, which contains approximately 1mL of liquid in its pore space.
- 3mL of 0.1M HNO_3 or in the case of a standard or calibration vial – a volume of ^{99}Tc standard and a volume of 0.1M HNO_3 which brings the final volume of acid + standard to 3mL.

8.4 PREPARATION OF REFERENCE STANDARD VIALS FOR GAMMA COUNTING

NOTE: Reference standard vials should be prepared at the time of spiking/tracing samples.

8.4.1 Prepare three Tc-99m reference standard vials for gamma counting as follows: Into three clean LS vials, pipet the appropriate volume of Tc-99m spiking solution, as described in Section 8.2.1 or 8.1.1. Add a

volume of 0.1M HNO_3 to the vial that will result in a final volume of 3mL. Typically, this is 1mL standard + 2mL 0.1M HNO_3. Add the same amount of wet, unused, TEVA Resin™, slurried in DI water, as that used in the columns prepared for the samples. Cap the vial and mix thoroughly by inverting and vortexing.

8.4.2 Submit the sample vials, Tc-99m reference standard vials, and benchsheet to the instrument lab for analysis of Tc-99m tracer by gamma counting and analysis of ^{99}Tc by LS counting. **It is extremely important that gamma analysis of Tc-99m be done within 24 hours since Tc-99m has a very short half-life (6.02 hrs).** The instrument lab should allow a time period of at least 72 hours to elapse from the spike date/time until beta analysis of the samples by LSC. This time may be shortened with the Department Manager's approval.

9. PREPARATION OF CALIBRATION VIALS (FOR QUENCH CURVE)

Twelve spikes and twelve blanks are prepared with increasing volumes of nitromethane for calibration. Details follow:

9.1 Blank preparation: Add the same amount of wet, unused, TEVA Resin™, slurried in DI water, as that used in the columns prepared for the samples (Section 8.3.1) to each of twelve vials (Blk1-Blk12). Add 3mL 0.1M HNO_3 and 15mL Ultima Gold AB™ LS cocktail to each vial. Blank1 vial does not receive nitromethane. Add nitromethane to each subsequent vial in 15µL increments (i.e., Blk2 receives 15µL, Blk3 receives 30µL, and so on). Cap the vial and mix thoroughly by inverting and vortexing to homogenize. Wipe the outside of each vial with methanol in ensure a clean optical surface.

9.2 Spike Calibration Vial preparation: Add the same amount of wet, unused TEVA Resin™, slurried in DI water, as that used in the columns prepared for the samples (Section 8.3.1) to each of twelve vials (S1-S12). Add a known volume of ^{99}Tc standard (approximately 1500dpm) to each vial. Add a volume of 0.1M HNO_3 to the vial which will result in a final volume of standard + 0.1M HNO_3 of 3mL. Spike1 vial does not receive nitromethane. Add nitromethane to each subsequent vial in 15µL increments (i.e., S2 receives 15µL, S3 receives 30µL, and so on). Cap the vial and mix thoroughly by inverting and vortexing to homogenize. Wipe the outside of each vial with methanol to ensure a clean optical surface.

10. QUALITY CONTROL

10.1 Acceptance criteria for QC samples and other quality indicating parameters can be found in SOP 715 and in the LIMS program specifications.

10.2 One method blank is prepared and analyzed per batch of 20 samples (5% frequency).

In the event that the method blank analysis results in activity above the calculated MDC, the three reference vials used to calibrate the gamma spectrometer should be counted on the LSC for the same length of time as the blank. The results of these counts will be used to determine whether the blank activity is due to laboratory contamination, or due to the potential contamination of the Tc-99m source, as described in Section 4.6. The Department Manager should be consulted in the interpretation of the count data.

10.3 One sample duplicate is prepared and analyzed per 10 samples (10 % frequency).

10.4 One LCS (spiked blank) is prepared and analyzed per batch of 20 samples (5% frequency). If there is insufficient sample to prepare a sample duplicate, a duplicate spiked blank (LCS-D) should be substituted.

11. CALCULATIONS

11.1 TPU FACTORS

As defined in SOP 743, the following 1σ preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty:

11.1.1 Water samples require a preparation uncertainty factor of 0.0564. This factor is based on one gross aliquotting (sample homogeneity), one volumetric measurement, one pipetting of Tc-99m standard, and one quantitative transfer. See the following equation:

$$0.0564 = \sqrt{0.05^2 + 0.006^2 + 0.004^2 + 0.025^2}$$

11.1.2 Soil samples require a preparation uncertainty factor of 0.0561. This factor is based on one gross aliquotting (sample homogeneity), one mass measurement, one pipetting of Tc-99m standard, and one quantitative transfer. See the following equation:

$$0.0561 = \sqrt{0.05^2 + 0.003^2 + 0.004^2 + 0.025^2}$$

11.1.3 To simplify analytical reporting, the larger of the two preparation uncertainties calculated above, 0.0564, will be used for both soil and water matrices.

11.2 CHEMICAL YIELD

11.2.1 Technicium-99m should be analyzed by gamma spec (140.5 keV) as soon as possible after sample preparation. The three reference vials should be counted on the same gamma detector for a sufficient period of time to acquire a total of 10,000 counts which is approximately 1% (1σ) counting uncertainty. Samples should be counted for a sufficient period of time to acquire 5% (1σ) counting uncertainty, or 400 counts.

Results for all samples must be decay corrected to the same date and time.

11.2.2 Chemical yield is calculated as the sample result for Tc-99m divided by the mean of the Tc-99m results for three reference standards prepared in Step 8.4.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Technicium-99m is a strong gamma emitting radionuclide and must be stored in a lead shield for at least 72 hours after receipt to allow for decay prior to disposal.

12.1.2 The building is equipped with a safety shower, eyewash station, fire extinguisher and fire blanket as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

12.1.3 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.4 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

12.1.5 Gloves, safety glasses and a lab coat must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

12.1.6 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.7 below.

12.1.7 All non-original containers used to hold reagents (e.g. wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.1.8 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

12.2 WASTE DISPOSAL

12.2.1 The instrument lab will analyze and ultimately dispose of the scintillation vials in the manner described in SOP 704. Emptied columns may be soaked in a RadiacWash® solution, rinsed in tap water and discarded into the sanitary trash.

12.2.2 Sample effluent from Section 8 can be disposed of by discharging into the PAR waste water treatment facility (i.e., down the laboratory sink with plenty of cold tap water), unless special instruction is given in the project instructions by the RSO.

12.2.3 Wastes that are "corrosive only", such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the Paragon waste water treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

12.2.4 The Tc-99m standard, which is delivered in a sterile saline solution, can be disposed of in the sanitary sewer AFTER allowing complete decay of the Tc-99m for at least one week. The glass ampoules may be discarded into the lab's broken glass receptacle.

13. REFERENCES

13.1 ATSM Method C1387-98: "Standard Guide for the Determination of Technetium-99 in Soil".

13.2 DOE Method RP550: "Technetium-99 Analysis Using Extraction Chromatography". DOE Methods for Evaluating Environmental and Waste Management Samples, (DOE Methods Compendium), Battelle Press.

13.3 DOE Method RS551: "Rapid Isolation and Measurement of Technetium-99 Using Anion-Exchange Filter Membranes". (DOE Methods Compendium), Battelle Press. 1997.

13.4 Eichrom Industries, April 2, 2002. Technetium-99 in Water, Procedure TCW01.

13.5 Mann, D.K. 1993. Determination of 99Tc in K-25 Cooling Tower Wood Leachates. Proceedings from the 39th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry. October 11-15, 1993. Colorado Springs, CO.

13.6 Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual, Vol. II, Draft Document. Section 10.3.3.1 and 14.10.9.8. August 2001.

13.7 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.8 Experiments to Investigate Volatilization of 99Tc from Soil During Drying. PAR Internal Work Order 03-13-020, 03-15-031, and 03-15-033. February 2003 through March 2003.

13.9 Experiment to Investigate Heating Time in Leaching 99Tc from Soil. PAR Internal Work Order 03-20-031. August, 2003.

DOCUMENT REVISION HISTORY

4/10/06: RESPONSIBILITIES updated to include ordering, use, storage, and disposal of Tc-99m and notifications to the instrument lab and the RSO. Muffling temperature was changed to 600°C. Other clerical changes were made to clarify the language. DOCUMENT REVISION HISTORY added.

9/27/07: Published SOP was amended as follows: Section 7.2 - updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57).

7/17/08: Incorporated previous amendment into SOP. Fixed header (was an error in previous published file) so that proper updated iteration is shown throughout. Removed PAR SOP 743 (TPUs) from Section 13 REFERENCES. Added DOE Method RS551 citation to REFERENCES. Added Form.

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

Ammended 9/27/07 (Section 7.1): Hold for 24hrs (not 16) after pH adjustment (consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57) DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 758 REVISION 2

TITLE: DETERMINATION OF PROMETHIUM-147 IN WATER

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 7/21/06

QUALITY ASSURANCE MANAGER _____ DATE 7/21/06

LABORATORY MANAGER _____ DATE 7-21-06

HISTORY: NEW, 4/14/94; Rev1, 7/7/2003; Rev2, 7/24/06.

1. SCOPE AND APPLICATION

This standard operating procedure describes the steps necessary for preparation of environmental water samples for quantitative measurement of Pm-147.

2. SUMMARY

The sample is spiked with samarium (Sm) carrier. Pm, Sm and other rare earth elements (REE) are initially pre-concentrated by co-precipitation with $Fe(OH)_3$. Promethium is isolated, along with other REEs, by passage through two anion exchange columns (nitrate and chloride) and by coprecipitation with SmF_3. The SmF_3 is dissolved for beta counting of the Pm-147 on a low background liquid scintillation counter (LSC). Chemical yield is determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of Sm.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.2 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specifications related to the client, project, and test method being performed.

3.3 It is the responsibility of the preparation technician to coordinate with the metals Department to facilitate the determination of chemical yields by ICP analysis.

3.4 It is the responsibility of the LSC instrument technician to properly optimize the

instrument window settings (regions of interest, ROI) so as to eliminate or reduce the potential interference from other beta-emitting rare earth isotopes, such as Sm-151.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who perform this procedure to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented, and approved by the Department Manager.

4. INTERFERENCES

Note that the chemical separation process described in this SOP does not separate Pm from other rare earth elements (REE), such as Sm-151.

5. APPARATUS AND MATERIALS

5.1 combination magnetic stirring/heating plate

5.2 steam bath

5.3 PTFE™-coated magnetic stirring bars (cleaned per SOP 720)

5.4 Pasteur pipets, disposable

5.5 mechanical pipets, Eppendorf™, or equivalent

5.6 centrifuge bottles, conical, polypropylene, 250mL

5.7 specimen cups, polypropylene, 220mL

5.8 Pyrex™ beaker, 1L

5.9 scintillation vials, low-potassium borosilicate glass, 20mL

5.10 test tubes, plastic with caps, 20mL

5.11 analytical balance with resolution to 0.0001g

5.12 ion exchange columns, disposable, Environmental Express #R10204 or equivalent

5.13 glass beads, solid, 3mm diameter

5.14 fitted funnels

5.15 graduated cylinder, 500mL or 1L

5.16 centrifuge

6. REAGENTS - All reagents must be, at minimum, reagent grade

6.1 Deionized (DI) water, obtained from Paragon's DI water system

6.2 Nitric acid (HNO_3), conc. reagent grade. TLV=2ppm. Irritant, corrosive.

6.3 Nitric acid (HNO_3), 8M: Cautiously add 1000mL conc. HNO_3 to 900mL DI water. Dilute to 2L with DI water. TLV=2ppm. Irritant, corrosive.

6.4 HNO_3, 2M: Cautiously add 130mL conc. HNO_3 to approximately 600mL DI water and dilute to 1L. TLV=2ppm. Irritant, corrosive.

6.5 Hydrochloric acid (HCl), conc. TLV=5ppm (ceiling). Irritant, corrosive.

6.6 Hydrochloric acid (HCl), 10M: Cautiously add 830mL conc. HCL to approximately 100mL of DI water and dilute to 1L. TLV=5ppm (ceiling). Irritant, corrosive.

6.7 ICP Diluting Solution: Carefully add 10mL of conc. nitric acid and 50mL of conc. hydrochloric acid to 940mL of DI water. TLV=5ppm (ceiling) for HCl irritant, corrosive. TLV=2ppm (TWA) for nitric acid, irritant, corrosive.

6.8 Ammonium hydroxide (NH_4OH), 15M, conc. TLV=25ppm (for ammonia).

6.9 Hydrofluoric acid (HF), 29M, conc. TLV=3ppm (ceiling). Irritant, burns, bone, teeth, fluorosis.

6.10 Sodium hydroxide (NaOH) TLV=2 mg/m^3 = 1.2 ppm (ceiling), irritant.

6.11 Sodium hydroxide (NaOH), 6M: Cautiously dissolve 120g NaOH pellets in 500mL of DI water. Allow solution to cool. Store in a plastic container. TLV=2 mg/m^3 = 1.2 ppm (ceiling), irritant.

6.12 Boric acid (H_3BO_3)

6.13 Boric acid, 1M: Dissolve 30.9g H_3BO_3 in 500mL of DI water.

6.14 Ammonium bifluoride (NH_4HF_2)

6.15 Ammonium bifluoride (NH_4HF_2), 1M: Dissolve 22.8g NH_4HF_2 in 500mL of DI water.

6.16 Samarium (Sm_2O_3), **primary standard grade**.

6.17 Samarium carrier (10mg Sm/mL): Dissolve 1.160g of primary standard grade Sm_2O_3 in conc. reagent grade HNO_3 and dilute with DI water to 100mL in a Class A volumetric flask.

6.18 Samarium ICP calibration standard (20µg/mL): Pipet 0.20mL of 10mg/mL Sm carrier into a Class A 100mL volumetric flask and bring to volume with DI water. To be delivered upon request to the metals Department for calibration of the ICP.

6.19 Iron chloride ($FeCl_3.6H_20$)

6.20 Ferric iron carrier (5mg Fe^{+3}/mL): Dissolve 24.2g $FeCl_3.6H_2O$ in 1 L of 0.5M HCl.

6.21 Methanol (CH_3OH). TLV=200 ppm. Neuropathy, vision, central nervous system effects.

6.22 Ultima Gold AB™ liquid scintillation cocktail.

6.23 Anion exchange resin, AG 1x8, Bio-Rad® or equivalent.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough HNO_3 to bring the pH to less than 2. The volume of nitric acid should be minimized to avoid significant dilution of the sample. If samples are to be collected without preservation, they should be brought to the laboratory within 5 days then preserved, with a minimum volume of concentrated HNO_3, to a pH less than 2. After preservation, the samples should be held in the original container for a minimum of ~~16~~ 24 hours before analysis or transfer of the sample.

7.2 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 Using a graduated cylinder, measure a 500mL aliquot (or other appropriate volume) of water sample into a 1L Pyrex™ beaker. Record the sample volume on the benchsheet. Place a PTFE™-coated magnetic stir bar into the beaker. Place the beaker on a stirring/heating plate and begin stirring.

8.2 Prepare quality control (QC) samples per Section 11.

8.3 **How to take initial ICP aliquot**: Prior to adding any reagents to the sample, use a calibrated mechanical pipet to remove 1mL of sample and place into a clean test tube labeled with the sample ID and "initial ICP". Dilute to 10mL with ICP diluting solution. Cap and invert tube several times to mix thoroughly. Set aside until final ICP aliquot has been taken.

8.4 Acidify the sample to pH less than 2 with conc. HNO_3.

8.5 Spike the field and QC samples with 1mL of Sm carrier (10mg Sm/mL). Record the Sm carrier ID, spike volume, and pipet ID on the benchsheet.

8.6 In addition, a replicate 1mL aliquot (or similar known volume from a calibrated pipet) of Sm carrier is diluted with 5mL conc. nitric acid and DI water to the default volume used for the water samples. After mixing thoroughly, a 1 mL aliquot of this dilution is transferred to a culture tube labeled 'reference carrier', diluted up to 10mL with ICP diluting solution, and submitted with the initial samples to provide a reference concentration for the ICP calculations below.

8.7 Add 1mL of 5mg/mL ferric iron carrier.

8.8 Heat the solution to just below boiling for 10-15 minutes then make basic (pH~11) by adding 6M NaOH to precipitate $Fe(OH)_3$. Turn the stir mechanism off and remove stir bar. Allow precipitate to settle to the bottom of the beaker for 15-20 minutes.

8.9 After the precipitate has settled, decant the aqueous portion away from the precipitate. Reduce the volume to approximately 200mL or less with **minimal** loss of precipitate. If this cannot be accomplished without significant loss of precipitate, the option is to perform multiple centrifugations to separate the supernatant from the precipitate. The aqueous portion of the sample can be disposed down the drain in the fume hood with large amounts of water.

8.10 Transfer the remaining solution containing the precipitate to a labeled 250mL centrifuge bottle.

8.11 Rinse the sample beaker with a **minimum amount** of deionized water and add the rinse to the centrifuge bottle.

8.12 Centrifuge the samples at approximately 3500rpm for 15 minutes. Discard the supernatant down the drain with large amounts of cold water unless otherwise specified due to hazardous or radioactive waste concerns.

8.13 Precondition the frit of a disposable plastic column (approximately 15mm I.D., 18mL capacity) with methanol up to the 1cm line. Using a wash bottle, fill the column with a slurry (resin/DI water) of AG 1x8 anion exchange resin to a settled depth of approximately 7cm. Cover the top of the resin bed with glass beads to a depth of approx. 2cm to hold the resin in place. Attach a fitted funnel to each column.

8.14 Condition the column with two 10mL aliquots of 8M HNO_3.

8.15 Add 10mL of 8M HNO_3 to dissolve the $Fe(OH)_3$. After the precipitate is dissolved, load the solution onto the anion exchange column. Collect the effluent from the column in a 220mL polypropylene beaker.

8.16 Complete quantitative transfer by repeating Step 8.15 two more times.

8.17 Rinse the column 4 times with 10mL of 8M HNO_3.

8.18 Convert the effluent collected in Sections 8.15–8.17 to the chloride form by evaporating the solution to dryness on a steam bath and dissolving the residue in 30mL of 10M HCl.

8.19 Prepare an anion exchange column per Section 8.13.

8.20 Condition the column with two 10mL aliquots of 10M HCl.

8.21 Load the solution from Step 8.18 onto an anion exchange column. Rinse the beaker twice with 10mL of 10M HCl and apply the rinsate to the column. Collect the effluent from the column in a 250mL centrifuge bottle

8.22 Rinse the column four times with 10mL of 10M HCl, collecting the effluent in the same centrifuge bottle from Step 8.21.

8.23 To the effluent in the centrifuge bottle add approximately 60mL of DI water.

8.24 Add conc. NH_4OH as needed to bring to pH~11. Sm will precipitate as $Sm(OH)_3$. NOTE: Add NH_4OH **very slowly**, this is a very vigorous reaction. Centrifuge and discard the supernatant.

8.25 Dissolve the $Sm(OH)_3$ precipitate in 5mL of 2M HNO_3. Dilute with about 10mL of DI water.

8.26 Add 1mL of 1M NH_4HF_2 and three drops of conc. HF to precipitate SmF_3.

8.27 Using DI water, selectively balance the centrifuge tubes to minimize the addition of DI water.

8.28 Centrifuge at 3500rpm for 15 minutes and discard the supernatant.

8.29 Dissolve the SmF_3 precipitate by adding 1mL of conc. HNO_3 and 2mL of 1M H_3BO_3. Heat the centrifuge bottle on a steambath to aid dissolution.

8.30 Dilute the solution with 3mL of DI water. Centrifuge the sample for about 5 minutes @ 3000 rpm to bring all of the sample solution to the bottom of the centrifuge bottle.

8.31 Document the total volume in the centrifuge tube on the benchsheet.

8.32 **How to take final ICP aliquot**: After making certain that the solution in the centrifuge bottle is well mixed, pipet a 0.10mL aliquot of the solution into a 20mL plastic vial. Dilute the aliquot to 10mL with ICP blank solution. Label the vial with the sample ID and "final Sm". Present this solution and the standard prepared in Section 6.18 to the metals Department for ICP analysis of Sm to determine chemical yield.

8.33 Pipet a 5mL aliquot from the centrifuge bottle into a labeled scintillation vial.

8.34 Add 15mL of Ultima Gold AB™ cocktail to each sample. Cap and mix thoroughly.

8.35 Wipe the scintillation vials clean using methanol.

8.36 Submit the vials, and associated documentation, to the instrument lab for liquid

scintillation counting.

9. PREPARATION OF CALIBRATION STANDARDS

When needed for instrument calibration, prepare calibration standards as follows.

9.1 Background Calibrations

9.1.1 Prepare twelve method blanks with varying amounts of Sm carrier solution added at the beginning of the separation process, with increasing increments of carrier at approximately 0.25, 0.50, 0.75, 1.0, 1.5, and 2mL. Each level of carrier should be prepared in duplicate.

9.1.2 After ICP yield determinations have been completed and the background calibration vials have been counted on the liquid scintillation counter, the yield-corrected carrier volumes are plotted against the observed count rate to generate a calibration curve describing the expected background count rate for the sample-specific chemical yield.

9.2 Efficiency Calibrations

9.2.1 Prepare three calibration sources, which have been prepared as method LCSs, with the addition of 1,000 – 10,000 dpm NIST traceable Pm-147.

9.2.2 ICP yield determinations are used to correct the known activity value in the calculation of the counting efficiency.

10. CALCULATIONS

10.1 Calculate the barium chemical recovery for aqueous samples, Y, as a percentage, as follows:

$$Y_i = V_i * ICP_i * DF$$

$$Y_f = V_f * ICP_f * DF$$

$$Y_{RC} = V_{RC} * ICP_{RC} * DF$$

$$Y = \frac{Y_f}{Y_i + Y_{RC}} * 100\%$$

where:

V_i = initial sample volume (mL)

Y_i = samarium recovery from initial ICP aliquot (µg)

ICP_i = initial samarium concentration measured by ICP (µg/mL)

DF = dilution factor

V_f = final sample volume (mL)

Y_f = samarium recovery from final ICP aliquot (µg)

ICP_f = final samarium concentration measured by ICP (µg/mL)

Y_{RC} = samarium recovery from RC aliquot (µg)

V_{RC} = RC final volume (mL)

ICP_{RC} = RC samarium concentration measured by ICP (µg/mL)

10.2 Calculate the actual volume, V_A, analyzed for each sample (accounting for volumes of sample removed) as follows:

$$V_A = V * \frac{V_i - icp_i}{V_i} * \frac{5}{V_f}$$

where:

V = sample aliquot (L, g)

V_i = sample final dilution volume (mL)

icp_i = initial aliquot taken for ICP (mL)

V_f = sample volume in EDTA (mL)

And 5 is the volume, in mL, specified in Section 8.33.

10.3 Calculate the activity, A, in picoCuries per liter, as follows:

$$A = \frac{(GCPM - BKGCPM)}{2.22 * v * y * e * decay}$$

where:

GCPM = Gross counts per minute

BKGCPM = Background counts per minute

v = volume

y = chemical yield

e = efficiency for Pm-147

decay = decay factor

10.4 Calculate the one-sigma total propagated uncertainty, TPU, in picocuries per liter

as follows:

$$TPU = \sqrt{CU^2 + (PU * A)^2 + (IU * A)^2}$$

where:

CU = Counting uncertainty

PU = Prep uncertainty

IU = Instrument uncertainty

A = Activity

10.4.1 Calculate the one-sigma counting uncertainty, CU, as follows:

$$CU = \frac{\sqrt{\frac{GCPM}{CT} + \frac{BKGCPM}{BKGCT}}}{2.22 * v * y * e * decay}$$

where:

CT = Count time

BKGCT = Background count time

10.4.2 The Preparation Uncertainty, PU, is 10.93%. This is based on one gross aliquot, one volumetric measurement, one ICP determination, one spike/carrier addition, three quantitative transfers, and one pipetting.

$$0.1093 = \sqrt{0.05^2 + 0.006^2 + 0.083^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.004^2}$$

10.4.3 Instrument Uncertainty, IU, is based on SOP 743 and is 5.61%.

10.5 Calculate the Minimum Detectable Concentration, MDC, as follows:

$$MDC = \frac{4.65 * \sqrt{BKGCPM * CT} + 2.71}{2.22 * v * y * e * decay * CT}$$

11. QUALITY CONTROL

11.1 One blank is prepared per batch of 20 samples or less (5% frequency) and is prepared by aliquotting 500mL of DI water.

11.2 One sample duplicate is run per batch of 10 samples or at a 10% frequency.

11.3 One spiked blank is run per batch of 20 samples or less (5% frequency) and is prepared by aliquotting 500mL of DI water. Spike with Pm-147 at a known activity, close to 500dpm. NOTE**:** Spike the LCS as in Step 8.5.

12. DEVIATIONS FROM METHOD

As this is a proprietary technique, there are no deviations to be noted from a published method.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

13.2 Wear gloves, safety glasses, and lab coat when working with any samples or chemicals or when handling materials or equipment potentially contaminated with chemicals.

13.3 All work involving NH_4OH and acids should be done in a fume hood, as well as any work with material that has a Threshold Limit Value (TLV) less than 50ppm.

13.4 Care should be taken when diluting acids. Unless the method explicitly directs you to do otherwise, **always add acids to water**, not water to acids.

14. REFERENCES

14.1 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

14.2 PAR SOP 743 “Estimating Total Propagated Uncertainties for Radiometric Analyses”.

DOCUMENT REVISION HISTORY

7/7/03: Reactivated from retirement, reformatted and released without technical revision.

7/24/06: Replaced GFPC analysis technique with LSC technique. Updated RESPONSIBILITIES, added calibration procedures, removed inappropriate reference citations. Added DOCUMENT REVISION HISTORY.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 760 REVISION 6

TITLE: PREPARATION OF SOLID SAMPLES BY POTASSIUM PYROSULFATE FUSION

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER Renee Valles DATE 7/21/08
QUALITY ASSURANCE MANAGER Dee Schatz DATE 7/20/08
LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: Rev0, 4/29/02; Rev1, 12/24/02; Rev2, 8/26/03; Rev3, 10/3/2003; Rev4, 5/17/04; Rev5, 7/24/06; Rev6, 7/18/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes a method for the total dissolution of solid samples using potassium pyrosulfate fusion. A fusion cake is first produced with potassium fluoride, which is effective in dissolving silica and refractory silicates and some metallic oxides. In the final steps of the procedure, a pyrosulfate fusion is obtained that decomposes refractory oxides and volatilizes remaining HF and silica.

2. SUMMARY

A solid sample is decomposed completely with potassium fluoride in a 100mL platinum dish. The cake is then transposed with sulfuric acid and sodium sulfate to a pyrosulfate fusion with simultaneous volatilization of hydrogen fluoride and silicon tetrafluoride. The resulting fusion cake is dissolved in 2N hydrochloric acid. Actinides are co-precipitated with iron hydroxide and are sequentially isolated using anion exchange resin as outlined in the appropriate standard operating procedure.

3. RESPONSIBILITIES

3.1 The fumes evolved in this procedure are extremely hazardous and must be properly contained and exhausted in a laboratory fume hood. It is the responsibility of the technician performing this work to ensure that the fume hood being used is turned on, functioning properly, has a current calibration, and is used appropriately.

3.2 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review. These procedures are to be performed only by personnel who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the preparation of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 Be careful to keep the platinum dish out of the oxidizing portion of the flame. With the flame set low, keep the dish either above or below the apex of the oxidizing portion of the flame.

4.2 The platinum crucible is difficult to handle. Hold the crucible at the edge (inside and out), with platinum tipped tongs. **To ensure that no contamination occurs between samples, the tongs are cleaned after every sample. After fusing the sample, allow the tongs to cool. Then, rinse the tongs first with Radiacwash and then DI water. Dry the tongs with a clean paper towel**.

4.3 When lighting the blast burner, turn on the gas first, then slowly turn up the air and watch the flame. A low blue flame contains large amounts of O_2 and is very hot.

4.4 If a large mantle of high velocity gases from the burner is allowed to envelop the crucible, the liquid flux will be blown too high in the dish and **a crust will form on the outside rim of the dish and cannot be recovered.**

5. APPARATUS AND MATERIALS

5.1 Top loading balance, 0.01g sensitivity

5.2 Hot plates

5.3 Plastic funnels

5.4 Platinum crucibles, 100mL

5.5 Muffle furnace

5.6 Watch glasses

5.7 Fisher blast burner, or equivalent

5.8 Pipettes, Eppendorf or equivalent

5.9 Pipet tips

5.10 Wash bottles

5.11 Graduated cylinder, plastic, 25mL

5.12 Compressed air tank, with regulator and hose

5.13 Natural gas tank, with regulator or propane connected directly to blast burner

5.14 Ring stand, with Ni-Cr wire triangle

5.15 Desiccator (for reagents)

5.16 Weighing dishes, aluminum

5.17 Centrifuge bottles, 250mL

5.18 Flitz® metal polish

5.19 Dremmel® tool

5.20 Nylon bristle brushes, Forney Industries, Inc., Cat. No. 60240, or equivalent.

5.21 Filter papers, Whatman® #41

5.22 Transfer pipets, disposable

5.23 Plastic stir rods

5.24 Whatman Ashless Powder

6. REAGENTS

Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

6.1 Deionized (DI) water, ASTM Type II.

6.2 Hydrofluoric acid, HF, 48%. TLV = 3ppm

6.3 Citric Acid, 1M (for cleaning crucibles): Dissolve 210.14g of $C_6H_8O_7$ in DI water. Dilute to 1000mL.

6.4 Nitric acid, HNO_3, concentrated. TLV = 2ppm

6.5 Hydrochloric acid, HCl, concentrated. TLV = 5ppm

6.6 2M HCl: Cautiously add 170mL conc. HCl to approximately 600mL DI water

and dilute to 1L. TLV = 5ppm

6.7 Sulfuric acid, H_2SO_4, concentrated. TLV = 0.25ppm

6.8 Potassium fluoride, anhydrous. TWA = 2.5mg/m^3 as F

6.9 Sodium sulfate, anhydrous

6.10 Fe carrier (20mg Fe^3+/mL): Dissolve 96g of $FeCl_3 \bullet 6H_2O$ in 1.0L of 0.5N HCl.

6.11 Radiacwash® detergent or equivalent

6.12 Ammonium hydroxide, NH_4OH, 15N (conc.), reagent grade. TLV = 25ppm (for ammonia)

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

No sample collection, preservation, or handling requirements are specific to this method.

8. PROCEDURE

8.1 POTASSIUM PYROSULFATE FUSION

If greater than 1.0 gram of sample is needed for analysis, proportionally increase reagents. For example, if a 2.0 gram aliquot is prepared, double the amount of all other reagents used during the fusion process.

8.1.1 Weigh a 1.0g aliquot of sample (dried and ground per SOP 336), into a tared 100mL platinum crucible.

8.1.2 Fold a Whatman® #41 filter paper and place it into the crucible designated for the blank and LCS.

8.1.3 Using calibrated pipettes (SOP 321), add the appropriate volume of tracing and spiking solutions for the requested analysis. If there is standing liquid in the crucible after spiking and tracing, it is advisable to absorb this liquid by adding Whatman Ashless Powder, prior to muffling, to avoid splattering of the sample.

8.1.4 Cover each crucible with a watch glass and muffle at 600°C for at least 1 hour.

8.1.5 After cooling, remove the crucibles from the furnace and, using a marker, label the watch glass with the crucible ID. Place the watch glass aside on a clean surface for later use. Add 1.0mL of concentrated nitric acid around the edge of the sample in the crucible.

8.1.6 Using a transfer pipet, add approximately 3-6mL of 48% HF (concentrated HF) to wet the sample thoroughly and evaporate to NEAR dryness on a hotplate. DO NOT allow the sample to bake onto the dish.

8.1.7 Sprinkle 6g of anhydrous potassium fluoride over the residue. Fuse over a hot flame on a blast burner until a clear melt is obtained, swirling GENTLY to mix. Heat about 4 minutes to fusion temperature (approximately 900°C) and another 2 minutes to complete dissolution. Place the sample on a ring stand to cool.

8.1.8 While the melt is still warm, add at least 7mL (or about 3 transfer pipets full) of concentrated sulfuric acid drop wise down the edges of the dish to wash sample residue down the walls of the dish. If needed, additional sulfuric acid can be added up to a maximum of 15mL.

8.1.9 PREVENT FROTHING IN THE NEXT STEP. Be prepared to set the dish in a cold water bath if it threatens to froth over the sides of the dish. The crucible can also be set on a heat insulating pad to cool.

8.1.10 Using the blast burner, pass the crucible slowly over a cool flame (low compressed air) or heat on a hot plate set between 230°C-280°C, until vigorous reaction subsides and the melt from Step 8.1.7 has completely dissolved.

8.1.11 Place the sample on a hot plate (setting of 7) and add 4.0g of anhydrous sodium sulfate.

8.1.12 Over the blast burner, swirling gently, continue heating until a clear pyrosulfate fusion is obtained. The thick, almost solid, sample will dissolve to a thin one that is easily boiled. Then, increase the temperature as fast as boiling will permit until a clear solution is achieved. The sample will be a dark red, but clear, solution when finished. The blank and LCS will generally have a light pink appearance at this Step.

DO NOT HEAT LONGER THAN NECESSARY TO MINIMIZE DISSOLUTION OF PLATINUM FROM THE CRUCIBLE.

CAUTION: Large amounts of hydrogen fluoride and silicon tetrafluoride are expelled from the sample. Be sure to use a properly operating fume hood.

8.1.13 Set the dish on a ring stand and allow the sample to cool and solidify.

8.1.14 Place the sample on the hot plate (setting 180°C-200°C) with the crucible's watch glass cover used during muffling, leaving slightly off to vent the sample. Fill the crucible ¾ full with 2M HCl.

8.1.15 When the solid sample has entirely dissolved (~5 to 6 hours), transfer the sample solution to a 250mL centrifuge bottle using a clean plastic

funnel.

8.1.16 Rinse the crucible with additional 2M HCl and add this rinse to the centrifuge bottle for a quantitative transfer. Do not fill the centrifuge bottle more than 150mL. If this occurs, the bottle may be placed on the steambath with the cap off to evaporate the sample to less than 150mL.

8.1.17 Add 2mL of ferric chloride carrier (20mg Fe^{3}+/mL). Add DI water to the centrifuge bottle to bring the total volume to ~200mL. (This dilution helps prevent a vigorous reaction from occurring between the acidic sample solution and the conc. NH_4OH to be added in the next step.)

8.1.18 Note: A great deal of heat can be generated at this step of adding a base to an acidic solution. Slowly add ~50 mL of conc. NH_4OH to form $Fe(OH)_3$ precipitate. If a precipitate does not form after adding the 50mL of NH_4OH, consult an appropriate supervisor. Balance the centrifuge bottles with DI water and allow the sample in the bottle to cool before centrifuging.

8.1.19 Centrifuge the samples for 12 minutes at approximately 3500 rpm. Discard the supernatant (avoid losing any precipitate). Further separations are now performed following the appropriate actinides separation SOP 778 or 777.

8.2 CLEANING PROCEDURE FOR PLATINUM CRUCIBLES

NOTE: When cleaning the crucibles, NEVER use anything abrasive such as scrubbing pads, that will scratch the platinum.

8.2.1 After the samples have been quantitatively transferred from the crucible (Step 8.1.16), rinse the crucible with tap water to remove residual acid.

8.2.2 Soak the crucibles in Radiacwash® for 30-60 minutes.

8.2.3 Rinse the crucibles with DI water and place them in a large beaker. Crucibles should be placed in a single layer, not stacked. Add enough 1M citric acid solution to completely cover the crucibles. Place the beaker containing the crucibles on a hot plate and cover with a watch glass or an aluminum pie pan. Boil for a minimum of 1 hour.

8.2.4 After cooling, rinse the crucibles with DI water and dry. Discard the citric acid down the laboratory sink, flushing with cold water.

8.2.5 Re-shape the crucible using the provided epoxy form.

8.2.6 Using a Dremmel® tool fitted with a nylon-bristled polishing brush and

FLITZ® polishing compound, polish the crucibles until visible scratches and oxidation are removed.

8.2.7 Buff with a clean, soft cloth until a mirrored finish is obtained. Repeat Step 8.2.5 above, if necessary.

9. CALCULATION OF TPU FACTORS

The preparation uncertainty factors for this method are generally equivalent to those factors affecting samples that undergo a normal acid dissolution. Consequently, no additional consideration should be made for this method.

10. QUALITY CONTROL

Acceptance criteria for QC samples may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.1 One blank sample is prepared and analyzed with every batch of 20 field samples or less.

10.2 One sample duplicate is prepared and analyzed with every batch of 10 field samples or less.

10.3 One spiked blank sample (LCS) is prepared and analyzed with every batch of 20 field samples or less.

10.4 Where required, a well-characterized solid refractory reference material is analyzed with a frequency of approximately every 100 samples. Results are compared to expected values to ensure adequate fusion of the solid sample is being obtained.

11. DEVIATIONS FROM METHOD

This is a proprietary, confidential procedure developed by Paragon. Therefore, there are no deviations from a promulgated method.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 The fumes evolved in this procedure are extremely hazardous and must be properly contained and exhausted in a laboratory fume hood. It is the responsibility of the technician performing this work to ensure that the fume hood being used is turned on, functioning properly, has a current calibration, and is used appropriately.

12.1.2 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.3 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

12.1.4 Gloves, safety glasses and a lab coat must be worn when working with any chemicals (e.g., standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

12.1.5 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.6 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.1.7 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

12.2 WASTE DISPOSAL

12.2.1 Wastes that are "corrosive only", such as sulfuric acid waste, are disposed of by discharging into the Paragon waste water treatment facility. These "corrosive only" materials have been identified as having no hazardous components or characteristics other than corrosivity, and may, therefore, be neutralized in the waste treatment facility.

12.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. Notify waste management staff for disposal.

12.2.3 All acid wastes not containing HF that are generated in sample dissolution steps, are disposed of to the waste tanks (i.e., down the drain), unless otherwise specified due to hazardous constituents.

13. REFERENCES

13.1 C.W. Sill, K.W. Puphal and F.D. Hindman, Analytical Chemistry, 46, 1725 (1974).

13.2 C.W. Sill, Analytical Chemistry, 49, 618 (1977).

13.3 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

7/24/06: Augmented RESPONSIBILITIES and safety precautions. Other clerical changes. Added DOCUMENT REVISION HISTORY.

7/18/08 Minor procedural updates/clarifications made. Added introductory comments to QC Section 10.

Must Discard 30 Days from _____ (date printed)

Ammended 9/27/07 (Section 7.1): Hold for 24hrs (not 16) after pH adjustment (consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57) DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 765 REVISION 4

TITLE: **SEPARATION AND ANALYSIS OF ^{237}NEPTUNIUM IN ENVIRONMENTAL MATRICES**

FORMS: **NONE**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 8/31/06
QUALITY ASSURANCE MANAGER _____ DATE 8/31/06
LABORATORY MANAGER _____ DATE 8-31-06

HISTORY: Rev0, PCN #314, 12/28/94; Rev1, 10/8/99; Rev2, 4/10/02; Rev3, 4/7/03 and 1/31/05 (no revisions); Rev4, 9/1/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedure for the separation and purification of ^{237}Np in environmental samples using anion exchange chromatography and precipitation of this analyte for quantification by alpha spectroscopy.

2. SUMMARY

Solid samples are digested according to SOP 773 and water samples are prepared according to SOP 776 prior to this procedure. Pretreatment of solid samples (drying and grinding) is described in SOP 721. The actinides are co-precipitated with an iron hydroxide precipitate. Neptunium (Np) is separated and purified by anion exchange chromatography. The purified Np is co-precipitated with lanthanum fluoride (LaF_3) and mounted on a filter membrane for alpha spectroscopy counting.

Since there is no suitable alpha-emitting isotope of Neptunium available for use as a yield tracer, the chemical yield is determined using the method of standard additions. Replicate aliquots of each sample are transferred to a beaker. A yield spike (i.e., a known activity of NIST-traceable ^{237}Np) is added to one sample aliquot, while the replicate is processed unspiked. A composite measure of the chemical yield and counting efficiency (i.e., the 'total efficiency') is determined for the yield spike sample using results obtained for the sample pair. ***Note that reproducibility of the process is critical in generating accurate chemical yield information. The analyst should treat all samples identically and must note any anomaly, which could cause a significant variation in yield between a sample and its associated yield spike.*** Also note that the yield spike is NOT a 'matrix spike'. A matrix spike is a quality control (QC) sample and is NOT used to generate data for chemical yield corrections, rather, the matrix spike is used to provide quality control information about analyte recovery.

3. RESPONSIBILITIES

3.1 It is the responsibility of the laboratory staff to perform these tasks according to

this SOP and to complete all documentation required for review. Preparation, analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, or the performance of precision and accuracy tests, or by other suitable means.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalous or out-of-control events. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 The presence of any significant quantities of suspended solids is a physical interference. Samples containing perceptible quantities of suspended solids will be filtered prior to initiation of preparation and analysis.

4.2 The presence of a significant amount of ^{234}U in the sample may interfere with the ^{237}Np region of interest (ROI) in the analytical spectrum.

5. APPARATUS AND MATERIALS

5.1 Ion exchange columns, plastic, disposable, with fitted funnels

5.2 Filter membrane, 0.1µm, 25mm diameter, polypropylene

5.3 Suction filter for 25mm membrane

5.4 Repeator pipet, 0.5mL and 1.5mL, Eppendorf™ or equivalent, and pipet tips

5.5 Centrifuge bottles, 250mL

5.6 Wash bottle

5.7 Double-sided tape

5.8 Stainless steel planchets, 1.25" diameter

5.9 pH paper (strips)

5.10 Rubber policeman

5.11 Petri dishes

5.12 Plastic cups, 220mL, disposable

5.13 Glass beads

5.14 Vortex mixer

5.15 Centrifuge

5.16 Steam bath

5.17 Laboratory forceps

5.18 Fluorescent heat lamp

5.19 RadiacWash® solution

6. REAGENTS

NOTE: Threshold Limit Value (TLV) and other hazard information may be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Anion exchange resin, AG 1X8, 50-100 mesh, available from Biorad or Eichrom (or equivalent)

6.2 Ammonium hydroxide (NH_4OH), 15N (conc.) TLV = 25ppm (for NH_3)

6.3 Deionized (DI) water, obtained from the laboratory's DI water system

6.4 Ferric chloride carrier, 20mg Fe^{+3}/mL. Made in-house by dissolving 96g of $FeCl_3$•6 H_20 in 1000mL of 0.5N HCl. PEL = 0.15ppm

6.5 Hydrochloric acid (HCl), 12M (conc.). ACS reagent grade. TLV = 5ppm (ceiling)

6.6 HCl, 1M: Add 83mL conc. HCl to approximately 800mL of DI water. Bring to a final volume of 1L with DI water. Mix well.

6.7 HCl, 0.5M: Add 42mL conc. HCl to approximately 800mL of DI water and bring to 1L volume with DI water. Mix well.

6.8 Hydrofluoric acid (HF), 48%-51% (conc.). TLV = 3ppm

6.9 HF, 3M: Carefully dilute 104mL conc. HF to 1L with DI water. Use plastic

graduated cylinder and storage bottle. TLV = 3ppm (for concentrated HF)

6.10 Nitric acid (HNO_3), 16M (conc.) ACS reagent grade. TLV = 2ppm

6.11 Lanthanum carrier, 0.1mg La^{3+}/mL: Made in-house by dissolving 0.312g high purity $La(NO_3)_3 \cdot 6H_2O$ per 1000mL 1M HCl. Document in RadChem Reagent Prep Logbook and Paragon's Standards & Solutions database.

6.12 ^{237}Np, NIST-traceable

6.13 Methanol, reagent grade. TLV = 200ppm

6.14 Polyethylene glycol (PEG), average molecular weight 2000g/mol, 0.25 M: Make in-house by dissolving 50g of PEG in 40mL of DI water. Dilute to 100mL with DI water. Note that placing the container on a stirrer with a stir bar will help dissolve the PEG in water.

6.15 Hydrogen peroxide (H_2O_2), 30%, reagent grade. TLV = 1ppm. Potential carcinogen, irritation, pulmonary edema, central nervous system effects.

6.16 Ammonium Iodide (NH_4I) in concentrated HCl: Weigh out 0.73g of NH_4I and dissolve in 100mL of conc. HCl.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLD TIME

7.1 It is recommended that samples be preserved at the time of collection by adding enough concentrated HNO_3 to the sample to lower the sample's pH to less than 2. Addition of 5mL conc. HNO_3 per liter of sample is usually sufficient. If samples are to be collected without preservation, they should be brought to the laboratory within 5 days of collection and then preserved and held in the original container for a minimum of ~~16~~ 24 hrs before analysis or transfer of the sample from the original container.

7.2 The sample container should preferably be plastic rather than glass. This prevents loss due to breakage during transport and handling and minimizes any possible losses due to analyte plate out on container walls.

7.3 There is no regulatory holding time for this method. Paragon recommends a default holding time of 180 days for waters. There is no holding time for solids.

8. PROCEDURE

8.1 CREATION OF SAMPLE ALIQUOTS AND YIELD SPIKES

8.1.1 Two identical volumes (default -- 1.0L or a 2.0g equivalent of digestate) of each sample are aliquotted. Label the first volume per the RadChem ID convention of yy - mm - wo# - s# (e.g., 02-12-123-12). Add a "YS" designation to the labeled ID of the second aliquot of sample (e.g., 02-12-123-12-YS), to denote the replicate aliquot of sample that is spiked for yield determination.

8.1.2 Yield spikes should routinely contain at least 5-10 times the expected

activity of the associated field or QC sample. For routine environmental samples, the yield spike activity should be ~30-50dpm. A typical batch of samples is named and would be spiked as follows:

0212123-1	unspiked
0212123-1-YS	~30dpm of ^{237}Np spike added
0212123-2	unspiked
0212123-2-YS	~30dpm of ^{237}Np spike added
0212123-3	unspiked
0212123-3-YS	~30dpm of ^{237}Np spike added
0212123-3DUP	unspiked
AS040305-1MB	QC sample (method blank)
AS040305-1YS	yield spike aliquot for method blank, ~30dpm of ^{237}Np spike added
AS040305-1LCS	QC sample (laboratory control sample), ~5dpm of 237Np spike added

8.2 PURIFICATION BY ANION EXCHANGE

8.2.1 Dissolve the iron hydroxide precipitate from the previous dissolution procedure in 50-100mL of concentrated HCl. For samples with suspected high plutonium (Pu) content, dissolve the precipitate in 50-100mL of conc. HCl/NH_4I solution

8.2.2 Sample matrix constituents such as silicates may cause a cloudy or foamy appearance when the samples are dissolved in HCl. Samples may be compared with the QC samples of that batch for differences in appearance. If samples are noticeably different from the batch QC, a PEG treatment may be conducted as explained in Step 8.2.3 below, to keep the sample constituents from blocking column flow. Perform this treatment on the entire batch of samples, as well as the QC. If samples are clear, proceed to Step 8.2.4.

8.2.3 <u>PEG Treatment</u>: After quantitatively transferring the sample to a centrifuge bottle, add 3mL of 0.25M PEG to each sample. Vortex to mix and place samples in a refrigerator for ~30 minutes. The silicates will be trapped by the chelating action of the PEG and will slowly settle as a glassy precipitate in the bottom of the centrifuge bottle. Centrifuge the sample for 5 minutes at 3500rpm.

8.2.4 Prepare an ion exchange column (70mm X 10mm I.D.) using AG 1X8 anion exchange resin. Fill the disposable plastic column with resin to a

settled depth of 7cm. Cover the top of the resin bed with a 1-2cm layer of clean glass beads. Securely attach a fitted funnel to each column. Place a waste beaker under the column.

8.2.5 Label each column with the sample ID using a Sharpie marker.

8.2.6 Condition the column with 50mL of concentrated HCl. Discard the effluent in the drain inside the fume hood with large amounts of cold water (this flushes the effluent into the Paragon wastewater treatment system).

8.2.7 Slowly pour the sample from the centrifuge bottle into the funnel. Discard column effluents into the drain inside the fume hood with large amounts of cold water (discharges to the Paragon wastewater treatment system).

8.2.8 Rinse the column with 20mL of concentrated HCl/NH_4I solution. *This Step should be performed only after the original sample has completely passed through the column.* Discard column effluents into the drain with a large amount of cold water.

8.2.9 Rinse the column with 20mL of concentrated HCl/NH_4I solution an additional two times. Discard the effluent into the drain inside the fume hood with plenty of cold water.

8.2.10 Rinse the column with 25mL of concentrated HCl and discard the column effluents into the drain inside the fume hood with plenty of cold water.

8.2.11 Strip the Neptunium with three 20mL volumes of 1M HCl. Collect this strip solution in a clean plastic cup that is labeled with the sample ID and "Np mic". Add 10mL of concentrated HNO_3 to the Np micro cup and take it to dryness on the steam bath.

8.2.12 Used resin columns are discarded by extruding the resin from the column and placing the resin in the established waste stream labeled "Hazardous Waste – Used Acidic Resin" in the Satellite Accumulation Area in the lab. When the satellite container is full, notify the Waste Management Officer for further instructions. Emptied columns may be soaked in a RadiacWash® solution, rinsed in tap water and discarded into the sanitary trash.

8.2.13 Used disposable cups may be rinsed with RadiacWash® solution and tap water and re-used for collecting waste column effluent. If the cups are not needed, they may be soaked in RadiacWash®, rinsed with tap water and discarded into the sanitary trash.

8.3 MICROPRECIPITATION OF NEPTUNIUM

8.3.1 Dissolve the sample residue from the Np micro cup using 1mL of concentrated HCl. If necessary, heat the cup on a steam bath for few minutes for a better dissolution - do not allow the sample to go dry.

8.3.2 Add 14mL of DI water to the cup and mix well.

8.3.3 Add 1.0mL of lanthanum carrier and swirl gently.

8.3.4 Add 1.0mL of 30% hydrogen peroxide and 5mL of 3N HF and swirl to mix.

8.3.5 Allow samples to sit for 30 minutes to complete micro-precipitation.

8.3.6 Assemble the micro-precip funnel with 0.1µm, 25mm filter paper. Turn the vacuum on and pre-rinse the filter paper with few mL of methanol. This will make the filter less hydrophobic. When the methanol is almost passed through the filter, add approximately 5mL of DI water.

8.3.7 When the water is almost passed through the filter, pass the co-precipitated sample through the filter membrane.

8.3.8 Rinse the sample cup with 10mL DI water and add to the filter funnel, once the load solution has passed through. After the rinse has passed through, rinse the filter with an additional 10mL of DI water.

8.3.9 After filtration, keep vacuum on and remove the funnel. Use a "Sharpie" marker to place a dot on the outside edge of the filter. This helps identify the right side of the filter in case the filter flips during transaction. Carefully remove the filter membrane with a pair of forceps and fix it face up on the double-sided tape that was placed on the planchet. Dry the filter membrane with the planchet under the fluorescence light bulb for a minute. DO NOT KEEP THE PLANCHET FOR A LONG TIME UNDERNEATH THE LAMP AS IT MIGHT MELT THE DOUBLE SIDED TAPE.

8.3.10 Discard the waste in the suction flask into the appropriate waste carboy.

9. CALCULATIONS

9.1 The standard alpha spectroscopy calculations defined in SOP 714 are used with the following modifications -- the chemical yield is calculated from the results of the spike addition as follows:

$$CY = \frac{(C_{YS} / (T_{YS} * Eff_{YS})) - (C_S / (T_S * Eff_S))}{DPM}$$

where:

CY	=	fractional chemical yield
C_{YS}	=	net ^{237}Np counts from the spiked sample (cts)
T_{YS}	=	time elapsed for the count of the spiked sample (min)
Eff_{YS}	=	fractional detector efficiency for the spiked sample
C_S	=	net ^{237}Np counts from the sample (cts)
T_S	=	time elapsed for the count of the sample (min)
Eff_S	=	fractional detector efficiency for the sample
DPM	=	dpm ^{237}Np yield spike added per unit mass or volume (DPM/L or DPM/g)

9.2 TPU FACTORS

As defined in SOP 743, the following 1σ preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU).

9.2.1 Water samples (that require initial prep using SOP 776) require a preparation uncertainty factor of 0.192. This is based on one gross aliquotting (sample homogeneity), one volumetric measurement, one tracer addition, two quantitative transfers and one reagent addition. The TPU factor is modified to reflect the uncertainty in the measurement due to the use of yield spikes in the determination of chemical yield. 0.18 = 1σ estimated uncertainty in chemical yield. See the following equation:

$$0.192 = \sqrt{0.05^2 + 0.006^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2 + 0.18^2}$$

9.2.2 Solid samples (that require initial prep using SOP 773) also require a preparation uncertainty factor of 0.192. This is based on one gross aliquotting (sample homogeneity), one mass measurement, one tracer addition, two quantitative transfers and one reagent addition. The TPU factor is modified to reflect the uncertainty in the measurement due to the use of yield spikes in the determination of chemical yield. 0.18 = 1σ estimated uncertainty in chemical yield. See the following equation:

$$0.192 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2 + 0.18^2}$$

10. QUALITY ASSURANCE REQUIREMENTS

10.1 One Method Blank must be analyzed with each batch of 20 or fewer samples. Acceptance criteria are described in SOP 714 or in the applicable client statement of work (SOW).

10.2 One Laboratory Control Sample (LCS) must be analyzed with each batch of 20 or fewer samples. Acceptance criteria are described in the SOP 714 or in the applicable client SOW.

10.3 Sample Duplicates are processed at a minimum frequency of 10%. Acceptance criteria are described in the SOP 714 or in the applicable client SOW. If insufficient sample is provided to perform sample duplicates, an LCS Duplicate may be run in lieu of the sample duplicate.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFTEY AND HAZARDS

11.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

11.1.2 Safety glasses, and lab coats must be worn in the radiochemistry prep labs at all times.

11.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.2 below.

11.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

11.1.6 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation and personnel safety features. Never inhale or allow skin or clothing to be exposed to HF fumes.

11.1.7 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

11.2 WASTE DISPOSAL

11.2.1 Wastes that are "corrosive only" " (i.e., have no hazardous components or characteristics other than corrosivity), such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the Paragon wastewater treatment facility, where they may be subsequently neutralized.

11.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Management Officer for disposal.

11.2.3 All acid wastes NOT containing HF that are generated in ion exchange operations are disposed of to the waste tanks (down the drain) unless otherwise specified due to hazardous constituents.

12. METHOD COMPLIANCE

This is a proprietary procedure developed by Paragon. Therefore, there are no deviations from promulgated methods for this procedure.

13. REFERENCES

13.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Herman L. Krieger and Earl L. Wittaker, EPA-600/4-80-0, August 1980.

13.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.3 Paragon SOP 743, "Estimating Total Propagated Uncertainties for Radiometric Analyses".

DOCUMENT REVISION HISTORY

9/1/06: No technical changes. Augmented LIMS program specification language. Corrected an editorial error in the yield calculation. Added DOCUMENT REVISION HISTORY section. Other minor clerical corrections.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 766 REVISION 6

TITLE: **WITNESSING THE ADDITION OF CARRIERS, TRACERS, AND STANDARDS IN RADIOCHEMISTRY SAMPLES**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/4/06

QUALITY ASSURANCE MANAGER _____ DATE 8/4/06

LABORATORY MANAGER _____ DATE 8-4-06

HISTORY: Rev0, 12/14/94; Rev1, PCN #345, 1/26/95; Rev2, 10/5/99; Rev3, 4/10/02; Rev4, 3/28/03; Rev5, 5/17/04; Rev6, 8/4/06. re-released w/o revision 7/17/08 DAS

1. SCOPE AND APPLICATION

This procedure describes the actions necessary to add carriers, tracers, and spiking solutions to samples being prepared for radiochemistry analyses.

2. SUMMARY

Element-specific carriers and isotopic tracers are added to samples being prepared for radiochemistry analyses, where available and necessary to the method. Laboratory Control Samples (LCS, Blank spike) are created by addition of a spike solution containing one or more of the target analytes. Target tracer and spike values are determined on a case-by-case basis. Specific spike and tracer solution activity values can be obtained from the reference spreadsheet (r:\forms\mda_list.xls). Target carrier concentrations are specified in the individual method SOPs. This procedure provides generic guidance for spike and tracer additions.

2.1 Carrier, tracer, and spike additions are witnessed by an analyst other than the primary analyst to ensure that all samples receive the correct volume and type of carrier, tracer, and/or spike solution. The witness must initial and date the appropriate section of the LIMS benchsheet.

2.2 Occasionally, a suitable element-specific tracer or carrier may not be available for use (e.g., ^{237}Np analysis). In these cases, a replicate split of each field and QC sample may be spiked and processed parallel to the original sample. The spike recovery (corrected for native sample activity) is used to generate chemical yield corrections for calculation of sample results. Alternately, a single matrix spike may be prepared, per batch of samples, at the Technical Manager's direction.

2.3 Calibrations of Eppendorf™ pipettes shall be verified immediately prior to use (SOP 321).

2.4 Carrier, tracer, and spike verification and expiration should be confirmed before a solution is released for general use in the laboratory (SOPs 300, 798).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst performing this procedure to remove from service and to notify the Department Manager, any pipette for which the calibration cannot be reliably verified.

3.2 It is the responsibility of the analyst performing this procedure, and the witnessing technician, to assure that all samples in the batch, including the batch QC samples, receive the appropriate volume of the correct solutions.

3.3 It is the responsibility of the analyst performing this procedure, and the witnessing technician, to prevent the use of expired or non-conforming carriers, tracers, and spiking solutions.

3.4 It is the responsibility of the Department Technical Manager to review the NIST traceability certificate and to evaluate the working-level dilution for the presence of interfering radionuclides.

3.5 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review.

3.6 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.7 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Tracer activity amounts may require adjustment if knowledge of the sample activity indicates potential for dramatic mismatches between the tracer amount and sample activity. Carrier amounts may require adjustments based on the expectation of interfering native sample constituents. Likewise, sample volumes may require adjustment to avoid excessive planchet activity, or other potential matrix interference issues.

4.2 Occasionally, nuclides specified as tracer in this and other SOPs may be sought as

target analytes. In such cases, samples are routinely traced using the nuclides otherwise designated as spikes, and LCS and matrix spike (MS) samples are spiked with the target analyte. The parallel analysis of splits of each sample may be necessary to determine the concentration or presence of 'interfering' native analyte in the sample. Results are calculated by correcting the added nuclide (non-target analyte used as tracer) amount for the native activity of that nuclide in the sample.

4.3 The NIST certificate for all radioactive standards should be reviewed by Supervisory and Management personnel prior to determining appropriate spiking levels. Some standards contain measurable amounts of impurities in the form of the actual analytes of interest. For example, the ^{243}Am tracing solution may contain ^{241}Am impurities. If ^{241}Am is the analyte of interest, care must be taken to ensure that the amount of ^{241}Am impurities introduced with the tracer solution is significantly below the client's requested detection limit.

5. APPARATUS

Pipettes, Eppendorf™ or equivalent, various volumes

6. REAGENTS

NIST-traceable or equivalent spiking and tracing solutions and reagent grade carriers, specific to the analysis to be performed as specified in the individual SOPs.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Not applicable.

8. PROCEDURE

8.1 Prior to the addition of carriers, tracers, and spiking solutions, a LIMS benchsheet will have been generated that indicates the samples to be analyzed and includes the required information about the tracer and the spike to be used. In addition, the appropriate sample aliquots will have been transferred to the proper container for digestion/preparation, per the SOP for that method.

8.2 Arrange for another analyst to watch and witness the addition of tracer and spike solutions. The spike witness must verify that:

8.2.1 Each carrier, tracer, and standard solution is properly labeled and not expired at the time of use. Radioactive standards must have a printed label, issued by the Department Manager, indicating that the verification procedure has been successfully completed. Carrier solutions may have hand-written labeling. The expiration date of the standard should be written on the benchsheet by the witnessing analyst.

8.2.2 The solution ID, radionuclides or carrier element, reference concentration, pipette ID and volume added have been recorded

properly on the benchsheet and match the spiking action.

8.2.3 Carrier, tracer and/or spike information corresponds with each sample listed on the benchsheet.

8.2.4 The witness must initial and date the appropriate section of the benchsheet after witnessing the addition of carriers, tracers, and spiking solutions.

8.2.5 If applicable, the information is then transferred to LIMS.

9. QUALITY ASSURANCE

Quality Assurance requirements for this procedure are contained in the appropriate actinides preparation SOP.

10. DEVIATION FROM METHOD

This is a proprietary procedure developed by and for Paragon. Therefore, there are no deviations from promulgated methods.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

11.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.4 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

All empty radionuclide standard solutions are disposed of by rinsing the standard container a minimum of three times with tap water. The container must be surveyed prior to release. Please note that all labels and markings must be defaced or removed prior to disposal.

12. REFERENCES

Not applicable.

DOCUMENT REVISION HISTORY

8/4/06: Use of stable carriers incorporated. Practice expanded to entire Radiochemistry Department. Other clerical changes. Added DOCUMENT REVISION HISTORY Section.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 767 REVISION 7

TITLE: SAMPLE PREPARATION -- FILTER LEACHING

FORMS: 631 (use current iteration)

APPROVED BY:
TECHNICAL MANAGER _____ DATE 5/2/07
QUALITY ASSURANCE MANAGER _____ DATE 5/2/07
LABORATORY MANAGER _____ DATE 5-2-07

HISTORY: Rev0, PCN #400, 3/25/95; Rev1, PCN #556, 10/25/95; Rev2, 10/6/99; Rev3, 1/26/00; Rev4, 4/26/02; Rev5, 4/4/03; Rev6, 11/29/04; Rev7, 4/27/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to prepare filters for multi-tests by leaching where total dissolution is not required.

The use of this procedure (i.e., nitric acid digestion, wet-ashing, muffling) is not appropriate for the preparation of leachates for certain tests such as tritium, carbon-14, radioiodine, technetium-99, or other nuclides that may be volatilized in an acidic environment or at elevated temperatures. Hence, this procedure may need to be modified to prevent volatilization of the analyte or to provide an appropriate matrix for subsequent processes.

All non-destructive testing must be completed and acceptable prior to initiation of destructive testing procedures. Depending on the mix of tests requested, it may be necessary to physically divide (cut) filters to allow for dissolution in two or more chemical systems.

2. SUMMARY

Many filters received by Paragon require multiple tests, or multiple filters (composites) are run for one or more tests utilizing the same client identification. Because the contaminants on these filters may or may not be homogeneously distributed, a method is necessary to ensure that a representative portion of the filter is measured for all tests. By leaching the filter in nitric acid and bringing the resultant volume to 1L, it is possible to aliquot a representative portion for each required analytical process.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform this procedure according to this SOP and to document all anomalous conditions on a Quality Assurance Summary Sheet (QASS, Form 302) or Non-Conformance Report (NCR, Form 313) and to obtain Supervisory approval in matters that affect data quality.

3.2 It is the responsibility of the Group Supervisor or Department Manager to notify the Project Manager in cases where data quality may be affected so that the Project Manager has ample opportunity to notify the client and discuss alternative analytical strategies.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

4. INTERFERENCES

Filters with high organic content may require the addition of hydrogen peroxide and/or muffling at approximately 450°C, prior to leaching, to facilitate dissolution of analytes in nitric acid.

5. APPARATUS AND MATERIALS

5.1 graduated cylinder, 1L

5.2 funnel, 15cm

5.3 filter paper, fluted

5.4 Pyrex® beakers, various sizes

5.5 ribbed watch glasses

5.6 hot plate

6. REAGENTS

6.1 Nitric acid, HNO_3, reagent grade, conc. TLV = 2ppm (TWA). Irritant, corrosive.

6.2 Nitric acid, 8N: Cautiously add 500mL conc. HNO_3 to 400mL DI water. Dilute to 1L with DI water. See above for TLV information.

6.3 Nitric acid, 1N: Cautiously add 63mL conc. HNO_3 to 800mL DI water. Dilute to 1L with DI water. See above for TLV information.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIME

7.1 The exact media used for sampling is typically determined and provided by the client. Filter samples are typically received in envelopes or other suitable containment.

7.2 No thermal (i.e., chilling) or chemical preservation is required.

7.3 See client specifications and individual analysis procedures for holding time requirements.

8. PROCEDURE

8.1 Read the project instructions to determine what information about the filter is required, (i.e., weight, # of filters, etc.). Always count the number of filters of each sample, and document on the sample condition form (Form 631).

8.2 Place filters in a 250mL beaker or larger if needed.

8.3 Add enough 8N HNO_3 to cover the filters.

8.4 Cover with a ribbed watch glass, and place the beakers on a hot plate. Bring to near boiling.

8.5 Maintain heat for half an hour.

8.6 Cool and transfer the liquid to a 1L graduated cylinder, using a funnel and fluted filter paper. Triple rinse the filters and beaker with 1N HNO_3, quantitatively transferring the rinsate to the 1L graduated cylinder.

8.7 Bring the leachate to full volume (1L) using 1N HNO_3. If volume is larger than 1L, evaporate leachate in a beaker on a hotplate to below 1 L, then dilute to 1L with 1N HNO_3.

8.8 Aliquot leachate as necessary.

9. QUALITY CONTROL

Refer to LIMS program specifications (project instructions) for QC sample requirements.

10. DEVIATIONS FROM METHOD

None. This procedure was developed in-house by Paragon.

11. SAFETY, HAZARDS, AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.2 Use extreme care when handling nitric acid. Work in a fume hood with adequate ventilation. Wear appropriate eye, face and body protection.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

11.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

11.2 WASTE DISPOSAL

11.2.1 RADIOCHEMISTRY ANALYTICAL EFFLUENT DISPOSAL
The sample preparation process effluent has been determined to not be hazardous other than corrosive. This material after all testing is completed and the proper archiving times have been met, may be discharged into the Paragon wastewater treatment facility. Here the solution will be neutralized prior to discharge and the activity will be monitored to ensure compliance with Colorado Rules and Regulations pertaining to Radiation Control, Part 4, regarding discharges to sanitary sewers.

11.2.2 All empty solvent bottles are disposed of according to the appropriate SOP. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

None.

DOCUMENT REVISION HISTORY

4/27/07: Corrected Sample Condition Form reference (631) in header and text, corrected form attachment. Added LIMS program specification language (3.3). Added Section 7 -- SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIME, to be consistent with Paragon SOP format. Added Sections 9 -- QUALITY CONTROL and 10 – DEVIATIONS FROM METHOD, to be consistent with Paragon SOP format. Added DOCUMENT REVISION HISTORY.

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 772 REVISION 4

TITLE: **PREPARATION OF WATER AND SOIL SAMPLES FOR THE ANALYSIS OF CARBON-14 USING POTASSIUM PERMANGANATE – EPA EERF METHOD C-01**

FORMS: **631** **(use current iteration)**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 8/16/07
QUALITY ASSURANCE MANAGER _____ DATE 8/12/07
LABORATORY MANAGER _____ DATE 8/16/07

HISTORY: Rev0, 3/17/95; Rev1, 3/24/00; Rev2, 4/26/02; Rev3, 4/07/03 and 3/15/05 (format updated); Rev4, 8/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used to prepare soil and water samples for the determination of ^{14}C. This procedure is based on Eastern Environmental Radiation Facility (EERF) Procedures Manual Method C-01.

2. SUMMARY

A measured aliquot of the sample is placed in a digestion tube. The organic and inorganic carbon in the sample is oxidized to CO_2 using sulfuric acid and potassium permanganate. The CO_2 gas is absorbed in a base solution. An aliquot of the base solution is added to a liquid scintillation cocktail. The sample is counted for low energy beta activity using a liquid scintillation counter (LSC).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.2 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specifications related to the client, project, and test method being performed.

3.3 Final review and sign-off of the data are performed by the Department Manager or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is satisfactory. Any errors that are

found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 The normal sample size for waters is 25mL to achieve a standard detection limit of 500pCi/L. Samples should not be preserved with acid. ^{14}C in inorganic forms cannot be determined in water samples that are received with an acid preservative because the addition of acid to a sample containing ^{14}C may result in the production and loss of $^{14}CO_2$ from the sample.

4.2 The normal sample size for soils is 1.0g to achieve a standard detection limit of 20pCi/g. Samples are routinely dried and ground per SOP 721.

4.3 Some organic compounds in solid matrices could become volatile during the drying stage, which may result in a low bias in the analytical results.

4.4 A maximum of 300 mg of carbon can be trapped by the system described in this SOP.

4.5 Incomplete recovery of carbon may result if the flow rate through the system is too fast or if the system is not properly sealed during use.

4.6 All glassware must be cleaned according to glassware washing SOP 720, and thoroughly dried prior to use in this procedure. Distillation apparatus should be thoroughly cleaned with Hydroxylamine Hydrochloride, as needed, to remove buildup of visible residues in the flasks.

4.7 The scintillation vial is an optical surface. Any markings or material on the outside of the scintillation vial will interfere with the detection of scintillation. These should be removed prior to analysis by wiping the vial with a lint-free lab wipe and alcohol. All labeling must be done on the cap of the vial.

4.8 The presence of visible coloration in the distillate will attenuate the light emitted from the scintillation cocktail. This effect, known as color quenching, is an interference to the detection of the scintillation. The quench indicating parameter or QIP (usually H-number or SQPe) should be monitored and variations in quench which could correspond to greater than 10% relative bias in the efficiency should be addressed by using standard additions to determine a sample specific efficiency.

4.9 The presence of particulate contaminant in the trap solution may interfere with the detection of the scintillation. This effect is known as 'physical quenching'. The symptoms, control limits, and corrective actions are identical to those mentioned in Section 4.7 above.

4.10 The presence of chemical contaminants in the trap solution may inhibit scintillation. This effect is known as 'chemical quenching'. The symptoms, control limits, and corrective actions are identical to those mentioned in Section 4.7 above.

5. APPARATUS AND MATERIALS

5.1 Midi cyanide distillation apparatus, including digestion tubes, cold finger, frit, and other glassware

5.2 vacuum pump or house vacuum

5.3 scintillation vials, low potassium borosilicate glass, 20mL, Wheaton™, or similar

5.4 graduated cylinder, 25 and 50mL

5.5 pipettors, 1mL, 5mL

5.6 pipet tips

5.7 pH paper, wide range

5.8 dispenser, repipette, 1-20mL adjustable, Brinkman™, or similar

5.9 aluminum weighing dish

5.10 plastic cups with lids, 100mL

5.11 analytical balance, capable of weighing to 0.0001g

6. REAGENTS

- Threshold Limit Value (TLV) and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Deionized (DI) Water, ASTM Type II or equivalent, obtainable from the laboratory's DI water system.

6.2 <u>5% (w/v) Potassium permanganate ($KMnO_4$) solution</u>: Dissolve 5g reagent grade $KMnO_4$ in 100mL DI water. Use a magnetic stirring bar and stir plate to speed dissolution.

6.3 <u>Sulfuric acid, 18N</u>: Cautiously add 500mL conc. H_2SO_4 to 500mL DI water. Allow to cool.

TLV = 0.25ppm. Irritant, corrosive. The Chemical Hygiene Plan requires the use of a rubber apron and face shield when handling concentrated sulfuric acid.

6.4 Scintillation cocktail - Ultima Gold™ LLT chemiluminescence-resistant cocktail or other equivalent.

6.5 ^{14}C standard solution, glucose form, approximately 100 $^{dpm}/_{mL}$, accurately calibrated.

6.6 Hydroxylamine Hydrochloride, 12%: Dissolve 12 g of $NH_2OH \bullet HCl$ in DI water, dilute to 100 mL final volume.
Severe irritant, reactive, corrosive, flammable.

6.7 Ammonium hydroxide base solution, 1N: Add 67 mL conc. NH_4OH to 500mL DI water. Dilute to 1L with DI water and mix well. Prepare fresh as needed.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Environmental and water samples for carbon analysis should be collected in amber glass containers. **The samples should not be chemically preserved.**

7.2 Keep all sample containers tightly closed. If samples are to be stored for an extended period of time, refrigeration is recommended to prevent biological growth in the sample.

7.3 At the current time, there is no regulatory holding time for ^{14}C. Many sampling and analysis plans, however, apply a default holding time of 180 days for this analysis. If samples are analyzed more than 180 days after collection, this fact should be noted in the case narrative.

8. PROCEDURE

8.1 SOLIDS PREPARATION

Solids are dried and ground per SOP 721 when appropriate. Record the condition of the sample on the sample condition form (Form 631).

Weigh 1g solid into a weighing dish using an analytical balance. Record weight to nearest 0.0001g on the benchsheet. A smaller aliquot must be weighed out for solids that have an unusually high total C content (>10%). Add the contents of the weighing dish to a clean, labeled digestion tube. Rinse the residue in the dish into the tube with a minimum of DI water. Proceed to Section 8.3.

8.2 WATERS PREPARATION

Check sample pH with wide range pH test paper. Record pH of each sample on the sample condition form (Form 631).

Water sample aliquots are measured with a graduated cylinder and transferred to clean, dry digestion tubes. The normal aliquot volume for water samples is 25mL. *A larger aliquot up to 50mL may be used to meet client detection criteria, but use caution when distilling on the Midi apparatus, as samples will have a tendency to overflow.* Proceed to Section 8.3.

8.3 SAMPLE PREPARATION

8.3.1 Prepare a Laboratory Control Sample (LCS) and a matrix spike (MS) per Section 9.2 below.

8.3.2 Label the receiving digestion tubes and fill with 50mL of freshly made 1N NH_4OH solution.

8.3.3 Finish assembling the distillation apparatus, ensuring a tight seal in the ground glass fittings. Start the water flow to the condensers at a flow rate of approximately 60gph (gallons/hour). Open the vacuum valve to begin aeration. Set vacuum so that the flow rate through the system is slow but continuous using the individual adjustable valves.

8.3.4 Add 5mL 5% $KMnO_4$ and 5mL 18N H_2SO_4 to the sample digestion tube through the air intake orifice.

8.3.5 Turn on the power to the Midi distillation apparatus. Turn on the heat to the digestion block by turning the timer knob. Set timer to 40 minutes.

8.3.6 Maintain the gas flow through the system by adjusting the vacuum, if necessary. The flow rate should be as slow as possible while avoiding backup.

8.3.7 Watch for foaming in the digestion tubes. Slowly turn down (or off) vacuum to any cell that foams excessively. Foaming may indicate excess carbon in the sample.

8.3.8 Continue to apply vacuum to the system and allow the cooling water to run for about fifteen minutes after the timer shuts the heating block off.

8.4 PREPARATION OF DISTILLATE FOR LIQUID SCINTILLATION COUNTING

8.4.1 Remove the fritted sparger from the 1N NH_4OH trap solution. Allow the fluid to drain back into the tube, with the aid of a pipet bulb, if necessary.

8.4.2 Pour the trap solution into a labeled 100mL poly cup. Dispose of the sample digestate into the carboy labeled “Carbon-14 Distillation and Tritium Distillation Waste”. Wash the glassware per SOP 720.

8.4.3 Label the cap of a 20mL glass scintillation vial for each sample.

8.4.4 Pipet a 5.0mL aliquot of the 1N NH_4OH trap solution from each sample into the scintillation vial. The remaining trap solution may be stored in the poly cup, capped, until the samples have been analyzed. After

satisfactory review of the data, the solution may be discarded into the carboy labeled "Carbon-14 and Tritium Distillate Remainders".

8.4.5 Add 15mL of Ultima Gold LLT^{TM}cocktail using a calibrated bottle-top dispenser.

8.4.6 Attach the labeled lid and shake each vial to mix well. Wipe off the outside of each vial using a laboratory wipe wetted with methanol.

8.4.7 Place the vials prepared for counting in a numbered rack, which fits into the LSC instrument.

8.4.8 Submit the samples to the Counting Lab where they will be analyzed and ultimately disposed of in the manner described in SOP 704.

9. QUALITY CONTROL

9.1 CALIBRATION

9.1.1 Repipettor calibration: The repipette dispenser is checked monthly (SOP 321) by dispensing a 10mL aliquot of scintillation cocktail into a 10mL graduated cylinder. The volume should be 10mL +/- 0.1mL, apply minor adjustment as necessary. Record the verification check in the pipet calibration logbook.

9.1.2 Efficiency calibration: While instructions are provided in Section 9.1.2.1 below for the preparation of a single point calibration standard, a quench curve is preferable and should be the default calibration unless otherwise instructed by the Radiochemistry Manager. Instructions for the preparation of a quench curve are provided in Section 9.1.2.2.

9.1.2.1 A single-point calibration is conducted as follows: At least 3 replicate standards are prepared by diluting ~ 500-5000dpm of NIST-traceable ^{14}C standard solution to the desired volume with 1N NH_4OH (default = 5mL, maximum using cocktails currently available). An appropriate volume of scintillation cocktail is added such that a stable emulsion will be formed (default = 15mL, minimum ratio of cocktail:sample, for Ultima-Gold LLT^{TM} = 3:1). The average efficiency is calculated as described below. Three Initial Calibration Verification (ICV) samples are prepared as described above, using an independent second source as the spiking standard, when available. The ICVs are submitted with the calibration vials. The radiometric recovery for the ICVs must meet the normal LCS acceptance

criteria for this method, as specified in the LIMS "Paragon Standard" program specification.

A single-point efficiency is accurate and may be used for the calculation of all results showing a QIP result corresponding to the average observed for the calibration standard (within +/- 10% relative efficiency or, lacking this calibrated range, +/- 15 of mean H# or SQPe number).

9.1.2.2 Quenched standards for the preparation of the quench curve are prepared as follows: Label 24 glass liquid scintillation vials (12 are spiked and 12 are for background). Spike 12 of the vials with ~500-5,000 dpm of NIST-traceable ^{14}C standard. Dilute to 5mL with 1N NH_4OH. Add nitromethane (or other suitable quenching agent) in 15µl increments ranging from 0µl to 165µl. Add 15mL of Ultima Gold LLT™ cocktail, cap, and shake to mix well.

For the 12 background vials, add a representative volume of the spike solution diluent, bring to a final volume of 5mL with 1N NH_4OH, then add nitromethane in the same increments as stated above. Add 15mL of cocktail, cap, and shake to mix well. Submit prepared vials to the Counting Lab. Three Initial Calibration Verification (ICV) samples are prepared as described above, using an independent second source as the spiking standard, and submitted with the calibration vials. In addition, the three ICVs should be quenched at the low, middle, and high ranges of the quench curve. The radiometric recovery for the ICVs must meet the normal LCS acceptance criteria for this method, as specified in the LIMS "Paragon Standard" program specification.

9.1.3 Background calibration (reagent blank): For single point calibrations, three reagent blanks are prepared and analyzed with each batch of efficiency calibration sources and each batch of samples, in the same solution ratios. These results are used to background-correct the current analysis batch.

In the use of quench curves, three reagent blanks are prepared and analyzed with each batch of samples. These results are used for batch-specific adjustments to the background quench curve, as described below:

9.1.3.1 Obtain a volume of blank (no radioactive standard added) diluent that was used to prepare the calibration standard solution.

9.1.3.2 To each scintillation vial, add blank diluent, 1N NH_4OH, and cocktail in the same ratios used in the efficiency calibration sources.

9.1.3.3 When using a quench curve, the three reagent blanks should be quenched at the low, middle, and high ranges of the quench curve.

9.1.3.4 The three reagent blanks are submitted for each preparation batch and counted for a time period equal to or longer than the longest sample count. For a single-point calibration, the average of these reagent blanks is used as the background correction for that particular batch. When using a quench curve, the average difference between the three reagent blank values and the corresponding points on the quench curve should be used to adjust the quench curve (up or down) for the current analytical batch.

9.1.3.5 For samples counted in the default calibration geometry, cpm results (as well as blank ID, batch, and QIP result) of the reagent blank count are entered into a spreadsheet (r:\inst\lsc*\CB's_BKGD_WIN2_CKS\rb_C14.xls, where * denotes the instrument used to count the reagent blanks), and compares each blank to historical control limits established from the first 30 data points in the population (+/- 3 sigma). The preparation of background calibration vials used in a quench curve calibration is described in Section 9.1.2.2 above.

9.2 QC SAMPLE PREPARATION

9.2.1 Method Blanks are analyzed at a frequency of 5% (i.e., one per 20 field samples) with a minimum of one per batch. Water and soil blanks consist of 25mL DI water.

9.2.2 LCSs are analyzed at a frequency of 5% (i.e., one per 20 field samples) with a minimum of one per batch. Spike ^{14}C at approximately 500dpm per LCS. Record the exact spike volume on the benchsheet. Spiked water blanks and soil blanks are prepared using 25mL of DI water. Appropriate spiking levels are approximately 10 times the requested minimum detectable concentration.

9.2.3 Matrix spikes are analyzed at the rate of one per batch of 20 or fewer samples. ^{14}C is spiked at approximately 500dpm. Record the exact spike volume on the benchsheet. If elevated ^{14}C activity in the sample is suspected, ensure that the spiking level is at least 4-10 times the estimated sample activity concentration.

9.2.4 Analyze one duplicate sample for every 10 samples or fewer for each matrix.

10. CALCULATIONS

10.1 The sample activity is calculated as described in SOP 708 -- Calculations for Radioanalytical Results.

10.2 The 1σ Total Propagated Uncertainty (TPU) is reported in association with each result. See SOP 708 for details regarding determination of the TPU.

10.2.1 TPU FACTORS. As defined in SOP 708, the following one-sigma preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU).

10.2.2 For water analyses the preparation uncertainty, per SOP 708 is 0.0509. This is based on one homogeneity estimate, one volumetric measurement of the sample volume, one volumetric measurement of the trap solution, and one pipetting of the trap solution aliquot for analysis.

$$0.0509 = \sqrt{0.05^2 + 0.006^2 + 0.006^2 + 0.004^2}$$

10.2.3 For soil analyses the preparation uncertainty, per SOP 708 is 0.0506. This is based on one homogeneity estimate, one gravimetric measurement of the sample mass, one volumetric measurement of the trap solution, and one pipetting of the trap solution aliquot for analysis.

$$0.0506 = \sqrt{0.05^2 + 0.003^2 + 0.006^2 + 0.004^2}$$

10.2.4 In practice, these values are substantially equivalent and the greater of the two, 0.0509, will be used for reporting both matrices.

10.3 The Minimum Detectable Concentration (MDC) and Decision Level (DL) activity are calculated as described in SOP 708.

10.4 The efficiency used for calculation of sample results is calculated as shown in the equation below:

$$\text{DetEff} = \frac{\text{Net Cpm}}{\text{SpkDPM}}$$

NOTE: Multiple standards are prepared and the measured values averaged for use in sample calculations.

For a quench curve calibration, the calculated efficiencies for each individual standard should be tabulated (in a spreadsheet, for example) and the data should be fit to a function that minimizes the difference between the individual data point and the fitted value. In no case should this difference be greater than 10%, except with the approval of the Department Technical Manager.

11. DEVIATIONS FROM METHOD

This procedure is compliant with Eastern Environmental Radiation Facility (EERF) Procedures Manual Method C-01 for water samples. The method has been modified to accommodate small aliquots of solid materials.

12. SAFETY HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents.

12.1.2 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

12.1.3 Cracked glassware should not be used in the Midi apparatus due to the risk of implosion under vacuum.

12.1.4 The spargers and plastic tubing should be rinsed with DI water. Allow to dry before next use.

12.1.5 The digestion tubes should be washed with lab detergent and rinsed with DI water. Allow to dry before next use.

12.1.6 Any chemicals with a TLV of less than 50ppm shall be worked within a laboratory fume hood (e.g., solvents and acids).

12.1.7 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health, Flammability, and Reactivity ratings, and date.

12.2 WASTE DISPOSAL

12.2.1 All empty radionuclide standard solutions are disposed of by rinsing the standard container a minimum of three times. The container must be surveyed prior to release. Please note that all labels and markings must be defaced or removed prior to disposal.

12.2.2 The residual sample in the digestion tube may be rinsed into the waste carboy provided by the Waste Compliance Officer. Rinse with a minimum of tap water in order to reduce the volume of waste produced.

12.2.3 Scintillation cocktails should not be disposed of down the drain but instead placed in a properly labeled carboy.

12.2.4 Vials of sample/cocktail mixture may be accumulated (intact) in a container provided by the Waste Compliance Officer.

13. REFERENCES

13.1 Eastern Environmental Radiation Facility (EERF) Procedures Manual, Method C-01, Carbon-14 in Water.

13.2 USEPA, EPA-R4-73-014, Procedures for Radiochemical Analysis of Nuclear Reactor Aqueous Solutions, Carbon-14, 1973. pp 38-42.

DOCUMENT REVISION HISTORY

6/04/07: Added this DOCUMENT REVISION HISTORY. Added LIMS program specification language. Changed the prep and analysis of the background determination (Section 9.1.3), and revised targeted spiking levels (Sections 9.1.2, 9.2).

8/12/07: Removed activity, TPU, and MDC calculations and referenced SOP 708 -- Calculations for Radioanalytical Results instead. Added Forms.

Paragon Analytics

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 773 REVISION 10

TITLE: **TOTAL DISSOLUTION OF SOLIDS FOR THE RADIOCHEMICAL DETERMINATION OF ACTINIDES AND OTHER NON-VOLATILE RADIONUCLIDES**

FORMS: **709**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 5/1/07

QUALITY ASSURANCE MANAGER _____ DATE 4/26/07

LABORATORY MANAGER _____ DATE 4-30-07

HISTORY: Rev0, 4/14/95; Rev1, PCN #532, 9/28/95; Rev2, PCN #561, 11/14/95; Rev3, 9/08/97; Rev4, 3/24/00; Rev5, 10/19/00; Rev6, 10/24/01; Rev7, 1/03/02; Rev8, 4/07/03; Rev9, 3/15/05; Rev10, 4/27/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the total dissolution of solids for the quantitative radiochemical measurement of actinides and other non-volatile constituents. After dissolution has been completed, the analytes are purified and prepared as described in the appropriate standard operating procedure.

This procedure is also amenable to dissolution of soils, non-soil solids, air filters, and materials containing significant organic content (biota, vegetation, oils, etc.).

2. SUMMARY

Samples are dried and ground per SOP 721 to a fine particle size. All solid samples are reported on a "dry weight" basis unless otherwise requested by client. Filters can be cut into pieces that will fit into muffling containers. **Where appropriate,** organic matter is removed by combustion in a muffle furnace.

Tracers are added and dissolution is accomplished using nitric, hydrochloric, and hydrofluoric acids. When actinides are being determined, a hydroxide co-precipitation is performed to pre-concentrate actinides and remove constituents that do not form insoluble hydroxides. The hydroxide precipitate is then re-dissolved and further purification is performed. Because any solid prepared by SOP 721 is dried prior to sieving, grinding, and dissolution, solid samples are automatically obtained on a dry weight basis.

A reagent blank is prepared with this procedure and used as a method blank in subsequent separations.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP

and to complete all documentation required for review.

3.2 Personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method perform analysis and interpretation of the results. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/ analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Combustible materials may flash-ignite during muffling and lead to uncontrolled sample loss or sample cross contamination. A slow ramped muffling procedure and covering the sample with a watch glass can be used to address this problem.

5. APPARATUS AND MATERIALS

5.1 Pyrex™ glass beakers, 50mL

5.2 muffle furnace

5.3 pipettes, Eppendorf™ or equivalent

5.4 polypropylene beakers, 110mL and 220mL

5.5 centrifuge bottles, 250mL

5.6 steam bath constructed to allow immersion of lower half of 220mL polypropylene beaker into steam

5.7 wash bottles

5.8 top loading balance, 0.01g sensitivity

5.9 centrifuge

5.10 vortex mixer

5.11 volumetric dispensers (Dispensette^{TM} or equivalent) designed for handling concentrated HNO_3 and HCl

5.12 graduated cylinder, plastic, 25mL

5.13 pH indicating paper, wide range (0-14 pH units)

5.14 RadiacWash^{TM}

5.15 liquid cleaning soap

5.16 analytical balance - to calibrate the pipettes

5.17 watch glasses

5.18 transfer pipets, plastic, disposable

5.19 plastic stir rods

5.20 filter paper, ashless

5.21 furnace gloves

5.22 long tongs

5.23 steam bath

6. REAGENTS

Threshold Limit Value (TLV) and other hazard information may also be given here. The absence of this information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding. As stated in Section 11.1.4 of this SOP, any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood.

6.1 TRACERS AND CARRIERS

High purity, standardized solutions traceable to NIST are diluted to approximately 10-40dpm/mL of activity for tracing and spiking solutions. Solutions of the following elements/isotopes may be utilized:

- **Pu-ISO**: ^{242}Pu is the tracer and ^{239}Pu is the spike for the LCS.
- **U-ISO**: ^{232}U is the tracer and ^{238}U is the spike for the LCS.
- **Am-241/Cm-244**: ^{243}Am is the tracer and ^{241}Am and/or ^{244}Cm is the spike for the LCS.
- **Th-ISO**: ^{229}Th is the tracer and ^{230Th} is the spike for the LCS.

- **Other Tests**: Spikes, tracers and carriers are defined in the applicable preparation SOP for the test being performed.

6.2 Nitric acid, HNO_3, concentrated, 16N, reagent grade. TLV = 2ppm (TWA). Irritant, corrosive.

6.3 Hydrofluoric acid, HF, concentrated, 29N, reagent grade. TLV = 3ppm (ceiling). Irritant, burns, bone, teeth, fluorosis.

6.4 Hydrochloric acid, HCl, concentrated, 12N, reagent grade. TLV= 5ppm (ceiling). Irritant, corrosive.

6.5 Boric acid, H_3BO_3, reagent grade.

6.6 Ammonium hydroxide, NH_4OH, concentrated, 15N, reagent grade. TLV = 25ppm for ammonia (TWA). Irritant.

6.7 Ferric chloride carrier, 20mg Fe^{3+}/mL: Dissolve 96g $FeCl_3 \bullet 6H2O$ in one liter of 0.5N HCl.

6.8 Deionized (DI) water, from the laboratory's DI water systems..

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 The minimum sample size required for this procedure is 30 grams. If samples scheduled for this procedure have a high moisture content (they are very wet or are sludge-like materials), more sample (up to 60 grams) may be required to properly perform this procedure. If the analysis procedure requires the generation of sample duplicates or sample matrix spikes, additional sample aliquots will be needed to generate these quality control (QC) samples.

7.2 The sample collection containers should be clean glass or plastic with a screw-cap top. They should be of adequate size to hold the required sample weight for this procedure.

7.3 The samples processed through this procedure do not need to be chilled or chemically preserved during shipment or storage unless otherwise required by project-specific requirements.

7.4 See client specifications and individual analysis procedures for holding time requirements.

8. PROCEDURE

8.1 Samples that require grinding are processed through the grinding steps of SOP 721. According to the analyst's judgment, samples with high organic content may be muffled prior to dissolution. Solid samples with high organic content characteristically are dark in color, are oily, or contain visible organic material

(i.e., vegetation).

8.2 SAMPLE ALIQUOT

8.2.1 Samples that do not require muffling can be aliquoted directly into a 220mL plastic cup. Weigh a 2g up to 10g aliquot (to the nearest 0.01g) of the ground sample into a clean, labeled 220mL plastic cup.

8.2.2 **IMPORTANT**: For samples that require muffling, the Pyrex™ brand glass beaker number (all labware to be used for muffling must have a permanent ID engraved on its surface) is written on the benchsheet in association with the corresponding sample number. For the blank and blank spike, a beaker containing a piece of ashless filter paper will be muffled.

Weigh a 2g up to 10g aliquot (to the nearest 0.01g) of the ground sample into **the corresponding** labeled Pyrex™ beaker. Filters should be cut or folded such that they fit into the bottom of the beaker. Cover the dishes using watch glasses to protect the content from material that could drop into the sample during the muffling.

8.2.3 Consult the Spike/Tracer Data Sheet (R:\forms\mda_list.xls) for information about the volume/activity and standard identification to be used. Add calibrated volumes of tracer and spike solutions to samples, blank and blank spike as per SOP 766 (Alpha Spectroscopy) or other appropriate SOP. For samples that require muffling, proceed to Section 8.2.4 of this SOP. If muffling is not necessary, proceed to Section 8.3.3 of this SOP. **NOTE: In cases where a common digestion of the sample is required for multiple analyses in addition to alpha spectroscopy, skip this Step; the spiking and tracing of the samples are performed after muffling, at Step 8.3.4.**

8.2.4 Place the beaker without the watch glass on a hot plate and take to dryness to prevent splattering in the muffle furnace.

8.2.5 Place the beaker with a watch glass in the muffle furnace and heat at 550- 600°C for at least 4 hours after the furnace reaches full temperature. Highly organic materials (or oil matrices) should be muffled overnight. Filters should be muffled at a setting of 450 ºC for a minimum of 12 hours.

8.3 SAMPLE DISSOLUTION

8.3.1 Where applicable, carefully remove dish from the muffle furnace using thick furnace gloves and long tongs. Allow the samples to cool.

8.3.2 After cooling, wet the sample in the beaker using conc. HNO_3 to

prevent any loss of powdered sample during transfer. Transfer the ignited sample to a 220mL polypropylene beaker using a plastic stir rod and about 25mL of conc. HNO_3. For the blank and blank spike, the corresponding empty beaker will be rinsed with acid just like the samples.

8.3.3 For samples that were not muffled, carefully add 25mL of conc. HNO_3 to the sample in the plastic cup and proceed to Section 8.3.5 of this SOP.

8.3.4 If the spiking and tracing of the samples was done prior to muffling, skip this Step, otherwise, consult the Spike/Tracer Data Sheet (R:\forms\mda_list.xls) for information about the volume/activity and standard identification to be used. Add calibrated volumes of tracer and spike solutions to samples, blank and blank spike as per SOP 766 (Alpha Spectroscopy) or other appropriate SOP.

8.3.5 Add 25mL of conc. HCl to each beaker using a volumetric dispenser. Using a **plastic** graduated cylinder, carefully add 25mL of conc. HF to each beaker. **Do not bring HF into contact with any type of laboratory equipment made of glass because HF will dissolve glass.**

8.3.6 Place a 110mL polypropylene beaker as a cover onto the 220mL beaker containing the sample.

8.3.7 Allow the samples to pre-digest about 1 hour at room temperature in a fume hood to allow any vigorous reaction to subside.

8.3.8 Place the beakers on the steam bath and heat for four (4) hours, with the hot plates set at at least 5, with the covers in place. Rinse (with DI water) and remove the cover. Allow the sample to go to dryness. After sample has dried, there should be a visible white residue on the bottom of the beaker. If significant amounts of non-white solids are observed in the container, an additional 25mL of HF, 25mL of HCl, and 25mL of HNO_3 are added and this Step (8.3.8) is repeated.

8.3.9 If actinides are being performed by alpha spectroscopy, continue with Section 8.3.10. If other tests such as gamma or non-routine tests are to be performed, the solution is taken to dryness, and the appropriate SOP must be consulted before continuing with the analysis. A Senior analyst may be consulted regarding conversion from the $HNO_3 \mid HCl \mid HF$ system to other appropriate solutions prior to continuing.

8.3.10 Remove from the steam bath and add 10mL conc. HNO_3, 100-150mL DI water (to solubilize the solids) and 2g H_3BO_3. Mix well by swirling contents of beaker. Return beakers to steam bath for approximately 15 minutes to warm solution and enhance dissolution of salts.

8.3.11 Transfer sample to a 250mL labeled centrifuge bottle using deionized water.

8.3.12 Using a repeater pipet, add 2mL of ferric chloride carrier. If the sample size is more than 2.0g, the addition of iron carrier may be skipped as the sample may have enough iron content to make a sufficient amount of precipitate.

8.3.13 Add 20-25mL of conc. NH_4OH to form an $Fe(OH)_3$ precipitate. Make sure that the precipitate forms and that the solution is basic. If there are any doubts, check the solution with pH paper. If no precipitate forms, keep adding NH_4OH dropwise with a transfer pipet until a precipitate does form.

8.3.14 Centrifuge the sample for 15 minutes at approximately 3500rpm. Discard the supernatant (avoid losing any precipitate). Further separations are now performed following the appropriate separation SOP.

9. QUALITY CONTROL

9.1 One reagent blank is prepared per batch of 20 samples or at a 5% frequency.

9.2 One sample duplicate is prepared per batch of 10 samples or at a 10% frequency. If there is insufficient sample for a duplicate, a blank spike will be prepared.

9.3 One laboratory control sample (spiked blank) is prepared for each batch of 20 samples (5% frequency) with a range of 10 to 30 dpm of analyte.

9.4 The same blank and duplicate may serve for any batch in which multiple analytes are being determined.

NOTE: Project-specific requirements may supersede default QC requirements.

10. DEVIATIONS FROM METHOD

This is a proprietary procedure developed by Paragon Analytics. Therefore, there are no deviations from promulgated methods for this procedure.

11. SAFETY HAZARDS AND WASTE

11.1 SAFETY AND HAZARDS

11.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

11.1.2 Safety glasses and lab coats must be worn in the radiochemistry prep. labs at all times.

11.1.3 Gloves, safety glasses and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

11.1.4 Any chemicals with a TLV of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

11.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with the compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.6 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation and personnel safety features. **Never inhale or allow skin or clothing to be exposed to HF fumes.**

11.1.7 Care should be taken when diluting acids. **Always add acids to water, NOT water to acid**.

11.2 WASTE DISPOSAL

11.2.1 Wastes that are "corrosive only," such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the Paragon wastewater treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

11.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Disposal Manager for disposal.

11.2.3 All acid wastes not containing HF that are generated in ion exchange operations are disposed of into the wastewater tank system (i.e., down the drain), unless instructed otherwise due to identified or suspected hazards.

12. REFERENCES

U.S.A.C. Reg. Guide 4.5 "Measurement of Radionuclides in the Environment - Radiochemical Analysis of Plutonium in Soil."

DOCUMENT REVISION HISTORY

4/27/07: Revision 10. Added LIMS program specification language (3.3). Added ashless filter paper, furnace gloves, long tongs, and steam bath to the equipment list (5.20 – 5.23). Added DI water to REAGENTS (6.8). Added DOCUMENT REVISION HISTORY. Attached form.

Paragon Analytics

_____ A **WORKSHEET FOR IN-HOUSE OR RUSH SAMPLES / ACTINIDES**

Matrix _____ **Prep Analyst** _____ **Prep Date** _____ **Analyte** 1) _____ 2) _____ 3) _____ 4) _____ **Analytical Batch** _____

Pretreatment? (Y / N) **Batch** _____ **Count Date / Time** _____ **Superseded** _____

Paragon WO No.	Sample Wt. (g / L)	Sample Aliq. (g / L)	Aliquot Basis (Dry / AR)	Micro-Precip Init / Date	Tracer / Spike Information	Remarks	Det. No.	Filename	POS Ckd By

Balance No. _____ **Spiked By** _____ **Date** _____ **Spike Witness** _____ **Date** _____ **QASS?** (Y / N) **No.** _____

	Isotope	*No*	*Act / mL*	*Vol*	*Pipet No.*	*Total Act (dpm)*	*Decay Corrected*		*Relinquished by / Date*	*Received by / Date*
Tracer 1								1		
Tracer 2										
Tracer 3								2		
Tracer 4										
Spike 1								3		
Spike 2										
Spike 3								4		
Spike 4										

Electronic Benchsheet No. (if / when generated) _____ Reviewed by / Date _____ Page 1 of 2 Form 709r7.doc (4/22/04)

Paragon Analytics

_____ B **WORKSHEET FOR IN-HOUSE OR RUSH SAMPLES / ACTINIDES**

Initials _____ **Date** _____ **Method (SOP / Rev)** _____ **Matrix** _____

COMMENTS

Reviewed by / Date _____ Page 2 of 2 Form 709r7.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 774 REVISION 1

TITLE: **$^{59/63}$NI IN WATER AND SOIL SAMPLES USING EICHROM NICKEL RESIN**

FORMS: **631, 311** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER Renee Kellogg DATE 7/21/08

QUALITY ASSURANCE MANAGER Deb Schatz DATE 7/20/08

LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: DRAFT 1/12/04, NEW, Rev0, 2/27/06; Rev1, 7/18/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references, Eichrom™ Method NIW01, Rev. 1.1, describes a procedure to determine ^{63}Ni in aqueous and solid matrices. It can also be used to analyze samples for ^{59}Ni. The method utilizes Eichrom™ Ni resin, which complexes the Ni in a sample with dimethylglyoxime (DMG). The DMG complex can be stripped from the resin and used to measure the Ni activity in the samples by liquid scintillation counting (LSC).

2. SUMMARY

A portion of the sample is removed for inductively coupled plasma (ICP) atomic emission spectrometry determination of the pre-separation concentration of nickel in the sample. An aliquot of the sample is digested in acid and taken to dryness. The sample is re-dissolved and run through a Ni resin column. The Ni-DMG complex is eluted from the column, taken to dryness, and re-dissolved prior to aliquotting a portion for counting by liquid scintillation.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of supervisory/ training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Cobalt and other metals that form complexes with DMG may be interferences to this method, as they may take up sites within the resin and not allow Ni-DMG complexes to form. ICP results should be closely monitored for interfering metals. Reduced aliquot sizes may be necessary in some cases to remediate poor recoveries.

4.2 The pH of the solution loaded onto the resin column is very important. Samples that have not been adjusted to a high enough pH (9-11) will run through the column without forming the Ni-DMG complex. If this should begin to occur, the pH can be adjusted while the sample is on the column to prevent gross nickel losses. Any Ni losses will be measured by ICP.

4.3 The scintillation vial is an optical surface. Any markings or material on the outside of the scintillation vial will interfere with the detection of scintillation. These should be removed prior to analysis by wiping the vial with a lint-free lab wipe and alcohol. **All labeling must be done on the cap of the vial.**

4.4 The quench indicating parameter (QIP) (usually H-number) should be monitored and variations in quench that could correspond to greater than 10% relative bias in the efficiency, should be addressed by using standard additions to determine a sample-specific efficiency.

4.1.1 The presence of visible coloration in the final sample will act as an ‘inner filter’. This effect, known as ‘color quenching’ is an interference to the detection of the scintillation.

4.1.2 The presence of chemical contaminants in the sample may inhibit scintillation. This effect is known as ‘chemical quenching’.

4.1.3 The presence of particulate contamination in the final sample may interfere with the detection of the scintillation. This effect is known as ‘physical quenching’.

5. APPARATUS AND MATERIALS

5.1 analytical balance, capable of reading to 0.0001g

5.2 graduated cylinder, 500mL

5.3 plastic cups, 150 and 250mL

5.4 test tubes, disposable, 15mL

5.5 transfer pipettes, plastic, ~3mL

5.6 Pasteur pipettes, glass

5.7 adjustable mechanical pipette, disposable pipette tips

5.8 steam bath

5.9 Parafilm™

5.10 beakers, glass, 400mL

5.11 centrifuge

5.12 centrifuge tubes with caps, 50mL

5.13 pH paper

5.14 repeater pipettors

5.15 scintillation vials, low-potassium borosilicate glass, 20mL

5.16 liquid scintillation counting racks

5.17 sand, clean, laboratory

5.18 Kimwipes™

5.19 Bio-Rad™ columns
To prepare for use: Add Ni resin to the column as a slurry with deionized water to the 1.8mL mark. Place a small layer of clean laboratory sand on top to hold the resin in place. Store in a capped 250mL plastic cup with a small amount of DI water to prevent drying.

6. REAGENTS

NOTE: TLV and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 NIST-traceable ^{59}Ni or ^{63}Ni spiking solution (source independent from that used for calibration)

6.2 Deionized (DI) water

6.3 Nickel + cobalt carrier, standardized: Dissolve 5.0g $Ni(NO_3)_2 \cdot 6H_2O$ and 5.0g $Co(NO_3)_2 \cdot 6H_2O$ in deionized (DI) water and dilute to 1000mL.

TLV for Ni = 0.04ppm (TWA) and the TLV for Co = 0.008ppm (TWA).

Standardization of Ni + Co carrier by ICP analysis: Prepare in triplicate a 1000-fold dilution of the Ni + Co carrier using the ICP solution described in Section 6.13 below. Submit to the metals lab for analysis. Average the results and record in the Reagent Prep Logbook.

6.4 Ammonium citrate, 1M: Dissolve 226.19g ammonium citrate in approximately 800mL of water and dilute to 1L. Note: The pH of this reagent may be adjusted to 9-11 using concentrated NH_4OH after preparation or just prior to use.

6.5 Ammonium citrate, 0.2M: Dissolve 45.24g ammonium citrate in approximately 800mL of water and dilute to 1L. Note: The pH of this reagent may be adjusted to 9-11 using concentrated NH_4OH after preparation or just prior to use.

6.6 Ammonium Hydroxide, 15N NH_4OH (conc.)
TLV = 25ppm (TWA for NH_3)

6.7 Hydrochloric acid, 12N: HCl (conc.)
TLV = 5ppm (ceiling)

6.8 Hydrochloric acid, 1N: Add 8mL of concentrated HCl to approximately 500mL of water and dilute to 1L
TLV = see Section 6.7

6.9 Nitric acid, concentrated (16N), ACS grade
TLV = 2ppm (TWA) Irritant, corrosive

6.10 Nitric acid, 8N: Cautiously add 500mL of reagent grade concentrated HNO_3 to approximately 400mL of DI water and dilute to 1.0L
TLV = see Section 6.9

6.11 Nitric Acid, 3N: Add 191mL of concentrated HNO_3 to approximately 500mL of water and dilute to 1L
TLV = see Section 6.9

6.12 Liquid scintillation cocktail, Ultima Gold LLT™ or equivalent

6.13 ICP diluting solution: Add 10mL 16N HNO_3 and 50mL 12N HCl to approximately 500mL of DI water. Then bring to 1L with DI water
TLV = See Sections 6.7 and 6.9

6.14 Methanol, reagent grade

TLV = 200ppm (TWA)

6.15 Eichrom™ Ni resin, 100-150µm

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Liquids: A sample should be collected in a manner that will provide the most representative sample. Collect a 1liter sample in a plastic container, from a free - lowing source when possible.

7.2 Although the client is responsible for conducting the sampling process, it is emphasized that water samples be collected in a manner that addresses the considerations discussed in EPA 900.0 Section Three or Chapter Nine of EPA SW-846, as appropriate. Also, it is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15mL 1N HNO_3 per liter of sample is usually sufficient). If not preserved upon collection, then the sample should be preserved within 5 days. If preservation is delayed, hold samples for a minimum of 24 hours after preservation to solubilize any possible activity on the container.

7.3 For a dissolved sample analysis, use a 0.45-micron membrane filter to remove the solids from the sample. Then acidify the sample with nitric acid to a pH < 2.0.

7.4 The container should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 AQUEOUS SAMPLE PREPARATION

8.1.1 Verify and record the pH of the sample on a liquid sample condition form (Form 631) according to SOP 733.

8.1.2 It may be necessary to filter the samples through a 0.45µm or other filter prior to analysis if excessive solids are present in the sample. Consult with the Radiochemistry Supervisor or Project Manager prior to analysis of heavily-sedimented samples.

8.1.3 Using a graduated cylinder, aliquot the sample into a labeled 400mL beaker. A sample aliquot of 300mL is typical for this method, but may need to be reduced due to matrix interference or volume limitations. All samples should be brought to a final volume of 300mL

8.1.4 Prepare batch QC samples per Section 10.

8.1.5 Using a calibrated pipette (SOP 321), add Ni spiking solution per Section 10.2.2 to LCS and any matrix spikes; add 1mL Ni + Co carrier

solution to all samples. Record all pertinent spiking information on the benchsheet (expiration dates, pipettes, solution IDs).

NOTE: A "reference carrier" should also be prepared by adding 1mL Ni + Co carrier to 300mL of DI water. Mix thoroughly, remove 1mL of solution and dilute to 10mL as stated in Step 8.1.7 for samples. Submit with samples for ICP analysis to provide a reference concentration for the yield calculations.

8.1.6 Place the sample on a stirring hotplate, add a stir bar, and stir at a moderate speed to thoroughly mix the sample.

8.1.7 How to take initial ICP aliquot: Use a calibrated pipette (SOP 321) to remove 1mL of sample and place into a clean test tube labeled with the sample ID and "initial ICP". Dilute to 10mL with ICP diluting solution. Cover with ParafilmTM and invert tube several times to mix thoroughly. Set aside until final ICP aliquot has been taken.

8.1.8 Remove the stir bar from the sample, rinsing with DI water.

8.1.9 Evaporate the sample to dryness. Be sure the sample does not boil or bake while on the hotplate.

8.1.10 Add 5mL 12N HCl to convert nitrate salts to chloride salts.

8.1.11 Evaporate the samples to dryness - **do not bake!**

8.1.12 Dissolve the residue in 5mL 1N HCl. Add an additional 5mL 1N HCl, if necessary, to dissolve all of the residue.

8.1.13 Proceed to Section 8.3 of this SOP.

8.2 SOLID SAMPLE PREPARATION

8.2.1 Verify and record the sample condition on a solids sample condition form (Form 631).

8.2.2 Solid samples used in this method should be dried and ground per SOP 721 prior to analysis. If the samples are not conducive to grinding, consult with the Radiochemistry Supervisor prior to analysis of samples.

8.2.3 Weigh 0.5g of solid into a labeled centrifuge tube. Record this initial weight on the benchsheet.

8.2.4 Prepare batch QC samples per Section 10.

8.2.5 Using a calibrated pipette (SOP 321), add Ni spiking solution per Section 10.2.2 to the LCS and any matrix spikes. Add 1mL Ni + Co carrier solution to all samples. Record all pertinent spiking information on the benchsheet (expiration dates, pipettes, solution IDs).

NOTE: A "reference carrier" should also be prepared by adding 1mL Ni + Co carrier to a centrifuge tube and bringing to a final 50mL volume with 10mL 8N HNO_3 and 39mL DI water. Mix thoroughly, remove 1mL of solution and dilute to 10mL as stated in Step 8.2.13 for samples. Submit with samples for ICP analysis to provide a reference concentration for the yield calculations.

8.2.6 Carefully add 10mL 8N HNO3 to each tube. **Watch out for vigorous reaction.**

8.2.7 Place the samples on the steam bath and digest for an hour with the caps on loosely.

8.2.8 Remove the samples from the steam bath and allow to cool. Vortex the samples to mix well and centrifuge them for 10 minutes.

8.2.9 Decant the leachate from the tubes into new, labeled centrifuge tubes.

8.2.10 Rinse the soil left in the original tube with 10mL DI water, mix and centrifuge, and decant the rinsate into the new tube from Step 8.2.9.

8.2.11 Bring all tubes from Step 8.2.10 up to a 50mL final volume with DI water.

8.2.12 The tubes containing the leached soil may be dried in a fume hood and disposed of in the proper SAA waste container, depending on prescreen radioactivity information.

8.2.13 How to take initial ICP aliquot: Use a calibrated pipette (SOP 321) to remove 1mL of sample and place into a clean test tube labeled with the sample ID and "initial ICP". Dilute to 10mL with ICP diluting solution. Cover with Parafilm™ and invert tube several times to mix thoroughly. Set aside until final ICP aliquot has been taken.

8.2.14 Transfer the samples to clean, labeled 250mL plastic cups, rinsing the centrifuge tubes with DI water.

8.2.15 Take the samples to dryness on the steambath - **do not bake!**

8.2.16 Add 5mL 12N HCl while the samples are still on the steambath to convert nitrate salts to chloride salts.

8.2.17 Evaporate the samples to dryness on the steambath- do not bake!

8.2.18 Dissolve the residue in 5mL 1N HCl. Add an additional 5mL 1N HCl, if necessary, to dissolve all of the residue.

8.2.19 Proceed to Section 8.3 of this SOP.

8.3 SEPARATION OF NI USING EICHROM NICKEL RESIN

NOTE: Wherever the method indicates an ammonium citrate solution, regardless of concentration, an ammonium citrate solution that has already been adjusted to pH 9-11 should be used. Be sure to check the pH of the solution just prior to use.

8.3.1 Add 1mL 1M ammonium citrate. Add 15N NH4OH dropwise until the pH of the sample is between 9-11. This usually takes about 10-15 drops. Check the pH of the sample using a glass Pasteur pipette to remove as little of the sample as possible.

8.3.2 Place a prepared, labeled Bio-Rad™ column in a rack for each sample. See Section 5.20 for column preparation. Place a cup or a waste tray under each column.

8.3.3 Condition each column with 5mL 0.2M ammonium citrate.

8.3.4 Load the sample onto the appropriate column using a transfer pipette. A red band will appear on the column as the Ni-DMG complex forms. The sample should be loaded as soon as possible after adjusting the pH in Step 8.3.1. If the sample is allowed to sit for too long, the sample may buffer to a lower pH.

NOTE: The pH of the solution on the column is crucial to the success of this method. The pH of the sample should be between 9-11 prior to loading on the column. If the pH is too low, the sample will drain through the column. If this occurs, the drainage may be stopped by adding the first 0.2M ammonium citrate rinse from Step 8.3.5 to the column. Since recovery is monitored by ICP, the amount of Ni lost will be accounted for. Document the event on a QASS (SOP 928).

8.3.5 Rinse the cup with 5mL 0.2M ammonium citrate. Add the rinse to the column.

8.3.6 Repeat Step 8.3.5 two more times.

8.3.7 Rinse the column with 5mL 0.2M ammonium citrate.

8.3.8 The eluate from Steps 8.3.3-8.3.7 has been determined not to be hazardous other than corrosivity. It may be discharged down the laboratory sink with plenty of tap water.

8.3.9 Strip Ni from the column using 10mL 3N HNO_3 (added in 5mL increments) into labeled 250mL plastic cups. The sample has been completely dissolved when the red band disappears entirely. If necessary, add additional 3N HNO_3 in 5mL increments until the red band is completely eluted from the column

8.3.10 The resin is inactive at this point and the column may be dried and emptied into the resin waste container.

8.3.11 Dry the samples on a steambath. Be sure not to bake the samples, as a hard, black residue may result.

8.3.12 Re-dissolve the samples with 0.25mL 16N HNO_3 and 5.75mL DI water.

NOTE: Since there is no pipette that will accurately deliver 5.75mL, this step currently takes three pipettes to perform. Calibrate three pipettes (SOP 321) in the following volumes: 0.25, 5.0, and 0.75mL. The use of three pipettes is reflected in the TPU calculation.

8.3.13 How to take final ICP aliquot: Swirl the sample to mix thoroughly. Using a calibrated pipette (SOP 321), aliquot 0.1mL of sample into a clean test tube labeled with the sample ID and "final ICP". Dilute with 9.9 or 10mL of ICP diluting solution, cover with Parafilm™, and invert several times to mix completely. Be sure to note the final volume of the dilution. Submit the initial and final test tubes to the metals lab with proper bench sheets for analysis.

8.3.14 Swirl the sample to mix thoroughly and pipette a 5.0mL aliquot into a labeled scintillation vial (label the cap only) using a calibrated pipette (SOP 321).

8.3.15 The remainder of sample after performing Step 8.3.14 must be disposed of in the appropriate SAA container.

8.3.16 Add 15mL Ultima Gold LLT™ scintillation cocktail to each vial, close tightly, and shake to mix thoroughly.

8.3.17 Clean the outside of the scintillation vial using a lint-free lab wipe and methanol to remove dust, smudges, and fingerprints; place the vials in liquid scintillation racks.

8.3.18 Deliver the samples to the counting lab with the necessary documents. Place the racks in the liquid scintillation counter and allow at least 3 hours for samples to "dark-adapt" prior to counting. The counting lab will analyze and ultimately dispose of the scintillation vials in the manner described in SOP 704.

9. CALCULATIONS

9.1 CORRECTED SAMPLE VOLUME CALCULATION (V_c)

The sample aliquot volume to be used in calculating the final result must be reduced slightly because aliquots were removed from the sample for chemical recovery determination. Also, not all of the final purified solution is pipetted into the scintillation vial for counting.

$$V_c = V_i\left(\frac{V_1 - ICP_i}{V_1}\right)\left(\frac{V_2 - ICP_f}{V_2}\right)\left(\frac{V_a}{V_2 - ICP_f}\right)$$

where:

V_i = Initial sample aliquot (typically 300mL for aqueous samples, 0.5g for solid samples)

V_1 = Sample dilution volume for initial ICP (typically 300mL for aqueous samples, 50mL for solid samples)

ICP_i = Volume removed for initial ICP (typically 1mL)

V_2 = Sample dilution volume for final ICP (typically 6mL)

ICP_f = Volume removed for final ICP (typically 0.1mL)

V_a = Volume submitted for LSC analysis (typically 5mL)

9.2 CHEMICAL RECOVERY DETERMINATION (Y)

Calculate the percent nickel recovered as follows:

$$m_i = (V_1)(C_i)(DF_1)\left(\frac{V_1 - ICP_i}{V_1}\right)$$

$$m_f = (V_2)(C_f)(DF_2)$$

where:

m_i = Mass of initial Ni present in sample (μg)
C_i = Concentration of Ni in initial ICP aliquot ($^{\mu g}/_{mL}$)
DF_1 = Dilution factor (due to dilution made in Steps 8.1.7 or 8.2.13, typically 10)
m_f = Mass of final Ni present in sample (μg)
C_f = Concentration of Ni in final ICP aliquot ($^{\mu g}/_{mL}$)
DF_2 = Dilution factor (due to dilution made in Step 8.3.13, typically 100 or 101)

NOTE: The mass of Ni present in the reference carrier (m_{RC}) is calculated in the same manner as that of m_i. Volumes and dilution factors are typically the same for samples and the reference carrier. Be sure to note differences on the benchsheet, if any. If $m_{RC} > m_i$, m_{RC} is substituted for m_i in the denominator of the yield calculation.

$$Y = \frac{m_f}{m_i} \times 100\%$$

10. QUALITY CONTROL

10.1 REPIPETTOR CALIBRATION

The re-pipette dispenser is checked monthly, before use, by dispensing a 10mL aliquot of scintillation cocktail into a 10mL graduated cylinder. The volume should be 10mL +/- 0.1mL; if not, adjust the dispenser and re-check. Record the calibration check in the pipette calibration logbook (Form 311).

10.2 EFFICIENCY CALIBRATION

10.2.1 **A one-point calibration source is conducted as follows:** Prepare six blank samples (three for spikes and three for blanks) as described in Sections 8.1 and 8.3, without spiking samples (no ICP recovery is necessary for these). Spike three empty LSC vials with a NIST traceable Ni standard. The spiking level should be 6-10 times the standard MDC. Dry down the vials slowly on a hotplate. Using a calibrated pipette (SOP 321), add 5mL of the prepared blank solution to each vial. Add 15mL UG LLTTM scintillation cocktail to bring the vials to a standard geometry. **The average efficiency is calculated as described below.**

A one-point efficiency is highly accurate and will be used for the calculation of all results showing QIP results corresponding to the average observed for the calibration standard (within +/- 10% relative efficiency or lacking this calibrated range, +/- 15 of mean H-numbers). Any sample falling outside this range will be calibrated by sample specific addition of a minimum known volume (<200μL) of NIST traceable Ni spiking solution. The efficiency from sample specific standard additions is calculated as defined in Section 9.3.

10.2.2 **Background calibration (reagent blank):** An aliquot of 0.67N HNO_3 equivalent to the calibration geometry is transferred to a scintillation vial independent of the preparation process and cocktail added such that the calibration geometry is reproduced. One calibration blank is submitted for each preparation batch and counted for a time period equal to or longer than the longest sample count. For samples counted in the default calibration geometry (5mL water + 15mL cocktail), cpm results (as well as blank ID, batch, and QIP result) of the calibration blank count are entered into a spreadsheet which tracks the running mean of the last seven calibration blanks, and compares each blank to historical control limits established from the first 20 data points in the population (+/- 3 sigma). The current running mean of the calibration blank cpm is used as the background in the calculation of associated results for the associated prep batch.

10.3 BATCH QC PREPARATION

Acceptance criteria for QC samples may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.3.1 A blank, prepared in 300mL of DI water for aqueous samples, and an empty centrifuge tube for solid samples, must be analyzed with each batch of 20 or fewer field samples (i.e., at a five percent frequency).

10.3.2 One blank spike (LCS), prepared in 300mL of DI water for aqueous samples, and an empty centrifuge tube for solid samples, must be analyzed with each batch of 20 or fewer field samples (i.e., at a 5 percent frequency). The spiking level for LCSs should be at least 4-10 times the requested MDA, or 50-100 pCi, whichever is larger.

10.3.3 Duplicate sample analyses will be performed at a minimum frequency of ten percent. If there is insufficient sample volume for this frequency of duplicates, LCS duplicates may serve as a measure of batch reproducibility.

11. DEVIATIONS FROM METHOD

11.1 A procedure for chemical recovery determination by ICP measurement has been added to the method.

11.2 A procedure for the digestion and subsequent analysis of solid samples using Ni resin has been added to the method.

11.3 The Eichrom^{TM} Ni resin method states that the critical pH for loading samples onto the column is 8-9. It has been determined experimentally that this range is not high enough. The critical pH has been changed to 9-11.

12. SAFETY, HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Safety glasses, lab coats and gloves should be worn in the laboratory at all times.

12.1.2 Use care when handling mineral acids (e.g. HNO_3, H_2SO_4). Work only in a fume hood with adequate ventilation and wear appropriate eye, face, and body protection.

12.2 WASTE DISPOSAL

12.2.1 A SAA container is available for disposal of sample remainders after the aliquot has been removed for analysis.

12.2.2 Other process waste, as indicated in Section 8, may be discarded into the laboratory wastewater treatment facility.

13. REFERENCES

13.1 Eichrom^{TM} Technologies, Inc., Analytical Procedures, NIW01 Rev. 1.1, $^{59/63}$Nickel in Water, February 13, 2002.

13.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

9/27/07: Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Section 7.1.

7/18/08. Removed activity, MDC, TPU calculations, referenced SOP 708 instead. Added Forms.

Paragon Analytics

PIPETTE TOLERANCE GUIDE

Nominal Dispensed Volume (mL)	Associated Weight Tolerance (g)
0.025	0.0248 - 0.0252
0.050	0.0495 - 0.0505
0.075	0.0742 - 0.0758
0.100	0.0990 - 0.1010
0.200	0.1980 - 0.2020
0.250	0.2475 - 0.2525
0.300	0.2970 - 0.3030
0.400	0.3960 - 0.4040
0.500	0.4950 - 0.5050
0.600	0.5940 - 0.6060
0.700	0.6930 - 0.7070
0.750	0.7425 - 0.7575
0.800	0.7920 - 0.8080
0.900	0.8910 - 0.9090
1.000	0.9900 - 1.0100
1.250	1.2375 - 1.2625
1.500	1.4850 - 1.5150
1.750	1.7325 - 1.7675
2.000	1.9800 - 2.0200
2.250	2.2275 - 2.2725
2.500	2.4750 - 2.5250
2.750	2.7225 - 2.7775
3.000	2.9700 - 3.0300
3.250	3.2175 - 3.2825
3.500	3.4650 - 3.5350
3.750	3.7125 - 3.7875
4.000	3.9600 - 4.0400
4.250	4.2075 - 4.2925
4.500	4.4550 - 4.5450
4.750	4.7025 - 4.7975
5.000	4.9500 - 5.0500
6.000	5.9400 - 6.0600
6.500	6.4350 - 6.5650
8.000	7.9200 - 8.0800
10.000	9.9000 - 10.1000

FORM 311r6.frm (9/10/2002)

Paragon Analytics

PIPETTE CALIBRATION VERIFICATION LOG

Balance ID_____

Date	Analyst	Pipet ID Number	Nominal Volume (mL)	Observed Wt. (g)	Pipet Setting	Comment

PIPETTE TOLERANCE: ±1.0 % (regardless of volume dispensed)

Reviewed by _____ Date: _____

FORM 311r6.frm (9/10/2002)

Paragon Analytics

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 776 REVISION 11

TITLE: PREPARATION OF WATER SAMPLES FOR ACTINIDES

FORMS: 631, 719 ~~(use current iteration)~~

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/7/07

LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, PCN #504, 7/10/95; Rev1, PCN #533, 9/28/95; Rev2, 9/9/97; Rev3, 4/30/98; Rev4, 3/24/00; Rev5, 10/19/00; Rev6, 10/24/01; Rev7, 4/29/02; Rev8, 4/4/03; Rev9, 1/31/05; Rev10, 9/8/06; Rev11, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes procedures for preparation of environmental and drinking waters for analysis of actinides. The SOP is based on EPA Method 908.0 for the preparation of waters for the separation of uranium. This SOP addresses only the initial concentration steps and is applicable to uranium, plutonium, thorium, americium, and curium.

2. SUMMARY

The water sample is made acidic by adding HCl and the sample is boiled to eliminate carbonate and bicarbonate ions. The actinides are co-precipitated with ferric hydroxide and separated from the sample. Once the hydroxide precipitate is centrifuged and the supernatant decanted as waste, further steps are performed per the appropriate actinide separation and purification SOPs 765, 777, 778 or 782. Please note that procedures for tracing and spiking samples are found in SOP 766.

3. RESPONSIBILITIES

3.1 It is the responsibility of the laboratory staff to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, performance of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard

criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 The presence of significant quantities of suspended solids is a physical interference. Samples containing perceptible quantities of suspended solids are filtered prior to initiation of preparation and analysis. If the sample needs to be analyzed including sediments, a modified procedure should be followed. This modified procedure will involve a soil digestion procedure to accommodate the sediment portion of the liquid.

4.2 The presence of significant quantities of carbonate (or bicarbonate) may complex uranium and interfere with the chemical exchange and co-precipitation steps. The routine addition of acid to samples followed by boiling should purge carbonates from the sample and address the interference.

5. APPARATUS AND MATERIALS

5.1 Pyrex™ beakers, 400mL and 1500mL - 2000mL or other appropriate size

5.2 Watch glasses

5.3 Stirring hot plates

5.4 Graduated cylinder, 1.0L

5.5 Stir bars

5.6 Centrifuge bottles, 250mL

5.7 Wash bottles

5.8 Repeator Eppendorf™ pipet or equivalent and disposable pipet tips

5.9 pH paper, acidic

5.10 Muffle furnace

6. REAGENTS

NOTE: Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

6.1 Deionized (DI) water, obtained from the laboratory's deionized water system.

6.2 Nitric Acid (HNO_3), conc., reagent grade.

6.3 Ammonium hydroxide (NH_4OH), 15N, (conc.). TLV = 25ppm (for NH_3)

6.4 Ferric chloride carrier, 20mg Fe^{+3}/mL HCl. Made in-house by dissolving 96g $FeCl_3 \bullet 6H_2O$ per 1000mL of 0.5N

6.5 Hydrochloric acid (HCl), 12N, (conc.), specific gravity 1.19, 37.2%, reagent grade. TLV = 5ppm (ceiling)

6.6 Actinides Tracer and Spike Solutions. High purity, NIST-traceable or equivalent, approximately 10-30dpm/mL activity (unless otherwise specified). A second source for tracer and/or spiking solutions should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification). Tracer and spiking nuclide defaults are as follows:

6.6.1 For Pu-239/240, Pu-238 Tracer = Pu-242, Spike = Pu-239

6.6.2 For U-238, U-235/236, U-233/234, Tracer = U232, Spike = Nat-U

6.6.3 For Am-241, Tracer = Am-243 or Cm-244, Spike = Am-241

6.6.4 For Th-232, Th-230, Th-228, Tracer = Th-229 Spike = Th-230

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to adjust the pH of the sample to less than 2. Addition of 5mL conc. HNO_3 per liter of sample is usually sufficient. If samples are to be collected without preservation, they should be brought to the laboratory within 5 days of collection and then preserved and held in the original container for a minimum of 24hrs before analysis or transfer of the sample from the original container (SOP 733). The container should preferably be plastic rather than glass. This prevents loss due to breakage during transport and handling and minimizes any possible losses due to analyte plate out on container walls.

8. PROCEDURE

8.1 DISSOLVED ANALYSIS

8.1.1 Before starting the procedure, check the pH of the sample. If the sample is unpreserved, add 5mL concentrated HNO_3 or enough to make the sample pH<2.

If the sample was not preserved, hold sample for 24 hours before aliquotting (refer to SOP 733 for sample preservation procedure).

If significant solids are present, filter the sample through a fluted qualitative filter paper (refer to SOP 721).

8.1.2 Aliquot 1.0L of sample (or appropriate volume adjusted to reach MDA or account for sample activity) into a Pyrex™ beaker. Record the volume of each sample on the benchsheet.

8.1.3 Consult the benchsheet for information about the volume, activity and standard identification to be used for tracing and spiking. Add calibrated volumes of tracer and spike solutions to the samples, blank and blank spike per SOP 766.

NOTE: It is important protocol to always add QC spikes *before* any chemical treatments applied during sample processing.

8.1.4 Add 5mL 12N HCl.

8.1.5 Using a repeater pipet (verify pipet per SOP 321), add 2mL of ferric chloride carrier.

8.1.6 Place a stir bar in each beaker, cover with a watch glass and set each sample on a hotplate. Stir and heat the water sample to boiling. When samples begin to boil, turn heat down to just maintain boiling temperature. Boil for 30 minutes.

8.1.7 After boiling sample for 30 minutes, turn hotplate heat setting to off and allow samples to stir and cool for 15-20 minutes.

8.1.8 After sample has sufficiently cooled, slowly add concentrated NH_4OH (carbonate free) to the sample. Add NH_4OH until the $Fe(OH)_3$ precipitate forms and turbidity persists while stirring continues. Then add an additional 10mL of NH_4OH. Turn the stir mechanism off and remove stir bar. Allow precipitate to settle to the bottom of the beaker for 15-20 minutes.

8.1.9 After the precipitate has settled, decant the aqueous portion away from the precipitate. Reduce the volume to approximately 200mL or less with **minimal** loss of precipitate. If this cannot be accomplished without significant loss of precipitate, the option is to perform multiple centrifugations to separate the supernatant from the precipitate. The aqueous portion of the sample can be discharged to Paragon's wastewater system (i.e., disposed down the drain in the fume hood with

large amounts of water).

8.1.10 Transfer the remaining solution containing the precipitate to a labeled 250mL centrifuge bottle.

8.1.11 Rinse the sample beaker with a **minimum amount of deionized** water and add the rinse to the centrifuge bottle.

8.1.12 Centrifuge the samples at approximately 3500rpm for 15 minutes. Discard the supernatant down the drain with large amounts of cold water unless otherwise specified due to hazardous or radioactive waste concerns.

8.1.13 Proceed to the appropriate separation and purification procedure, SOP 765, 777, 782 or 778.

8.2 TOTAL ANALYSIS

8.2.1 Before starting the procedure, check the pH of the sample. If the sample is unpreserved, add 5mL concentrated HNO_3 or enough to make the sample pH<2 and hold for 16 hours. Refer to SOP 733 for sample preservation procedure.

8.2.2 Shake the sample container to homogenize and mix the sediment and measure a volume of one liter (or other appropriate volume to reach requested detection limits) of the water sample to be analyzed. Record the volume on the benchsheet.

8.2.3 Consult the benchsheet for information about the volume, activity and standard identification to be used for tracing and spiking. Add calibrated volumes of tracer and spike solutions to the samples, blank and blank spike as per SOP 766.

8.2.4 Heat the sample on a hot plate at a low temperature and take it to near dryness. Transfer the sample into a 400mL Pyrex™ glass beaker using 8N HNO_3. Heat the sample to dryness.

8.2.5 If the sediment portion contains any organic material, the samples should be muffled. If muffling is required, cover the sample with a ribbed watch glass and muffle the sample at approximately 600°C for at least 4 hours.

8.2.6 From this point, follow the soil digestion procedure outlined in SOP 773. Following solid digestion, refer to the appropriate actinides separation SOPs (765, 777, 778, or 782) for further separation.

9. CALCULATIONS

TPU FACTORS. As defined in SOP 708, the 1σ preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU).

10. CALIBRATION STANDARDS

Calibration standards are not required for this procedure.

11. QUALITY CONTROL

11.1 A method blank, utilizing one liter of DI water, is prepared with each batch of up to 20 field samples (i.e., at a five-percent frequency).

11.2 One laboratory control sample (LCS or blank spike), prepared in one liter of DI water, is prepared with each batch of up to 20 field samples (i.e., at a five-percent frequency). Consult the Spike/Tracer Data Sheet Table for identification and volume of spiking standard.

11.3 Duplicate sample analyses are prepared at a minimum frequency of ten-percent, with at least one duplicate for each batch. If there is insufficient sample volume for this frequency of duplicates, a blank spike duplicate may serve as a measure of batch reproducibility.

12. DEVIATIONS FROM METHOD

12.1 This method has been modified from EPA Method 908.0 to enable determination of total uranium concentration of the sample by alpha spectroscopy. A known quantity of Uranium-232 tracer is equilibrated with the sample prior to separation. The tracer activity is used to calculate the concentration of uranium isotopes in the sample. The total uranium concentration is calculated as the sum of the U-234/235/238 activities.

12.2 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the lab's internally derived acceptance criteria.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 SAFETY AND HAZARDS

13.1.1 Read the MSDSS prior to preparing standards or using any solvents or reagents for the first time.

13.1.2 Wear gloves, safety glasses, and lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or handling materials or equipment potentially contaminated with chemicals.

13.1.3 Care must be used during handling of mineral acids (e.g., HCl) and

caustic solutions (e.g., ammonium hydroxide). Proper hand, body and face protection shall be worn and operations carried out in a fume hood with adequate ventilation.

13.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

13.1.5 Any non original containers may be used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with compound name, NFPA Health ,Flammability, and Reactivity ratings, and date.

13.2 WASTE DISPOSAL

The water actinide preparation process has been determined to not be hazardous, other than corrosivity. This material may be discharged into the Paragon waste tanks. Here the solution will be neutralized prior to discharge and the activity will be monitored to ensure compliance with Colorado Rules and Regulations pertaining to Radiation Control Part 4 regarding discharges to sanitary sewers.

14. REFERENCES

14.1 EPA Method 908.0, "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA-600/4-80-032, August, 1980.

14.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

9/11/06: No technical changes, minor clerical corrections made. Augmented LIMS program specification language. Added DOCUMENT REVISION HISTORY section. Attached Forms.

8/31/07: Clarified use of second independent source for spiking (SECTION 6), clarified order (switched 8.1.3 and 8.1.4) and added note that it is important protocol to add spikes before any chemical processing. Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Sections 7 and 8.1. Removed activity calculations from SECTION 9 and referenced SOP 708 instead.

Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

WATER ACTINIDES WORKSHEET

Prep Analyst:_____ **Analyte** **#1** **#2** **#3** **#4**
Preparation Date:_____ **Count Date/Time:**_____

ATI WORKORDER NUMBER:	CLIENT SAMPLE ID	SAMP VOL (L)	SAMP ALIQ (L)	Diss	Anion Col	Solv. Ext.	Cation Col	Micro	Remarks	DET. NO	FILENAME	POS CKD BY

ATI FRM 719FC3 -02/14/94

BALANCE #_____
Spike Witness_____ Date_____
Spiked by_____ Date_____

	Isotope	NO	ACT/ml	Vol	PIPET NO	TOTAL ACT (ppm)	Decay Corrected
Tracer 1							
Tracer 2							
Tracer 3							
Tracer 4							
Spike 1							
Spike 2							
Spike 3							
Spike 4							

#1 Relinquished by_____ Date_____
Received by_____ Date_____
#2 Relinquished by_____ Date_____
Received by_____ Date_____
#3 Relinquished by_____ Date_____
Received by_____ Date_____
#4 Relinquished by_____ Date_____
Received by_____ Date_____

Reviewed by_____ Date_____

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 777 REVISION 9

TITLE: **ACTINIDES -- THORIUM AND PLUTONIUM SEQUENTIAL SEPARATION BY ANION EXCHANGE**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07
QUALITY ASSURANCE MANAGER _____ DATE 9/3/07
LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 7/10/95; Rev1, PCN #534, 9/08/95; Rev2, 5/22/97; Rev3, 10/02/00; Rev4, 12/10/01; Rev5, 3/11/02; Rev6, 4/10/02; Rev7, 4/07/03; Rev8, 3/15/05; Rev9, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the sequential separation and purification of thorium (Th) and/or plutonium (Pu), including ^{241}Pu, using anion exchange chromatography for quantification by alpha spectroscopy. Before using this procedure, an aqueous or solid sample must be prepared as described in one of the appropriate sample preparation SOPs.

2. SUMMARY

2.1 The ferric hydroxide precipitate (from previous dissolution SOPs) is dissolved in either hydrochloric acid or nitric acid depending on the column to be used. The sample solution is passed through a column containing anion exchange resin that is pre-equilibrated in either 9M HCl or 8M HNO_3. If Th and Pu are run sequentially or only Pu is being analyzed, a chloride column is utilized, followed by a nitrate column. If only Th is needed, a nitrate column can be used without the further purification provided by a chloride column (please see Section 4.3, for further discussion). The chloride column does not reatain Th, which passes directly through the column when the sample is loaded. Pu is retained on a chloride column and is selectively stripped with an HCl/NH_4I solution. Th and Pu are retained on a nitrate column while other sample constituents pass through. The resin is rinsed with 8M HNO_3 to complete the isolation of Th and Pu from the sample solution. The Th and Pu remain on the column, and other interferents are discarded with the rinsate.

2.2 After loading on the nitrate column, Th is selectively stripped by rinsing with 9M HCl. Finally, Pu is stripped from the column by rinsing with 0.5M HCl. The purified Th and Pu are co-precipitated with lanthanum fluoride and mounted on a filter membrane for quantification by alpha spectroscopy. Either of the two elements, Pu or Th, can be isolated using this procedure. If ^{241}Pu is being analyzed, the Pu filters can be removed from their planchets, after performing the

^{242}Pu yield determination by alpha spectroscopy, and placed into a liquid scintillation vial with 0.1M HCl and Ultima Gold™ LLT cocktail and counted for beta-emitting ^{241}Pu. When spiking samples for ^{241}Pu, it is important to note that the detection limit is significantly higher for liquid scintillation counting than for alpha spec. Therefore, the spiking level should be much higher (about 500dpm vs. 10dpm). Consult the Instrument Lab for appropriate spiking levels, if necessary. If a particular element (Th or Pu) is not an analyte of interest, the column eluate (strip solution) is discarded as lab waste, rather than collected for analysis, at that step of the procedure.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of supervisory training and review, the performance of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Pu can exist in several different oxidation states in aqueous solutions. Pu must be present as Pu(IV) to be successfully purified by anion exchange chromatography, as described in this procedure. It is therefore essential that as little time as

possible elapse between the addition of $NaNO_2$ (in dissolution/concentration procedures) and completion of the anion exchange process.

4.2 In 8M HNO_3, Th and Pu(IV) form negatively charged complexes (anions) with NO^{3-} ions. Therefore, in 8M HNO_3, Th and Pu(IV) are retained by the anion exchange resin. In 9M HCl, Pu(IV) forms negatively charged complexes with Cl^- ions but Th does not. Hence, when the anion exchange column is washed with 9M HCl, Pu is retained by the resin and Th elutes.

4.3 In some cases, sample matrix constituents may interfere with the complete purification of Th on a single nitrate column. At the analyst's discretion, both the chloride and nitrate columns may be run, as if a Th/Pu sequential analysis were being performed. In this case, the chloride column may remove significant interferences to the nitrate column separation technique. No plutonium fraction is collected and the chloride column feed solution effluent and subsequent rinses are collected for further nitrate column purification.

4.4 The presence of lanthanides could be a significant interference in the analysis of Th, which is not addressed in the routine separation process. Lanthanides are stripped from the column along with the Th fraction. During micro-precipitation these lanthanides that are native to the sample are combined with the lanthanum carrier added as a reagent and an excessive amount of lanthanide-fluoride precipitate is formed and deposited on the filter membrane. This excessive precipitate may cause a "mass attenuation" problem in the spectrum, which significantly degrades spectral resolution. If the sample has significant lanthanides present, the Th fraction must be further purified as described in Section 8.3 below.

4.5 In some cases, the sequential separation of Pu and Am is desirable. When ^{241}Pu is one of the Pu analytes of interest, however, caution must be used in the creation of the batch LCS samples. Plutionium-241 is a beta-emitting radionuclide that produces ^{241}Am as the first daughter product. Consequently, the ^{241}Pu spiking solution contains significant ^{241}Am activity, which will confound the accurate quantification of ^{241}Am in the LCS. The most convenient approach, when creating batch LCSs in a sequential Pu/Am analysis where ^{241}Pu is also required, is to create the Pu and Am LCSs separately. Create a single Am LCS, traced with ^{243}Am and spiked with ^{241}Am, and a single Pu LCS, traced with ^{242}Pu and spiked with <u>both</u> ^{239}Pu and ^{241}Pu. Other tracing and spiking schemes may be acceptable, with supervisory approval.

5. APPARATUS AND MATERIALS

5.1 Ion exchange columns, plastic, disposable, Environmental Express™ R1020 or equivalent

5.2 Filter paper, Whatman™ 41 or equivalent

5.3 Fitted funnel, disposable

5.4 Plastic funnel

5.5 Glass beads, 3mm diameter

5.6 Suction filter apparatus, polysulfone filter holder and funnel, 25mm, or equivalent

5.7 Membrane filter, 0.1µm pore size, 25mm

5.8 Cupped planchets, stainless steel, 32mm diameter

5.9 Heat lamp

5.10 Pipettors, Eppendorf™ or equivalent

5.11 Wash bottles

5.12 Graduated cylinder, plastic, 25mL

5.13 Vortex mixer

5.14 Centrifuge bottles, 250mL disposable, conical

5.15 Hot plate

5.16 Steam bath

5.17 Forceps, fine tipped

5.18 Tape, double-sided

5.19 pH paper

5.20 Scintillation vials, glass

5.21 Kimwipes™

5.22 Plastic cups, disposable, 220mL

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) of less than 50 ppm, shall be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Ammonium Iodide, NH_4I, reagent grade. TLV = 25 ppm (TWA, as NH_4; STEL = 35 ppm). Irritant.

6.2 Nitric acid, HNO_3, 8M: Cautiously add 500mL conc. reagent grade HNO_3 to 400mL DI water. Dilute to 1L with DI water. TLV = 2 ppm (TWA, conc. HNO_3). Irritant, corrosive.

6.3 Nitric acid, HNO_3, 3M: Cautiously add 190mL of conc. HNO_3 to approximately 600mL DI water and dilute to 1L. See 6.2 above for TLV.

6.4 HCl/NH_4I Reagent: Dissolve 0.73g of NH_4I (reagent grade) in 100mL of 9M HCl. ***MAKE FRESH DAILY.***

6.5 Hydrochloric acid, HCl, concentrated. TLV = 5 ppm. Irritant, corrosive.

6.6 9M HCl: Cautiously add 750mL conc. reagent grade HCl to 100mL DI water. Dilute to 1L with DI water. See 6.5 above for TLV.

6.7 6N HCl: Cautiously add 500mL conc. reagent grade HCl to 400mL DI water. Dilute to 1L with DI water. See 6.5 above for TLV.

6.8 1M HCl: Cautiously add 83mL conc. reagent grade HCl to 800mL DI water. Dilute to 1L with DI water. See 6.5 above for TLV.

6.9 0.1M HCl: Cautiously add 8.3mL of conc. reagent grade HCl to 900mL DI water. Dilute to 1L with DI water. See 6.5 above for TLV.

6.10 0.5M HCl: Cautiously add 42mL conc. reagent grade HCl to 800mL DI water. Dilute to 1L with DI water. See 6.5 above for TLV.

6.11 Hydrofluoric acid, HF, 3M: Dilute 104mL conc. reagent grade HF to 1L with DI water. Use plastic graduated cylinder and storage bottle. TLV = 3 ppm (ceiling, conc. HF). Irritant, burns, bone, teeth, fluorosis.

6.12 Hydrogen peroxide, H_2O_2, 30% reagent grade. TLV = 1 ppm. Potential carcinogen, irritation, pulmonary edema, central nervous system effects.

6.13 Anion exchange resin, 1X8 Eichrom™ resin or equivalent.

6.14 Lanthanum carrier, 0.1 mg La^{3+}/mL: Dissolve 0.078 g high purity $La(NO_3)_3 \bullet 6H_2O$ in 250mL of 1M HCl.

6.15 Polyethylene glycol, average molecular weight of 2000 g/mole (0.25 M): Dissolve 50 g in 40mL DI water and dilute to 10 0mL with DI water.

6.16 Sodium nitrite, $NaNO_2$, saturated: Dissolve 85 g of $NaNO_2$ in 100mL of DI water. MAKE FRESH DAILY.

6.17 Ultima Gold™ LLT cocktail.

6.18 Methanol, reagent grade. TLV = 200 ppm. Neuropathy, vision, central nervous system effects.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Not applicable for this procedure. See the appropriate sample preparation SOP.

8. PROCEDURE

8.1 PURIFICATION BY ANION EXCHANGE-CHLORIDE COLUMN

8.1.1 **NOTE:** If analyzing for Th only, skip this Section and proceed to Section 8.2.1 of this SOP. Estimate the volume of the ferric hydroxide precipitate in the bottom of the conical 250mL centrifuge bottle. To dissolve the precipitate, add three times the volume of conc. HCl and mix by vortexing. Add 50mL of 9M HCl to assist in solubilizing any salts that may be present. Final volume depends on the amount of ferric hydroxide precipitate.

8.1.2 Sodium nitrite must be added to the sample prior to loading the sample on the column. The column separation must then be carried out on the same day. Add 3 drops of sodium nitrite to each sample.

8.1.3 Sample matrix constituents such as silicates may cause a cloudy or foamy appearance when the samples are dissolved in HCl. Samples may be compared with the QC samples of that batch for differences in appearance. If samples are noticeably different from the batch quality control (QC) samples, a polyethylene glycol (PEG) treatment may be conducted as explained in Section 8.1.4 to keep the sample constituents from blocking column flow. Perform this treatment on the QC samples as well. If samples are clear, proceed to Section 8.1.5.

8.1.4 PEG Treatment: Add 3mL of 0.25M polyethylene glycol to the sample. Vortex to mix and place samples in a cooler for ~30 minutes. The silicates will be trapped by the chelating action of the PEG and will slowly settle as a glassy precipitate at the bottom of the centrifuge bottle. Centrifuge the sample for 5 minutes at a 3500 rpm setting.

8.1.5 Precondition the frit of a disposable plastic column (approximately 15 mm I.D., 18mL capacity) with methanol up to the 1 cm line. Using a wash bottle, fill the column with a slurry (resin/DI water) of AG 1x8 anion exchange resin to a settled depth of approximately 7 cm. Cover the top of the resin bed with glass beads to a depth of approximately 2 cm to hold the resin in place.

8.1.6 Place a fitted plastic funnel on top of the ion exchange column. Place a regular funnel on the top of the fitted funnel. Fold a Whatman™ 41 filter paper and place it inside the funnel. Wet the filter paper with 9M HCl.

8.1.7 Condition the resin with 50 mL of 9M HCl. Discard the effluent down the back of the hood (discharges into Paragon's wastewater treatment system) followed with plenty of cold water.

8.1.8 If Th analysis is required, place a clean specimen cup, labeled with the sample ID and "Th", under the column. If Th analysis is not required place an empty waste collection cup under the column.

8.1.9 Load the sample solution onto the column through the filter. If the volume is more than 100 mL, pour the sample into the filter in portions until the entire solution has passed through the filter and the resin bed. If analyzing for Th, collect the effluent and the subsequent rinses in a clean, labeled cup. If not analyzing for Th, discard the column effluent and rinses into the appropriate waste container.

8.1.10 Rinse the centrifuge bottle two times with 20 mL volumes of 9M HCl. Add the first rinse to the filter (and column). Allow the first rinse to pass completely through the column before adding the second rinse. After the second rinse has passed through the column, discard the filter. Dry the filter on a tray and dispose of it in the contaminated soils and solids bucket.

8.1.11 Rinse the column with six additional 20mL volumes of 9M HCl. An additional 220 mL cup may be necessary to collect all of the rinses. This cup should also be labeled with the complete sample ID and "Th". The cups can be designated "A" and "B". Heat the cups containing the Th fraction on a steam bath until the volume is reduced enough to allow the sample to fit into one cup. Quantitatively transfer the sample solution, using 9M HCl to rinse, into one cup. Continue heating on a steam bath until dry. If Th is not to be analyzed, the effluent may be discarded as waste (i.e., down the drain with plenty of cold water).

8.1.12 To strip the Pu from the column, rinse the column with three 20mL portions of HCl/NH_4I reagent. (Allow each rinse to pass completely through the column before adding the next). Collect the effluent from these rinses in a clean 220 mL cup labeled with the sample ID and "Pu".

8.1.13 Add 10mL of conc. HNO_3 to the Pu fraction and take to dryness on a steam bath.

8.1.14 Used resin columns are treated and disposed, as described in Section 8.2.11.

8.1.15 Once the Th and Pu fractions have gone to complete dryness, dissolve the residue in 1mL of concentrated nitric acid. Add 50mL of 8M HNO_3 and 3 drops of sodium nitrite to the Pu fraction. The Th and Pu fractions will be further purified on separate nitrate columns. Proceed to Section 8.2.3.

8.2 PURIFICATION BY ANION EXCHANGE-NITRATE COLUMN

8.2.1 If analyzing for Th only, a chloride column is not usually necessary (please see section 4.3 for further discussion). The Th will be sufficiently isolated by using a nitrate column only. Estimate the volume of the ferric hydroxide precipitate in the bottom of the conical 250 mL centrifuge bottle that was produced in the previous prep SOP. To dissolve the precipitate, add an equal volume of concentrated nitric acid and mix by vortexing. Add 50mL of 8M HNO_3 to bring the solution to volume.

8.2.2 If analyzing for Th only, sample matrix constituents such as silicates may cause a cloudy or foamy appearance when the samples are dissolved in HNO_3. Samples may be compared with the QC samples of that batch for differences in appearance. If samples are noticeably different from the batch QC, a PEG treatment may be conducted as explained in Section 8.1.4 above to keep the sample constituents from blocking column flow. Perform this treatment on the QC samples as well. If samples are clear, proceed to Section 8.2.3.

8.2.3 Precondition the frit of a disposable plastic column (~15 mm I.D. with 18mL capacity) with methanol up to the 1 cm mark. Using a wash bottle containing a slurry of AG 1 X 8 anion exchange resin and DI water, fill the column to a settled depth of about 7 cm. Cover the top of the resin bed with glass beads to a depth of ~2 cm to hold the resin in place. Precondition the resin with 50 mL of 8M HNO_3 and discard the effluent down the back of the hood followed by plenty of water.

8.2.4 Firmly twist a fitted plastic funnel on top of the column. If samples have already gone through a chloride column, filtering is not necessary. For Th that is going on a nitrate column only, place a regular funnel on top of the fitted funnel and place a folded Whatman™ 41 filter inside. Wet the filter paper with 8M HNO_3.

8.2.5 Load the sample onto the column in portions. Rinse the cup or centrifuge bottle with 25mL of 8M HNO_3. Add this rinse to the column. Repeat this rinse. If applicable, the filter paper can be removed after the first rinse.

8.2.6 Rinse the column with a third 25mL volume of 8M HNO_3. Discard the column effluent down the drain with plenty of water unless otherwise specified.

8.2.7 Rinse the resin four times with 20mL volumes of 9M HCl. Allow each rinse to pass completely through the column before adding the next rinse. If the samples are being analyzed for thorium collect the column effluent in a 220 mL plastic disposable beaker, or other suitable

container, labeled with the sample ID and the symbol "Th". Dispose of this fraction down the drain followed with plenty of water if Th is not needed.

8.2.8 Heat the solution, containing the Th, to dryness on a steam bath. If lanthanides are present in the Th fraction, follow the procedure explained under Section 8.3 below, otherwise, the Th fraction can be taken to microprecipitation.

8.2.9 If analyzing for plutonium, strip the Pu by rinsing the resin three times with 20mL volumes of 0.5N HCl. Allow each rinse to pass completely through the column before adding the next. Collect the column effluent in a 220mL plastic disposable container, or other suitable container, labeled with the sample ID and the symbol "Pu".

8.2.10 Take the solution to dryness by heating on a steam bath. This sample fraction is now ready for Pu microprecipitation.

8.2.11 Used Resin columns are discarded by extruding the resin from the column and placing the resin in the established waste stream labeled "Hazardous Waste - Used Acidic Resin" in the Satellite Accumulation Area in the lab. When the satellite container is full, notify the site Waste Compliance Officer for further instructions. Emptied columns may be soaked in a RadiacWash™ solution, rinsed in tap water and discarded into the sanitary trash.

8.2.12 Used disposable cups may be rinsed with RadiacWash™ solution and tap water and re-used for collecting waste column effluent. If the cups are not needed they may be soaked in RadiacWash™, rinsed with tap water and discarded into the sanitary trash.

8.3 PROCEDURE TO CLEAN UP LANTHANIDES FROM THORIUM

8.3.1 The Th fraction from Step 8.2.8 is dissolved in 10mL of 3N nitric acid.

8.3.2 Prepare TEVA resin column: Fill disposable Bio-Rad™ ion exchange column to the 1.6mL mark. The TEVA resin is transferred into the column as a slurry with water. A layer of clean silica sand is placed on top of the resin bed to keep the resin in place.

8.3.3 Condition the TEVA column with 10mL of 3N nitric acid.

8.3.4 Transfer the sample solution onto the TEVA column using a transfer pipette. Wait until the entire sample has passed through the column before proceeding to the next step.

8.3.5 Rinse the sample cup with 5mL of 3N nitric acid and pass that solution through the TEVA column.

8.3.6 Repeat the preceding step one more time.

8.3.7 Replace the waste collection cup with a clean, labeled cup in order to strip the Th fraction. The cup should be labeled with the sample ID and "Th micro".

8.3.8 Strip Th from the column using three 5mL (15mL total) rinses of 9N HCl.

8.3.9 Add 5mL of 6N HCL to the column to strip any remaining Th from the column and collect it in the same cup.

8.3.10 Heat the Th fraction on the steam bath and take it to dryness. After drying the sample, proceed with Th microprecipitation.

8.4 THORIUM MICRO-PRECIPITATION

8.4.1 Add 1.0mL of concentrated HCl to the sample beaker labeled Th (from Step 8.2.8 or 8.3.10). Mix well to resolubilize the dried sample.

8.4.2 The plastic cup may be placed on a steam bath for about five minutes to aid dissolution. However, do not let the sample go completely dry. Add 14mL of DI water and mix well

8.4.3 Add 1.0mL lanthanum carrier. Mix well. Add 5mL 3N HF. Mix well. This will co-precipitate the thorium as La(Th)F.

8.4.4 Allow sample to stand for a minimum of 15-20 minutes.

8.4.5 Place a 25mm filter membrane on the supporting screen that sits on the top of the tapered funnel stem. Lock the funnel stem with a 25mm polysulfone filter funnel using a twist lock coupling, and turn the vacuum on. Rinse with 1-2mL methanol. (This will make the filter less hydrophobic.) Rinse further with DI water. NOTE: Do not let the filter membrane go dry before pouring the sample through.

8.4.6 Using suction, filter the precipitate through the filter membrane.

8.4.7 Rinse the sample beaker once with 5mL DI water and add to the filter funnel. After the sample has passed through, rinse the filter with an additional 10-15mL of DI water.

8.4.8 After filtration, remove the funnel, then turn the vacuum off. At the technician's discretion, a "Sharpie" marker may be used to print a mark on the edge of the filter. This helps identify the right side of the filter

in case the filter is dropped while transferring it to a planchet. Mount the filter membrane, **face up**, (side with the mark) on a 32mm stainless steel cupped planchet with double-sided adhesive tape. Dry the filter membrane under the heat lamp to dry any acid residue.

8.4.9 Submit the prepared samples and the updated benchsheet to the Instrument Lab, for analysis and subsequent disposal per SOP 714.

8.5 PLUTONIUM MICRO-PRECIPITATION

8.5.1 Add 1.0mL conc. HCl to the sample beaker containing the Pu fraction (from Step 8.2.10). Mix well to solubilize the dried sample.

8.5.2 If necessary, the cup may be placed on a steam bath for five minutes or until the residue breaks up. However, do not allow the sample to go completely dry. Add 14mL of DI water and mix well.

8.5.3 Add approximately 1.0mL of H_2O_2 and swirl gently.

8.5.4 Add 1.0mL lanthanum carrier. Mix well. Add 5mL 3N HF. Mix well. This will co-precipitate the plutonium as La(Pu)F.

8.5.5 Allow sample to stand for 15-20 minutes.

8.5.6 Place a 25mm filter membrane on the support screen that sits on the top of the tapered funnel stem. Lock the funnel stem with a 25mm polysulfone filter funnel using a twist lock coupling and turn the vacuum on. Rinse with 1-2mL alcohol. (This will make the filter less hydrophobic.) Rinse further with DI water. NOTE: Do not let the filter membrane to become dry before pouring the sample through.

8.5.7 Using suction, filter the co-precipitated sample through the filter membrane.

8.5.8 Rinse the sample beaker once with 5mL DI water and add to the filter funnel. After the sample has passed through, rinse the filter with an additional 10-15mL of DI water.

8.5.9 After filtration, remove the funnel, then turn the vacuum off. At the analyst's discretion, a "Sharpie" marker may be used to print a mark on the edge of the filter. This helps identify the right side of the filter in case the filter is dropped while transferring it to a planchet. Mount the filter membrane, **face up**, (side with the mark) on a 1.25in stainless steel cupped planchet with double-sided adhesive tape. Dry the filter membrane under the heat lamp to dry any acid fumes.

8.5.10 Submit the prepared samples and the updated benchsheet to the Instrument Lab. The Instrument Lab will analyze and ultimately dispose of the planchet and filter in the manner described in SOP 714.

8.6 PREPARATION OF SAMPLES FOR β-EMITTING Pu-241 LIQUID SCINTILLATION COUNTING

8.6.1 When the Instrument Lab has completed counting the micro-precipitated Pu samples for alpha-emitting Pu and the data has been reviewed and deemed acceptable for reporting, the samples and QC will be relinquished back to the Actinides Lab.

8.6.2 Carefully remove the sample filter membrane and double-sided tape with a pair of forceps and place into a properly labeled scintillation vial.

8.6.3 Add 5mL of 0.1N HCl to the vial containing the filter to help facilitate dissolution of the LaF_3 micro-precipitate on the filter.

8.6.4 Add 15mL of Ultima Gold™ LLT cocktail. Cap the vials tightly and invert several times to homogenize. Wipe the vials clean with a Kimwipe and methanol. Submit the vials and a ^{241}Pu liquid scintillation benchsheet to the Instrument Lab for analysis. The Instrument Lab will ultimately dispose of the scintillation vials in the manner described in SOP 704.

9. QUALITY CONTROL

Not applicable for this part of the procedure. Quality control samples are prepared prior to initiation of this SOP. See the appropriate sample preparation SOP for the kinds and numbers of QC samples prepared for this analysis.

10. CALCULATIONS

TPU FACTORS. As defined in SOP 708, the following one-sigma preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU).

10.1 Water samples (that require initial prep using SOP 776) require a preparation uncertainty factor of 0.0667. This is based on one gross aliquoting (sample homogeneity), one volumetric measurement, one tracer addition, two quantitative transfers and one reagent addition. See the following equation.

$$0.0667 = \sqrt{0.05^2 + 0.006^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2}$$

10.2 Solid samples (that require initial prep using SOP 773) require a preparation uncertainty factor of 0.0665. This is based on one gross aliquoting (sample

homogeneity), one mass measurement, one tracer addition, two quantitative transfers and one reagent addition. See the following equation.

$$0.0665 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2}$$

In practice, these two TPU factors are substantially equivalent. To simplify the data reporting procedure, the greater of the two (0.0667) may be used for both matrices.

11. DEVIATIONS FROM METHOD

This is a proprietary procedure developed by Paragon. The procedure draws upon several source methodologies. Therefore, there are no deviations from promulgated methods to be noted.

12. SAFETY HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.2 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

12.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (e.g., standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

12.1.4 Any chemicals with a TLV of less than 50ppm shall be used in a laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.3 below.

12.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with the compound name, NFPA Health, Flammability and Reactivity ratings, and date.

12.1.6 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation and personnel safety features. Never inhale or allow skin or clothing to be exposed to HF fumes. Immediately report any contact with HF to the lab Supervisor and Health & Safety Manager.

12.1.7 Care should be taken when diluting acids. **Always add acids to water, NOT water to acid.**

12.2 WASTE DISPOSAL

12.2.1 Wastes that are “corrosive only,” such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the Paragon

wastewater treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

12.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Compliance Officer for disposal.

12.2.3 All acid wastes not containing HF that are generated in ion exchange operations are disposed of to the waste tanks (i.e., down the drain) unless otherwise specified due to hazardous constituents.

13. REFERENCES

13.1 USDOE, RESL/ID, Procedure AS-5, 1979.

13.2 USEPA, EMSL/LV, Isotopic Determination of Plutonium, Uranium, and Thorium in Water, Soil, Air, and Biological Tissue, March 1979.

13.3 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

8/31/07: ^{241}Pu LCS discussion added to INTERFERENCES. Updated anion exchange resin to reflect current practice (use of Eichrom^{TM} instead of BioRad^{TM}), Section 5. Removed various calculations from SECTION 10 and referenced SOP 708 instead. DOCUMENT REVISION HISTORY Section added. Various clerical changes throughout.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 778 REVISION 12

TITLE: ACTINIDES – URANIUM, PLUTONIUM AND AMERICIUM/CURIUM (PARTIAL) SEQUENTIAL SEPARATION BY ION EXCHANGE

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/28/07

QUALITY ASSURANCE MANAGER _____ DATE 2/28/07

LABORATORY MANAGER _____ DATE 3-1-07

HISTORY: Rev0, PCN #506, 7/10/95; Rev1, PCN #535, 9/28/95; Rev2, 9/25/96; Rev3, 7/14/97; Rev4, 1/26/00; Rev5, 11/2/00; Rev6, 10/24/01; Rev8, 11/8/02; Rev9, 3/6/04; Rev10, 11/29/04; Rev11, 10/5/06; Rev12, 3/1/07.

1. SCOPE AND APPLICATION

Pretreatment and digestion of solids are described in SOP 721 - Solids Preparations For Radiochemistry Analysis, and SOP 773 - Dissolution Of Solids For The Determination Of Actinides. The preparation of waters is described in SOP 776. The procedure for tracing and spiking samples is found in SOP 766. At the conclusion of the preceding pretreatment and digestion steps, uranium, americium, curium, and plutonium are co-precipitated with ferric hydroxide.

This standard operating procedure (SOP) describes the sequential separation and purification of uranium (U), plutonium (Pu), and americium (Am)/curium (Cm) using anion exchange and the mounting of uranium for quantification by alpha spectroscopy (see SOP 777 for further details regarding the purification and mounting of the Pu). Where americium analysis is required, without curium, the separation and mounting of the americium fraction collected in this procedure is found in SOP 751. Where curium analysis is required, refer to SOP 780.

2. SUMMARY

The ferric hydroxide precipitate from previous dissolution procedures is dissolved in hydrochloric acid (HCl). The sample solution is passed through a column containing anion exchange resin that is equilibrated in 9N HCl. U and Pu are retained by the resin while other sample constituents, including Am/Cm, pass through. The resin is washed with 9N HCl to complete the isolation of U and Pu from the sample matrix. Pu is selectively stripped from the column by washing with a 9N HCl/NH_4I solution. Pu may be further purified by separation on a nitrate column as described in SOP 777. Finally, U is stripped by washing the resin with 0.5N HCl. The purified U and Pu are co-precipitated with lanthanum fluoride and mounted on a filter membrane for quantification by alpha spectroscopy. Any of the elements, Am, Pu, or U, can be isolated separately

using this procedure. The final steps of collecting rinses from the column are ignored if that respective element is not to be isolated for analysis.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specifications related to the client, project, and test method being performed.

3.3 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of supervisory training and review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Pu can exist in several different oxidation states in aqueous solutions. Pu must be present as Pu(IV) to be successfully purified by anion exchange as described in this procedure. It is essential that as little time as possible elapse between the addition of $NaNO_2$ (in the dissolution/concentration procedures) and completion of the anion exchange process.

4.2 In 9N HCl, U and Pu(IV) form negatively charged complexes (anions) with the ion-exchange chromatography resin. Therefore, in 9N HCl, U and Pu(IV) are retained by the anion exchange resin. In 9N HCl/NH_4I, Pu(IV) is reduced to Pu(III) which does not form the anionic complex. Hence, when the anion exchange column is washed with 9N HCl/NH_4I, Pu is eluted while U is retained. The subsequent washing of the column with 0.5N HCl breaks the U chloride complex and the U elutes from the column.

4.3 Excessive amounts of iron in the sample may co-precipitate with uranium, causing high precipitate masses and poor peak resolution in the analysis. This situation is avoided by reducing the iron in the microprecipitation stage with ascorbic acid in excess.

4.4 Excessive amounts of titanium chloride in the micro-precipitation steps will contribute additional mass to the lanthanum fluoride precipitate. This, in turn, may cause significant degradation of the alpha peak resolution in the analysis.

5. APPARATUS AND MATERIALS

5.1 plastic fitted funnels, disposable, Environmental Express #R10304 or equivalent

5.2 filter paper, Whatman® 41 or equivalent

5.3 laboratory funnel, plastic

5.4 glass beads, solid, 3mm diameter

5.5 vacuum filter apparatus for 25mm membrane ("The Whale")

5.6 filter, polypropylene, Environmental Express #F250100pp or equivalent

5.7 Stainless steel cupped planchet, 32 mm diameter

5.8 pipettes, Eppendorf® or equivalent, with disposable pipet tips

5.9 centrifuge bottles, disposable, conical, 250mL

5.10 transfer pipets, disposable

5.11 ion exchange columns, disposable, Environmental Express #R10204 or equivalent

5.12 plastic cups, disposable, 220mL

5.13 double-sided tape

5.14 steam bath

5.15 hot plate

5.16 vortex mixer

5.17 centrifuge

6. REAGENTS

NOTE: Threshold Limit Value (TLV) and other hazard information may be given here. The absence of this information does not imply that the substance is not hazardous. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The employee should be familiar with all pertinent Material Safety Data Sheets (MSDSs) before proceeding.

6.1 Methanol, reagent grade. TLV=200 ppm. Neuropathy, vision, central nervous

system.

6.2 Hydrochloric acid (HCl), concentrated, 12N. TLV=5 ppm (ceiling, conc. HCL).

6.3 9N HCl: Cautiously add 1500mL conc. reagent grade HCl to 500mL DI water. TLV=5 ppm (ceiling, conc. HCL).

6.4 0.5N HCl: Cautiously add 83mL conc. reagent grade HCl to approximately 1 liter DI water, bring to a final volume of 2L with DI water. Mix thoroughly. TLV=5 ppm (ceiling, conc. HCL).

6.5 Hydrofluoric acid (HF), 3N: Dilute 104mL conc. reagent grade HF to 1L with DI water. Use plastic graduated cylinder and storage bottle. TLV=3 ppm (ceiling, conc. HF). Irritant, burns, teeth, fluorosis.

6.6 Ammonium Iodide (NH_4I), reagent grade

6.7 Titanium Chloride ($TiCl_3$), 20% solution, reagent grade

6.8 Anion exchange resin, AG 1x8, Eichrom® or equivalent

6.9 Lanthanum Carrier, 0.1mg La^{3+}/mL: Dissolve 0.312g high purity $La(NO_3)_2 \bullet 6H_2O$ in 1000mL of 1N HCl. Prepare in a 1L volumetric flask.

6.10 HCl/NH_4I Reagent: Dissolve 0.73g NH_4I, reagent grade, in 100mL 9N HCl. Make fresh daily.

6.11 Nitric Acid, HNO_3, concentrated, 16N, reagent grade. TLV=2 ppm (TWA, conc. HNO_3). Irritant, corrosive.

6.12 Nitric acid, 8N: Cautiously add 500mL conc. reagent grade HNO_3 to 400mL DI water. Dilute to 1L with DI water. See TLV information above.

6.13 Safranine-O, 1% stock solution, reagent grade

6.14 Polyethylene glycol, average molecular weight 2000 g/mole (PEG 2000), 0.25M: Dissolve 50g PEG in 40mL of DI water and dilute to 100mL with DI water.

6.15 Deionized (DI) water, generated in-house by the DI water system.

6.16 Ascorbic Acid Solution, saturated: Add just enough DI water to dissolve approximately 2 grams of ascorbic acid. MAKE FRESH DAILY.

6.17 Sodium nitrite ($NaNO_2$), saturated: Dissolve 8.5g of $NaNO_2$ in 10mL of DI water. MAKE FRESH DAILY.

6.18 Hydrogen Peroxide, H_2O_2, 30%, reagent grade. TLV=1 ppm. Potential carcinogen, irritant, pulmonary edema, central nervous system effects.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

The samples should be collected according to an approved sampling plan.

8. PROCEDURES

8.1 PURIFICATION BY ANION EXCHANGE

8.1.1 Estimate the volume of the ferric hydroxide precipitate in the bottom of the conical 250mL centrifuge bottle. To dissolve the precipitate, add three times the volume of conc. HCl and mix thoroughly. Add 50mL 9N HCl to assist in solubilizing any salts that may be present. Final volume depends on the amount of ferric hydroxide precipitate.

8.1.2 If analyzing for Pu, add 3 drops of sodium nitrite to each sample, otherwise, skip this Step.

8.1.3 Sample matrix constituents such as silicates may cause a cloudy or foamy appearance when the samples are dissolved in HCl. Samples may be compared with the quality control (QC) samples of that batch for differences in appearance. If samples are noticeably different from the batch QC, a PEG treatment may be conducted as explained in Step 8.1.4 below, to keep the sample constituents from blocking column flow. Perform this treatment on the entire batch of samples, as well as, the QC. If samples are clear, proceed to Step 8.1.5.

8.1.4 PEG Treatment: Add 3mL of 0.25M polyethylene glycol to the sample. Mix and place samples in a cooler for ~ 30 minutes. The silicates will be trapped by the chelating action of the PEG and will slowly settle as a glassy precipitate at the bottom of the centrifuge bottle. Centrifuge the sample for 5 minutes at 3500 rpm.

8.1.5 MAKING THE ION-EXCHANGE COLUMN
Assemble a column support apparatus (PVC pipe). Twist a fitted plastic funnel tightly on top of a disposable plastic column (15mm I.D., 18mL capacity) and place into the pre-drilled holes in the PVC pipe. Position a waste cup under the column. Precondition the frit of the column with methanol up to the 1cm line. Using a squeeze bottle, fill the column with a slurry of AG 1x8 anion exchange resin that is a 1:1 ratio of resin to DI water. The final settled depth should be approximately 7cm. Add a layer of ~ 1-2 cm of glass beads to hold the resin in place.

8.1.6 Place a regular funnel on the plastic fitted funnel. Fold a Whatman® 41 filter paper and place it inside the regular funnel.

8.1.7 Condition the column by adding 50mL of 9N HCl through the filter paper. The effluent may be poured down the drain in the lab hoods with plenty of cold tap water. *If Am/Cm is to be analyzed, place a clean 220 mL plastic cup labeled with the sample ID and the notation "Am" under the column.* Otherwise, the waste cups may be left in place and the collected effluent may be discarded into the appropriate waste container. Load the sample solution onto the column by pouring the sample in portions through the filter until the entire solution has passed through the filter and the resin bed.

8.1.8 Rinse the column four times with 20 mL volumes of 9N HCl. Add the first two rinses from the centrifuge bottle to the filter (and column). After the solution has passed through, remove the filter and regular funnel. Filters should be dried on a tray in the hood, scanned, and disposed of in the proper waste bucket. Allow each rinse to pass completely through the column before adding the next rinse. *If americium is to be analyzed, collect the rinses in the "Am" plastic specimen cup. Take this fraction to dryness on a steam bath and proceed to SOP 751. If curium is to be analyzed, collect the rinses in the "Am/Cm" cup, take this fraction to dryness, and proceed to SOP 780.*

8.1.9 If analyzing for Pu, rinse the column with an additional four 20mL volumes of 9N HCl, collecting the effluent into a waste cup. Discard this rinse down the drain with plenty of cold water. This rinse should wash any residual Th (which will cause an interference in the Pu spectra) in the column through the resin bed. A nitrate column will be run on all Pu samples, following the chloride column, in order to remove interfering Th.

8.1.10 Rinse the resin with three 20 mL portions of HCl/NH_4I Reagent. Allow each rinse to pass completely through the column before adding the next. If the samples are being analyzed for plutonium, collect the column effluent from these rinses in a 220mL plastic specimen cup labeled with the sample ID and the symbol "Pu".

Add 10mL of conc. HNO_3 to the Pu fraction collected from the column. Dry the Pu fraction on a steam bath. When dry, dissolve residue in 1mL of concentrated nitric acid. Add 50mL of 8N nitric acid and 3 drops of sodium nitrite. Proceed to SOP 777 Section 8.2.3.

8.1.11 If analyzing for U, rinse the column with two 20mL volumes of 9N HCl, collecting the effluent into a waste cup. Discard this rinse down the drain with plenty of water. This rinse should wash any residual NH_4I through the resin bed.

8.1.12 Strip the U by rinsing the resin with four 20mL volumes of 0.5N HCl. Collect the column effluent in a 220mL polypropylene cup, or other suitable container, labeled with the sample ID and the symbol "U". Add 2.5mL of concentrated HNO_3 and 7.5mL of concentrated HCl to the "U" fraction and take it to dryness by heating on a steam bath. Proceed to Section 8.2 below.

8.2 URANIUM MICRO-PRECIPITATION

8.2.1 In the micro-precipitation lab, add 1mL conc. HCl to the sample cup. Mix well. Let stand for 15-20 minutes to resolubilize the residue. If sample does not completely dissolve during this time, it may be necessary to place the plastic cup on a steam bath for a few minutes.

8.2.2 Add 14mL of DI water and mix well.

8.2.3 Add 1.5mL of lanthanum carrier.

8.2.4 Add ascorbic acid solution drop wise, with swirling, until any yellow color from remaining ferric iron disappears. Add approximately 1mL extra.

8.2.5 Add one drop of Safranine-O indicator solution to each sample and mix thoroughly.

8.2.6 Add approximately 0.5mL of $TiCl_3$ and swirl constantly. The solution should lose the Safranine-O color and be reasonably colorless. If the solution does not lose the Safranine-O color, up to 5 additional drops may be added while swirling until the color changes. If the solution still does not become reasonably colorless, proceed to the next step.

8.2.7 Add 5mL 3M HF. Mix well.

8.2.8 Allow sample to stand for approximately 20 minutes. If the Safranine-O color returns during this period, add up to an additional 5 drops $TiCl_3$, drop wise while swirling, until the solution again loses the Safranine-O color. If the solution does not lose the Safranine-O color, document the appearance on a Quality Assurance Summary Sheet and proceed to the next step.

8.2.9 Label planchets and petri dish with sample ID, batch ID and analyte.

8.2.10 Turn the vacuum on low (about ¼ to ½ turn). Place a 25mm filter membrane on the support screen that sits on top of the tapered funnel stem. Lock the funnel stem with a 25mm polysulfone filter funnel using a twist lock coupling. Using a squeeze bottle, thoroughly rinse the filter with methanol (this will make the filter less hydrophobic.)

Before the filter goes dry from the methanol rinse, add at least 5mL of DI water.

8.2.11 Before the water rinse completely passes the filter, transfer the coprecipitated sample to the filter apparatus.

8.2.12 After the sample passes through the filter, rinse the sample cup once with approximately 10mL of DI water and add to the filter funnel, once the sample has passed completely through the filter. After the first rinse has passed completely through the filter, rinse the sides of the funnel with approximately 10mL of DI water.

8.2.13 After filtration, keep the vacuum on and remove the funnel. A "Sharpie" marker may be used to place a dot on the outside edge of the filter. This helps identify the right side of the filter in case the filter flips during the transaction. Carefully remove the filter membrane with a pair of forceps and fix it face up on the double-sided tape that was mounted on the planchet. Dry the mounted filter membrane under a heat lamp on low setting until dry. THE FILTERS MUST BE THOROUGHLY DRY TO PREVENT DAMAGE TO THE ALPHA SPECTROMETRY DETECTORS. HOWEVER, DO NOT LEAVE THE PLANCHET UNDERNEATH THE HEAT LAMP FOR TOO LONG AS IT MIGHT DEFORM THE FILTER OR MELT THE DOUBLE SIDED TAPE.

8.2.14 Rinse the support screens with dilute RadiacWash® followed by a thorough rinse with DI water. The PVC pipe containing the sample waste must be drained into the appropriate HF waste carboy after the completion of each batch of samples to avoid overflow.

8.2.15 Used polysulfone funnels are soaked in concentrated RadiacWash®, gently cleaned with a non-abrasive sponge, soaked in a dilute RadiacWash® solution, and then rinsed thoroughly with DI water.

8.2.16 Arrange the planchets in a labeled petri dish and submit the prepared samples and the updated benchsheet to the Counting Lab. The Counting Lab will analyze and ultimately dispose of the planchets and filters in the manner described in SOP 714.

9. CALCULATIONS

TPU FACTORS. As defined in SOP 743, the following one-sigma preparation uncertainty factors should be applied during the final reporting stage of the uranium analysis as a component of the Total Propagated Uncertainty (TPUs for plutonium and americium analyses are defined in SOPs 777 and 751, respectively):

9.1 Water samples (that require initial prep using SOP 776) require a preparation uncertainty factor of 0.0711. This factor is based on one gross aliquoting (sample homogeneity), one volumetric measurement (initial aliquot), one tracer addition by pipetting, one tracer activity determination, and three quantitative transfers (hydrox. ppt. from beaker, cent. bottle to column, and from cup to filter in microppt.). See the following equation:

$$0.0711 = \sqrt{0.05^2 + 0.006^2 + 0.004^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2}$$

9.2 Solid samples (that require initial prep using SOP 773) require a preparation uncertainty factor of 0.0709. This factor is based on one gross aliquoting (sample homogeneity), one mass measurement (initial aliquot), one tracer addition by pipetting, one tracer activity determination, three quantitative transfers (digestion cup to cent. tube, tube to column, cup to filter in microppt.). See the following equation:

$$0.0709 = \sqrt{0.05^2 + 0.003^2 + 0.004^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2}$$

9.3 In practice, the water and solid sample TPU values are substantially equivalent. For simplification in reporting, the first factor of 0.0711 shall be used for both matrices.

10. QUALITY CONTROL

Refer to SOP 773 for the "Dissolution of Solids for the Determination of Actinides" and SOP 776 for the "Preparation Of Water Samples For Actinides".

11. DEVIATIONS FROM METHOD

This method is substantively compliant with ASTM method D3972 and DOE U-02 in the chemical separation, which is performed by anion exchange chromatography. The ASTM method, however, specifies electro-deposition as the technique for presenting the sample for analysis. This method uses microprecipitation, which is substantively compliant with DOE U-02 except that the DOE method uses neodymium fluoride as the precipitate, where this method uses lanthanum fluoride. The two are believed to be equivalent, particularly in light of the use of the radioactive tracers used for chemical yield determination.

12. SAFETY HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.2 Safety glasses, lab coats and gloves must be worn when working in the radiochemistry prep. labs.

12.1.3 Any chemicals with a TLV of less than 50ppm shall be worked with in

the laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.4 below.

12.1.4 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.1.5 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation and personnel safety features. Never inhale or allow skin or clothing to be exposed to HF fumes.

12.1.6 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

12.2 WASTE DISPOSAL

12.2.1 Wastes that are "corrosive only", such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into Paragon's wastewater treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) are neutralized in the waste treatment facility.

12.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Compliance Officer for disposal.

12.2.3 All acid wastes not containing HF that are generated in ion exchange operations are disposed of to the wastewater treatment system (i.e., down the drain with plenty of tap water) unless otherwise specified due to hazardous constituents.

13. REFERENCES

13.1 USDOE, RESL/ID, "Procedure AS-5", 1979.

13.2 USEPA, EMSL/LV, "Isotopic Determination of Plutonium, Uranium, and Thorium in Water, Soil, Air, and Biological Tissue", March 1979.

13.3 ASTM Method 3972, "Determination of Isotopic Uranium in Water".

13.4 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.5 Paragon SOP 743, current revision, "Estimating Total Propagated Uncertainties for Radiometric Analyses".

DOCUMENT REVISION HISTORY

10/5/06: Deviations Section updated to discuss electro-deposition vs. microprecipitation.

3/1/07: Rev12. Added some additional detail to INTERFERENCES. Added direction to use methanolic column for Cm separations. Clarified acid additions and reagent volumes in microprecipitation, with instructions for completing QASSs. Also updated TPU factors.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 780 REVISION 8

TITLE: **ACTINIDES - AMERICIUM / CURIUM SEPARATION -- PURIFICATION BY METHANOLIC ANION EXCHANGE AND TEVA SPEC COLUMN**

FORMS: **NONE**

APPROVED BY:
TECHNICAL MANAGER Renee Hallez08 DATE 7/21/08
QUALITY ASSURANCE MANAGER Dan Schenk DATE 7/20/08
LABORATORY MANAGER K. Thiel DATE 7/21/08

HISTORY: Rev0, 11/8/95; Rev1, 4/19/96; Rev2, 5/3/96; Rev3, 1/26/00; Rev4, 10/19/00; Rev5, 3/14/02; Rev6, 4/7/03; Rev7, 7/5/06; Rev8, 7/18/08.

1. SCOPE AND APPLICATION

This procedure describes the isolation of americium (Am) and curium (Cm) in water samples, filter leachates, vegetation, and soil digestate solutions using methanolic anion exchange followed by purification using TEVA-Resin. Also described is the mounting of Am onto a filter membrane for quantification by alpha spectroscopy. Before using this procedure, an aqueous or solid sample must be prepared as described in one of the appropriate sample dissolution and ion exchange separation SOPs. The Am/Cm fraction separated from the preceding procedure should be co-precipitated with ferric hydroxide or calcium oxalate prior to separation by methanolic anion exchange.

2. SUMMARY

For normal water samples, soil samples and filter leachates, the Am/Cm fraction from previous dissolution and ion-exchange SOPs is co-precipitated as iron hydroxide and dissolved in 1N HNO_3/93% methanol solution. For soil samples with higher interference of constituents, such as iron and samples with larger aliquots, Am in the acidic solution from previous prep SOPs is precipitated with calcium oxalate. The precipitate is ignited in a muffle furnace and the ash is dissolved in 1N HNO_3/93% methanol solution. The sample solution is passed through a column containing anion exchange resin that is equilibrated in 1N HNO_3/93% methanol. Am/Cm is held by the resin while other sample constituents pass through. The resin is washed with 1N HNO_3/93% methanol to complete the isolation of Am/Cm from the sample matrix. Am/Cm is stripped from the column by washing with 8N HNO_3. The Am/Cm is further purified from interfering rare earth elements using TEVA resin. Finally, the Am/Cm is co-precipitated with lanthanum fluoride and mounted on a filter membrane for quantification by alpha spectroscopy.

NOTE: *After the methanolic anion exchange column has been prepared, the separation procedure should be carried out without interruption. In other*

words, the analyst should plan to begin the procedure early enough so that the methanolic column work can be done from start to finish in the same workday.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

The presence of Thorium in the sample may be an interference. When the aliquot size for analysis is larger than normal (default = 2g), and if the sample is a sequential analysis of Pu, U, and Am, care must be taken to remove Th from the sample. Th-228 may appear in the Am-241 Region Of Interest (ROI) and give a false positive if Th-228 is not sufficiently removed from the sample. The analyst must run a nitrate column (SOP 777), prior to running a methanolic column to remove Th if the sample is known to have elevated levels of Th activity.

5. APPARATUS AND MATERIALS

5.1 Ion exchange columns, disposable

5.2 Filter paper, Whatman™ #41 or equivalent

5.3 Filter paper, Whatman™ #42 or equivalent

5.4 Funnel, plastic

5.5 Glass beads, solid, 3mm diameter

5.6 Silica sand

5.7 Pyrex™ beaker, 250 and 600mL

5.8 Watchglasses, Pyrex™

5.9 Suction filter apparatus for 25mm membrane

5.10 Polypropylene filter membrane, 0.1 μm porosity, 25mm

5.11 Cupped planchets, stainless steel, 1.25in diameter

5.12 Drying oven, set at 105+5°C

5.13 Muffle Furnace, set at approximately 600°C

5.14 Pipets, Eppendorf™, or equivalent

5.15 Pipets, transfer, plastic

5.16 Centrifuge bottle, 250mL capacity

5.17 Centrifuge, capable of 3500rpm spin

5.18 Wash bottles

5.19 Graduated cylinder, plastic, 25mL

5.20 Polypropylene beaker, disposable, 220mL

5.21 Hot plates / magnetic stir plates

5.22 Magnetic stir bars, Teflon™-coated

5.23 Steambath

5.24 Disposable BIO-Rad® Ion exchange columns, or equivalent

5.25 SharpieTM marker, or equivalent

5.26 Double-sided tape

6. REAGENTS

Only reagent grade or better chemicals shall be used. Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents, acids).

6.1 Deionized (DI) water, obtained from the laboratory's deionized water system

6.2 HNO_3, conc. TLV = 2ppm. Irritant, corrosive.

6.3 HNO_3 8N: Dilute 500mL conc. HNO_3 with 500mL DI water. TLV = 2ppm. Irritant, corrosive.

6.4 HCl, conc. TLV = 5ppm (ceiling). Irritant, corrosive.

6.5 HCl, 2N: Dilute 150mL conc. HCl with 750mL DI water. TLV = 5ppm (ceiling). Irritant, corrosive.

6.6 Ammonium hydroxide, NH_4OH, conc. TLV = 25ppm for ammonia. Irritant.

6.7 Hydrofluoric acid, HF, 3N: Dilute 104mL conc. HF to 1L with DI water. *Use a plastic graduated cylinder and store in a plastic bottle.* TLV = 3ppm (ceiling). Irritant, bones, teeth, fluorosis.

6.8 Methanol, MeOH, 99.8%. TLV = 200ppm. Neuropathy, vision, central nervous system effects.

6.9 Formic acid, 98%. TLV= 5ppm (TWA). Irritant.

6.10 Ammonium oxalate or oxalic acid. TLV = $1mg/m^3$ (TWA for oxalic acid). Irritant, burns.

6.11 1N HNO_3/93% methanol: For 160mL of solution, dilute 10mL conc. HNO_3 with 150mL of methanol. Prepare daily as needed. TLV = 2ppm (HNO_3). Irritant, corrosive.

6.12 Ferric chloride carrier, 20mg Fe^{+3}/mL. Dissolve 96g $FeC_{l3}•6H_2O$ in one liter of 0.5N HCl. TLV = 5ppm (ceiling). Irritant, corrosive.

6.13 2M ammonium thiocyanate/0.1M formic acid, 2M NH_4SCN/0.1M HCOOH: For every 100mL of solution dissolve 15.2g NH_4SCN and 0.35mL 98% formic acid in 100mL DI water. TLV= 5ppm (TWA). Irritant.

6.14 1M ammonium thiocyanate/0.1M formic acid, 1M NH_4SCN/0.1M HCOOH: For every 100mL of solution dissolve 7.6g NH_4SCN and 0.35mL 98% formic acid in 100mL DI water. TLV= 5ppm (TWA). Irritant.

6.15 Lanthanum carrier, 0.1mg La^{+3}/mL: dissolve 0.2337g high purity $La(NO_3)_2•6H_2O$ in 250mL of 1N HCl. TLV = 5ppm (ceiling). Irritant, corrosive.

6.16 TEVA resin®, 100-150µ size

6.17 Anion exchange resin, AG 1x8, Eichrom™ or equivalent.

6.18 Calcium carrier solution, 50mg Ca/mL: Dissolve 295g $Ca(NO_3)_2•4H_2O$ in 1000mL DI water.

6.19 Methyl violet indicator, 0.02% aqueous

7. PROCEDURE

7.1 SAMPLE PRE-TREATMENT FOR SOIL/SOLID SAMPLES OF LARGE ALIQUOT SIZE

7.1.1 Sample aliquots greater than 2g and samples with excess iron may need additional pre-treatment in the form of a calcium oxalate precipitation
7.1.2 for removal of excess iron and aluminum. If a typical aliquot size was taken, interferences are not expected, proceed to Section 6.2.

7.1.3 The acidic effluent from the preceding chloride or nitrate column separation procedure should be collected in a 600mL Pyrex™ beaker. Dilute the solution by adding DI water so that the final acid concentration is less than 3N.

7.1.4 To the sample solution, add 1.0mL of Ca carrier (50mg Ca) and 5g of either ammonium oxalate or oxalic acid.

7.1.5 Place the beaker containing the sample on a magnetic stir plate. Place a magnetic stir bar in the beaker and begin agitation. Begin adding concentrated NH_4OH to the sample using a wash bottle to neutralize the acidity. Continue to add concentrated NH_4OH until a precipitate just begins to form. If reddish brown $Fe(OH)_3$ precipitate forms, add 8N HNO_3 dropwise from a wash bottle to lower the pH. At the endpoint, the sample should be cloudy with a **white calcium oxalate precipitate**.

7.1.6 At this point, add 2mL of methyl violet indicator. The solution color should be blue due to the methyl violet indicator. The exact indicator color can be obtained either by adding acid or base. NOTE: the purpose of this Step is to precipitate Am/Cm with calcium oxalate at a pH low enough that iron and aluminum stay in solution.

7.1.7 To recover the precipitate, pour the sample through a Whatman™ #42 filter paper (or equivalent). Complete the transfer by rinsing the beaker with DI water.

7.1.8 After all the solution has passed through, place the filter + precipitate in a beaker (same beaker as above can be used) and dry in a drying oven.

7.1.9 Cover the beaker containing the filter + precipitate with a Pyrex™ watch glass and place in a muffle furnace. The beaker ID must be marked permanently (ink will burn off). Record the beaker ID corresponding to the sample ID on the benchsheet. Ignite the sample by heating at approximately 600°C for at least 1 hr.

7.1.10 Allow the beaker + ash to cool. Dissolve the ash in about 3mL of conc. HNO_3. After the ash is completely dissolved, dilute the acid solution with 45mL of methanol. Proceed to Step 7.3.1.

7.2 WATER/FILTERS, AND SOIL/SOLID SAMPLES WITH STANDARD ALIQUOT SIZE

7.2.1 The acidic effluent from the preceding chloride or nitrate column separation procedure should be collected in a disposable plastic beaker. Place the container on a steam bath and take to dryness. Dissolve the residue in 5-10mL of conc. HNO_3 and add 100 to 125mL of DI water. Add 1.0mL of iron carrier to the sample solution. Transfer the solution to a 250mL centrifuge bottle. Rinse the cup with DI water and add to the centrifuge bottle. Precipitate ferric hydroxide using an excess of NH_4OH. Centrifuge at approximately 3500rpm for at least 15 minutes. Discard the supernatant.

7.2.2 Dissolve the ferric hydroxide precipitate in 3mL of conc. HNO_3. After the precipitate is completely dissolved, dilute the acid solution with 45mL of methanol and proceed to step 7.3.1. If the precipitate does not dissolve completely, add an additional volume of conc. HNO_3 and increase the volume of methanol **proportionally**. If the precipitate requires more than 9mL of conc. HNO_3 and 135mL of methanol, consult your Supervisor for alternative method to handle this situation.

7.3 ISOLATION OF Am BY METHANOLIC ANION EXCHANGE

7.3.1 Combine the needed volume of anion exchange resin with twice the volume of 1N HNO_3/93% methanol solution in a plastic bottle with a screw cap. Tighten the cap securely and let the resin condition overnight. *Do not allow the resin to be exposed to air.*

7.3.2 Pour the resin slurry into a disposable column and let settle to a resin bed height of approximately 10cm.

7.3.3 Insert a fitted plastic funnel on top of the ion exchange column. Place a layer of glass beads on top of the resin bed. **NOTE**: **Do not allow the resin to dry out at any point in the procedure.**

7.3.4 Condition the resin bed by rinsing the column with 40mL of 1 N HNO_3/93% methanol solution.

7.3.5 Load the sample solution from Step 7.1.10 or 7.2.2 onto the column through the filter. Pour the sample into the column until the entire solution has passed through the resin bed.

7.3.6 Rinse the centrifuge bottle two times with 20mL volumes of 1N HNO_3/93% methanol solution. Add the first rinse to the column. Allow the first rinse to pass completely through the column before adding the second rinse. Rinse the column with a third 20mL volume of 1N HNO_3/93% methanol solution. Discard the column effluent into the **methanolic waste receptacle**.

7.3.7 Strip Am/Cm by passing three 20mL volumes *of 8N HNO_3* through the column. Allow each rinse to drain completely before adding the next rinse. Collect the effluent in a *plastic beaker* labeled with the sample ID and "Am/Cm-TEVA". Discard the used column and resin into the resin waste receptacle.

7.3.8 Place the beaker containing the Am/Cm fraction on a steam bath and heat the solution to dryness.

7.4 PURIFICATION OF Am/Cm USING TEVA RESIN

7.4.1 Fill a BioRad® column (or equivalent) to the 1.6mL mark with a slurry of TEVA™ resin and DI water. Add a 4-5mm layer of clean silica sand to hold the resin in place.

7.4.2 Re-dissolve the sample from Step 7.3.8 in 10mL of 2M NH_4SCN/0.1M formic acid solution. Allow the sample to stand or heat briefly on the steam bath to ensure dissolution.

7.4.3 Condition a TEVA™ resin column by passing 5mL of 2M NH_4SCN/0.1M formic acid solution through it.

7.4.4 Transfer the sample solution onto the TEVA™ column in two portions using a disposable polyethylene transfer pipette. Rinse the sample container with 1mL of 2M NH_4SCN/0.1M formic acid solution. Apply the rinsate to the column. Repeat the rinse one more time with 2M NH_4SCN/0.1M formic acid solution to complete the transfer.

7.4.5 Rinse the sample cup with two 5mL volumes of 1M NH_4SCN/0.1M formic acid solution. Apply the rinsate to the TEVA™ column. Allow the first 5mL to pass through the column completely before applying the second 5mL. The purpose of this Step is to wash lanthanides from the column.

7.4.6 Strip Am/Cm from the column with three, 5mL volumes of 2N HCl. Collect the effluent from the column in a clean polypropylene beaker labeled with the sample ID and "micro for Am/Cm". Apply the 2N HCl in three 5mL portions. Allow each portion to drain completely before applying the next.

7.4.7 To decompose thiocyanate, add 2.5mL conc. HNO_3 and 7.5mL conc. HCl to the Am strip solution. Swirl gently to mix. Place the samples on a steam bath and heat until the volume is reduced to about one drop.

7.4.8 Add 5mL conc. HNO_3 to the sample from the previous Step only if any black or brown colored residue is noted and heat on the steam bath until the volume is reduced to about one drop.

7.5 AMERICIUM MICRO-PRECIPITATION

7.5.1 Add 1mL conc. HCl to the sample beaker from Step 6.4.7 or 6.4.8. Heat on the steam bath to aid in dissolution. Add 14mL DI water to the beaker.

7.5.2 Add 1.0mL lanthanum carrier. Mix well. Add 5mL 3N HF. Mix well.

7.5.3 Allow sample to stand for 30 minutes.

7.5.4 Place a 25mm filter membrane on a filter funnel assembly and turn the vacuum on. Rinse with 1-2mL methanol (this will make the filter less hydrophobic), followed by ~10mL of DI water. NOTE: *Do not let the filter become dry before pouring the sample through.*

7.5.5 Using suction, filter the co-precipitated sample through the filter membrane.

7.5.6 Rinse the sample beaker once with 5mL DI water and add to the filter funnel. After the sample has passed through, rinse the filter with an additional 10-15mL of DI water.

7.5.7 After filtration, turn the vacuum off. Remove the funnel. A "Sharpie" marker may be used to place a dot on the outside edge of the filter. This helps identify the right side of the filter in case the filter flips during the transfer. Carefully remove the filter membrane with a pair of forceps and fix it face up on the double-sided tape on a planchet. Dry the filter membrane with the planchet under a heat lamp until the filter is dry.

7.5.8 NOTE: DO NOT HEAT THE PLANCHET FOR TOO LONG - THE FILTER AND DOUBLE-SIDED TAPE MAY MELT.

7.5.9 The sample is analyzed by Alpha Spectroscopy and reported according to Paragon (PAR) SOP 714. Submit the prepared samples and the updated benchsheet to the Counting Lab. The Counting Lab will analyze and ultimately dispose of the planchet and filter in the manner described in SOP 714.

8. PREPARATION OF CALIBRATION STANDARDS

Calibration standards are not prepared for this method, however electroplated sources are purchased from an outside vendor, Isotope Products Laboratories, and used for instrument calibration. Refer to SOP 714 for calibration standards.

9. CALCULATIONS

As defined in SOP 743, the following one-sigma preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total

Propagated Uncertainty (TPU). TPU calculations for the chloride column along with soil/water preparation run previous to this method are stated in SOP 778.

9.1 Methanol columns require a preparation uncertainty factor of 0.0359. This is based on two quantitative transfer and one reagent addition. See the following equation:

$$0.0359 = \sqrt{0.025^2 + 0.025^2 + 0.006^2}$$

9.2 TEVA™ columns require a preparation uncertainty factor of 0.0257. This is based on one quantitative transfer and one reagent addition. See the following equation:

$$0.0257 = \sqrt{0.025^2 + 0.006^2}$$

9.3 Samples prepared according to SOP 778 have an additional preparation uncertainty of 0.1020 for a final TPU prep factor of 0.1111, as shown below:

$$0.1111 = \sqrt{0.0359^2 + 0.0257^2 + 0.1020^2}$$

10. QUALITY CONTROL

Acceptance criteria for QC samples and other quality indicating parameters can be found in SOP 715 and in the LIMS program specifications.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

11.1.2 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

11.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (*e*.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

11.1.4 Any chemicals with a TLV of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents, acids).

11.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

11.1.6 Use extreme care when using hydrofluoric acid (HF). Work only in a fume hood that has adequate ventilation and personnel safety features. **Never inhale or allow skin or clothing to be exposed to HF fumes.**

11.1.7 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

11.2 WASTE DISPOSAL

11.2.1 Wastes that are "corrosive only", such as glacial acetic acid and sulfuric acid waste, are disposed of by discharging into the PAR waste water treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

11.2.2 Hydrofluoric acid at any concentration is collected in a labeled waste carboy. This includes any excess HF from dissolution of samples and all solutions remaining from the micro precipitation process. Notify the Waste Disposal Coordinator for disposal.

11.2.3 The methanolic effluent that is generated in the anion exchange process is collected in a labeled waste carboy. Notify the Waste Disposal Coordinator for disposal.

11.2.4 The ammonium thiocyanate effluent that is generated using TEVA^{TM} resin is collected in a labeled waste carboy. Notify the Waste Disposal Coordinator for disposal.

11.2.5 All acid wastes not containing HF, MeOH or NH_4SCN that are generated in separation operations are disposed of to the waste tanks (down the drain) unless otherwise specified due to hazardous constituents.

12. REFERENCES

12.1 Schierman, M.J. 1994. "Characterization of Americium and Plutonium Concentrations in Soil Profiles at the Rocky Flats Plant". Thesis for Master of Science Degree, Dept. of Radiological Health Sciences, Colorado State University.

12.2 Yamato, A. "An Anion Exchange Method for the Determination of ^{241}Am and Plutonium in Environmental and Biological Samples", Journal of Radioanalytical Chemistry, Vol. 75, Nos 1-2 (1982), pages 265- 273.

12.3 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

7/5/06: Added LIMS Program Specification language and missing TLV information; augmented apparatus list; updated format. No technical revisions made.

7/18/08: Minor clerical corrections made, added introductory comments to QC Section 10. No technical revisions made.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 783 REVISION 8

TITLE: RADIUM-226 IN AQUEOUS AND SOIL MATRICES -- RADON EMANATION TECHNIQUE -- METHOD EPA 903.1

FORMS: 302, 631 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/4/07

LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: NEW, Rev0, 3/31/96; Rev1, 12/26/96; Rev2, 1/10/99; Rev3, 9/21/01; Rev4, 4/7/03; Rev5, 9/22/03; Rev6, 4/10/0; Rev7, 9/11/06; Rev8, 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references, EPA Method 903.1, describes a procedure to determine ^{226}Ra in soil and aqueous matrices. The method is based on the emanation and scintillation counting of ^{222}Ra and progeny produced by the decay of ^{226}Ra.

Due to the potential difficulty in obtaining a complete dissolution of some solid matrices, it is recommended that ^{226}Ra in soils and solids be routinely analyzed directly by gamma spectroscopic determination of ^{214}Pb and ^{214}Bi progeny. Radon emanation in soils should be performed only at the specific request of the client.

2. SUMMARY

2.1 The ^{226}Ra in aqueous samples is concentrated and separated by coprecipitation with barium sulfate. Prior to separation, a portion of the sample is removed for inductively coupled plasma atomic emission spectrometry (ICP-AES) determination of the preparation concentration of barium in the sample. The $Ba[Ra]SO_4$ precipitate is dissolved in basic EDTA solution, placed in a 40mL VOA vial, purged of any existing ^{222}Ra, and stored to allow quantitative in-growth of ^{222}Ra. After in-growth, the radon is purged into an alpha scintillation cell. The short-lived ^{222}Ra progeny are allowed to come to equilibrium with the parent radon (~4hrs) before the scintillation cell is counted for alpha activity. The 4hr in-growth period also allows for the decay of other radon isotopes.

2.2 In solids, ^{226}Ra is liberated from the solid matrix by a total digestion of the solid. The sample is muffled, transferred to a polypropylene beaker and digested in the presence of strong acids. After digestion, the sample is transferred to a VOA vial, purged, and counted, as stated in Section 8.1.

2.3 The absolute measurement of ^{226}Ra is effected by calibrating the scintillation cell (and emanation system) with a solution of NIST-traceable ^{226}Ra. Each alpha detector/cell combination must be calibrated individually and the cell constants applied to the specific detector/cell pairs when calculating results.

2.4 The detection limit for this method is dependent upon sample aliquot, sample count time, length of the in-growth period, the scintillation system background activity, and detection efficiency. The routine minimum detectable activity (MDA) is 1.0pCi/L for aqueous samples, and 1.0pCi/g for solid samples.

2.5 As a result of fluctuation of the background due to build-up and decay of Rn and its progeny, dedicated backgrounds must be counted for each detector/cell combination prior to emanation of each sample.

2.6 The emanation apparatus is set up as shown in Figure 1.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, performance of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 There are no known radiometric interferences to this method. Samples such as heavily sedimented samples and high brine content samples may require special treatment or a reduced aliquot prior to initiation of chemical separation procedures, as they might require more than 30mL of solvent to dissolve.

4.2 Water samples with high concentrations of sulfate-forming cations may present barium chemical recovery problems, but do not interfere with radiometric recovery in samples.

4.3 Soil samples in which visible precipitate accumulates in the bubbler during the ingrowth period may cause a low bias in the final results, as Ra-226 and the associated Rn-222 progeny may be sequestered in the precipitate and consequently be unavailable for radon emanation. Samples with visible sediment at the time of emanation require that the client be informed of the potential bias in the analytical results. Corrective action may involve either of the following options:

4.3.1 Disclose the potential bias to the analytical results in the case narrative and submit the results with that qualification.

4.3.2 Re-prepare the sample at a reduced aliquot, with a corresponding increase in detection limits. The reduced aliquot should be estimated at the sample mass that is unlikely to form precipitate in the bubbler.

4.4 Scintillation cells should be stored for at least four hours after purging with helium before background counts can be obtained. If cells are not stored for at least four hours before background counting, radon and its progeny that are not completely purged from the cell will not be in secular equilibrium and the background may be biased high, resulting in a low bias to the final analytical results.

5. APPARATUS AND MATERIALS

5.1 scalar, Ludlum Model 1000, or equivalent

5.2 photo multiplier tube, Ludlum Model 182, or equivalent

5.3 Tygon^{TM} tubing, various sizes

5.4 glass wool

5.5 gas regulator valve, 3000 PSIG, max

5.6 multi-turn needle valves, 75 PSIG, max, Cole Parmer, or equivalent

5.7 VOA vials, with septum lids, 40mL

5.8 vacuum pump, 2-Stage, GE, or equivalent

5.9 scintillation cells

5.10 stirring hotplate

5.11 laboratory balance, resolution 0.01g

5.12 centrifuge tubes

5.13 graduated cylinder, 1L

5.14 beakers, Pyrex™, 100mL and 1.5 or 2L sizes, or similar

5.15 specimen cups, polypropylene, 100mL and 250mL sizes

5.16 spatulas, plastic

5.17 test tubes, disposable, with polyethylene test tube caps, 15mL

5.18 BD™ syringe ,with luer-lock tip, or equivalent, 3mL

5.19 Deflected-point septum penetration needles

5.20 stopcocks

5.21 BD™ insulin syringe, 30 gauge x 8 mm, 0.5cc, short needle

5.22 Pipette, 1.0mL and 0.1mL sizes, with disposable pipette tips

5.23 Whatman™ filter paper, #42 (90mm), or similar

5.24 Parafilm™

5.25 stir bars

5.26 watch glasses

5.27 vortex mixer

5.28 Drierite™, or indicating desiccant, 10-20 mesh

6. REAGENTS

NOTE: TLV and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Distilled or deionized (DI) water, ASTM Type-II, or equivalent

6.2 Ascarite, drying reagent, 8-20 mesh.
TLV = 2mg/m3 = 1.22ppm (NaOH, ceiling)

6.3 Barium carrier, 16mg/mL, standardized: Dissolve 28.46g $BaCl_2 \cdot 2H_2O$ in DI water. Add 5mL 16NHNO_3 and dilute to 1000mL with DI water. See Paragon SOP 712 for standardization procedure.
TLV = 0.5mg Ba/m3 = 0.06ppm (TWA). Irritant.

6.4 EDTA reagent, basic 0.25M: Dissolve 20g NaOH in 750mL water and slowly add 93g Na2EDTA· 2H2O. Heat and stir until dissolved, filter through coarse filter paper and dilute to 1L in DI water. Adjust pH to 10 with sodium hydroxide. Irritant.

6.5 Helium, gas. Ultra high purity, 99.999%.

6.6 Hydrochloric acid (HCl), 12N, conc.
TLV = 5ppm (ceiling).

6.7 Nitric Acid (HNO_3), 16N, conc.
TLV = 2ppm (TWA). Irritant, corrosive.

6.8 ^{226}Ra standard solution, Traceable to NIST, or equivalent: Prepare stock dilution of approximately 50pCi/mL. Prepare one source for calibration purposes, and a different independent source for spiking purposes.

6.9 Sulfuric acid, 18N: Carefully add 500mL 36N H_2SO_4 to approximately 450mL of DI water. Dilute to 1L with DI water.

NOTE: A rubber apron and face shield must be worn when handling concentrated H_2SO_4. Add H_2SO_4 slowly with stirring to prevent boiling due to liberation of heat during mixing.
TLV = 1mg/m3 = 0.25ppm (TWA). Irritant.

6.10 Sulfuric acid, 0.1N: Dilute 120mL 18N H_2SO_4 to 22L with DI water.
TLV = 1 mg/m3 = 0.25ppm (TWA). Irritant.

6.11 Nitric Acid, 8N: Carefully add 500mL of concentrated HNO_3 to approximately 400mL of DI water. Then bring to 1 liter with DI water.
TLV = 2ppm (TWA). Irritant, corrosive.

6.12 ICP diluting solution: Add 10mL 16N HNO_3 and 50mL 12N HCl to approximately 500mL of DI water. Bring to 1 liter with DI water.
TLV = See Sections 6.6 and 6.7.

6.13 Hydrofluoric acid (HF), 48.0-51.0%, conc.
TLV = 3ppm (ceiling). Irritant, burns, bone, teeth, fluorosis.

NOTE: Employees must be familiar with the HF burn kit location and use before performing this procedure.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Liquids: A sample should be collected in a manner that will provide the most representative sample. Collect a 2 liter sample in a plastic container, from a free-flowing source when possible.

7.1.1 For a total sample analysis, preserve the sample with nitric acid to a pH<2.0 upon collection (15mL 1N HNO_3 / 1L H_2O). If not preserved upon collection, then the sample should be preserved within 5 days. For a total sample analysis, preserve the sample with nitric acid to a pH<2.0 upon collection (15mL 1N HNO_3 / 1L H_2O). If not preserved upon collection, then the sample should be preserved within 5 days. If preservation is delayed, hold samples for a minimum of 24 hours after preservation.

7.1.2 For a "dissolved" sample analysis, use a 0.45µm membrane filter to remove the solids from the sample. After filtering, acidify the sample with nitric acid to a pH<2.0.

7.2 Solids: Preservation is not required. A representative sample of 25-50 grams should be submitted for analysis.

8. PROCEDURE

8.1 CALIBRATION

8.1.1 BACKGROUND CALIBRATION

Prior to each sample analysis, the cell is purged with helium and stored for at least four hours. The number of background counts associated with the alpha scintillation cell is then obtained by counting the cell in the detector to be used. The background calibration must be counted for a duration equal to or longer than the planned sample count. If the sample and background count times differ (e.g. if the sample count is shorter than the background count), the number of background counts should be adjusted to match the sample count time. Record this adjustment on a Quality Assurance Summary Sheet (QASS), Form 302. The count rate of the empty cell is employed as the background count rate in calculated results.

8.1.2 PLATEAU CALIBRATION (OPERATING VOLTAGE DETERMINATION)

The purpose of the plateau calibration is to determine the optimum operating voltage for the photomultiplier tube. This optimized operating voltage minimizes the detector background, while stabilizing the counting efficiency, under normal operating conditions. Plateau calibrations must be performed prior to initial use of the instrument and at least annually, prior to the efficiency calibrations.

8.1.2.1 Adjust the voltage setting on the scalar to a low voltage of approximately 500 volts.

8.1.2.2 Count the daily check source for one minute and record the number of counts in the maintenance logbook.

8.1.2.3 Increase the voltage by 100 volt increments, repeating the previous Step each time.

8.1.2.4 Continue to increase the operating voltage past 1,000 volts until the count rate significantly increases, indicating that the voltage is no longer on the plateau. Do not exceed 1,500 volts.

8.1.2.5 Plot the voltage against the gross counts on a scatter plot.

8.1.2.6 Repeat the process described above, removing the daily check source and counting an empty detector instead. Count times should be increased to five minutes and the range of voltages need only encompass the "flat" part of the plateau.

8.1.2.7 Select an operating voltage on the "flat" part of the plateau, where the background count rate is lowest.

8.1.2.8 If the operating voltage is changed from the existing setting for sample analyses, all detector/cell combinations must be recalibrated for counting efficiency.

8.1.3 EFFICIENCY CALIBRATION

The calibration constant of each detector-scintillation cell combination must be determined, using NIST-traceable ^{226}Ra solution. This calibration is performed at least annually. The constant is determined as follows:

8.1.3.1 Prepare calibration sources by adding 25mL EDTA to a 40mL VOA vial. Be sure to prepare enough sources to count one in each cell and a few extra sources in case a cell needs to be recalibrated. Calibration sources may only be used once then must be discarded in the "Pb/Ba Aqueous Hazardous Waste" container.

8.1.3.2 Spike the samples with approximately 200dpm of ^{226}Ra spiking solution. The samples should be purged with helium to ensure that no radon is present prior to radon in-growth, see Section 8.2. The samples may be sealed immediately

after spiking, without purging with helium, as long as they are stored for at least 26 days to achieve >99% in-growth.

8.1.3.3 The calibration constant is a composite measure of the emanation efficiency of the sample, the collection efficiency of the system, and the counting efficiency of the cell. The calibration procedure is conducted, similar to sample measurements, after the alpha emitting radon daughters have come to equilibrium with ^{222}Ra (i.e., 4 hours after transfer to the scintillation cell). The duration of the calibration count should be sufficient to allow the collection of at least 10,000 counts. Record the detector, cell ID, count start time, and count duration on the appropriate benchsheets and logbook. If a given cell is to be used with multiple detectors, it may be recounted in those detectors and calibration constants generated for each detector/cell combination.

NOTE: If a cell is to be calibrated in multiple detectors, a background measurement must be obtained for that cell in each detector prior to transferring and counting the sample.

8.1.3.4 Each detector-scintillation cell combination should be calibrated with a NIST-traceable ^{226}Ra standard at least annually.

8.1.3.5 See Section 9.5.6 for calibration constant calculations.

8.1.4 INITIAL CALIBRATION VERIFICATION (ICV) AND CONTINUING CALIBRATION VERIFICATION (CCV)

8.1.4.1 ICV and CCV sources are prepared in the same manner as efficiency calibration sources, see Section 8.1.3, using an independent second source, instead of the calibration source.

8.1.4.2 To verify that the efficiency calibration is valid, count one ICV source per cell in each detector after the calibration is complete. As with the calibration sources, ICVs may be counted for the same sample in multiple detectors, as long as a background measurement is made for the cell in a specific detector.

8.1.4.3 Calculations for ICV sources are the same as those in Section 9 for samples, assuming a 100% chemical yield.

8.1.4.4 The efficiency determined for a specific cell in a specific detector is used to determine the radiometric recovery for each ICV. The radiometric recovery must be within ±15%; if the radiometric recovery is > ±10%, approval must be obtained from the Radiochemistry Technical Manager before the cell can be used.

8.1.4.5 CCVs are analyzed once every twenty analytical runs on each detector/cell combination and are subject to the same acceptance criteria as ICVs. If a CCV falls outside the ±15% acceptance criteria, the CCV is repeated. If the failure is confirmed, the cell is removed from service until it is recalibrated.

8.1.5 DAILY CHECK SOURCE
A NIST-traceable Thorium source is counted long enough to acquire at least 2,000 counts before and after samples are counted each day, bracketing the sample counts to ensure that the detector and scalar are working properly.

8.2 AQUEOUS SAMPLE PREPARATION

8.2.1 Verify and record (on Form 631) the pH of the sample according to SOP 733.

8.2.2 Using a graduated cylinder, aliquot the sample into a labeled 1.5L or 2L beaker. A sample aliquot of 1L is typical for this method, but may need to be reduced due to matrix interference or volume limitations. All samples should be brought to a final volume of 1L with DI water. Add a stir bar to each beaker and place on a stirring hot plate.

8.2.3 Prepare QC samples according to Section 10.

8.2.4 HOW TO TAKE INITIAL ICP ALIQUOT

8.2.4.1 Prior to adding any reagents, spikes, or carriers to the sample, use a calibrated pipette to remove 1mL of sample and place into a clean test tube filled with 9mL of ICP diluting solution and labeled with the sample ID and “i”, to indicate the initial ICP aliquot. Cover with a test tube cap and invert tube several times to mix thoroughly. Set aside until final ICP aliquot has been taken.

8.2.4.2 A “reference carrier” (RC) should also be prepared by adding 1mL Ba carrier to 1L of DI water. Mix thoroughly, remove 1mL of solution and dilute to 10mL as stated above

for samples. Submit with samples for ICP analysis to provide a reference concentration for the yield calculations.

8.2.5 To each water sample, add 20mL of 12N HCl, 1.0mL barium carrier, and appropriate amount of spiking solution to LCS and any MS samples. Cover with a watch glass and heat to a gentle boil.

8.2.6 Cautiously, with vigorous stirring, add 25mL 18N H_2SO_4. Continue boiling and stirring at least 10 minutes. Remove from heat. Remove stir bar, rinsing with 0.1N H_2SO_4. Let precipitate settle overnight, or at least four hours (overnight is recommended).

8.2.7 Aspirate the supernatant into the PAR waste water treatment facility.

8.2.8 Slurry the precipitate and transfer to a labeled centrifuge tube with a minimum amount of 0.1N H_2SO_4. Centrifuge at 3500rpm for 10-15 minutes and discard supernatant into the PAR wastewater treatment facility. Wash twice with 15mL of 0.1N H_2SO_4. Centrifuge and discard washes into the PA wastewater treatment facility.

8.2.9 Add 25mL basic EDTA reagent, heat in a water bath and stir well until dissolved. After dissolution, remove from the steam bath and allow the samples to cool.

NOTE: If the precipitate is difficult to dissolve, additional EDTA can be added; however, the maximum volume of EDTA that may be used is 30mL, as the VOA vials are only 40mL. Record the volume of EDTA used on the benchsheet.

8.2.10 HOW TO TAKE FINAL ICP ALIQUOT

8.2.10.1 Vortex the sample to mix thoroughly. Using a calibrated pipette, aliquot 0.1mL of sample into a clean, labeled test tube containing 9.9 or 10mL of DI water (record the volume of water used). Cover with Parafilm, and invert several times to mix completely. With a calibrated pipette, aliquot 1.0mL of the diluted sample into another clean test tube labeled with the sample ID and "f" and containing 9.0mL of ICP diluting solution. Cover with a test tube cap and mix well. Submit the initial and final test tubes to the Metals Lab with proper bench sheets for analysis.

8.2.10.2 Upon the return of ICP sample fractions to the radiochemistry lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the PAR waste water treatment facility (i.e., down the

laboratory sink with plenty of cold tap water). The test tubes may be soaked in a Radiacwash™ solution, rinsed with tap water and discarded into the sanitary trash. The tubes containing the intermediate, DI water diluted, sample may be disposed of in the same manner.

8.2.11 Transfer the solution remaining after Step 8.2.10 to a labeled VOA vial using approximately 2.5mL EDTA to rinse the centrifuge tube. The centrifuge tubes may be soaked in Radiacwash™, rinsed, and discarded into the sanitary trash.

8.2.12 Purge the samples in the VOA vials for approximately 20 minutes with helium to remove any radon from the solution prior to sealing the vial.

8.2.13 Seal the VOA vial and record the date and time that the purge ended as t_1, beginning of ^{222}Ra in-growth, on the benchsheet. Store the solution for at least 4 days for in-growth of ^{222}Ra (typical storage time is 7 days, full in-growth is achieved after 30 days).

8.2.14 At the end of the storage period, fill the upper half of a modified 3mL syringe with Drierite™ to about the 2.5mL mark and the lower half with ascarite to about the 3mL mark. Place a small amount of glass wool in the end of the syringe to secure the drying agents. The column is a single use column and can be discarded in the sanitary trash after transferring the sample. Store unused columns in the desiccator.

8.2.15 Assemble the radon emanation apparatus (see Figure 1), including a scintillation cell with a current background measurement, see Section 8.1. Evacuate the scintillation cell by applying vacuum to the cell for about 10 seconds and transfer the vacuum to the VOA vial after attaching it to the emanation apparatus by quickly opening and closing the stopcock on the cell.

8.2.16 Adjust the helium pressure to deliver a minimum flow rate. Fill the helium feed line with helium. Puncture the septum of the VOA vial with the helium feed needle.

8.2.17 After bubbling has subsided, gradually open the scintillation cell stopcock. Allow bubbling to proceed at a rate, as determined by experience, such that 15 to 20 minutes are required to complete the transfer. When the bubbling subsides the apparatus is essentially at ambient pressure.

8.2.18 When the system is at ambient pressure, remove the helium feed needles, close the scintillation cell stopcock, and dissemble the

apparatus. Record the ending transfer date and time as t_2, beginning of ^{222}Rn progeny in-growth, on the benchsheet.

8.2.19 Store the scintillation cell for at least 4 hours to ensure equilibrium between ^{222}Rn and its progeny, and to allow other isotopes of radon and their progeny to decay. Count the alpha scintillations from the cell in a scintillation cell counter with a light-tight enclosure that protects the photomultiplier tube. Record the beginning of the counting date and time on the benchsheet to correct for the decay of ^{222}Rn.

NOTE: After each analysis, flush the cell thoroughly with helium for at least 1 minute and store at atmospheric pressure to remove radon from the cell and prevent the build-up of radon daughter products. The cell must be stored for at least four hours prior to re-use.

8.3 PREPARATION OF SOLID SAMPLES

8.3.1 Weigh 1-4 grams dried, pulverized soil into a permanently labeled glass beaker. Typical aliquot size is 2.0g but may be adjusted due to MDA or matrix interference considerations. Record the sample weight and beaker number on the benchsheet.

8.3.2 Prepare QC samples according to Section 10.

8.3.3 Dry the beakers on a hotplate set at 2. Samples must not have any standing liquid prior to muffling. Cover the beakers with a watch glass and muffle at 600°C for at least 4 hours.

8.3.4 Transfer the sample to a 250mL polypropylene specimen cup, using at least 20mL 16N HNO_3 to rinse the beaker. Scraping with a plastic spatula may be necessary to remove all of the soil from the beaker.

8.3.5 Add 20mL HF, cover with a 100mL polypropylene specimen cup, and heat for 4 hours on a steam bath.

8.3.6 Remove the 100mL cup and evaporate to dryness. The 100mL cups may be rinsed thoroughly with tap water and discarded into the sanitary trash.

8.3.7 Add 10mL 8N HNO_3 to the samples while they are on the steam bath to facilitate dissolution. The samples may be covered with a 100mL polypropylene cup to prevent evaporation.

8.3.8 Transfer the solution to a labeled VOA vial, rinsing the beaker with three 5mL rinses of 8N HNO_3, for a total volume of 25mL. The

250mL cups may be soaked in Radiacwash™, rinsed, and discarded into the sanitary trash.

NOTE: If the digestate residue is difficult to dissolve, additional 8N HNO_3 can be added; however, the maximum volume of 8N HNO_3 that may be used is 35mL, as the VOA vial capacity is only 40mL.

8.3.9 Proceed to Step 8.2.12.

9. CALCULATIONS

9.1 Calculate the actual volume, V_A, of sample analyzed for aqueous samples (accounting for volumes of sample removed) as follows (Note: The actual volume for solid samples is the same as the initial sample volume because no sample is removed during the process):

$$V_A = V * \frac{V_i - icp_i}{V_i} * \frac{V_f - icp_f}{V_f}$$

where:

V = sample aliquot (L, g)

V_i = sample final dilution volume (mL)

icp_i = initial aliquot taken for ICP (mL)

V_f = sample volume in EDTA (mL)

icp_f = final aliquot taken for ICP (mL)

9.2 Calculate the barium chemical recovery for aqueous samples, Y, as a percentage, as follows (barium chemical recovery is assumed to be 100% for solid samples):

$$Y_i = (V_i - V_{ICP}) * ICP_i * DF$$

$$Y_f = V_f * ICP_f * DF$$

$$Y_{RC} = V_{RC} * ICP_{RC} * DF$$

$$Y = \frac{Y_f}{Y_i + Y_{RC}} * 100\%$$

where:

Y_i = barium recovery from initial ICP aliquot (µg)

V_{ICP} = volume removed for ICP analysis

ICP_i = initial barium concentration measured by ICP (µg/mL)

DF = dilution factor

Y_f = barium recovery from final ICP aliquot (µg)

ICP_f = final barium concentration measured by ICP (µg/mL)

Y_{RC} = barium recovery from RC aliquot (µg)

V_{RC} = RC final volume (mL)

ICP_{RC} = RC barium concentration measured by ICP (µg/mL)

9.3 The sample activity concentration, counting uncertainty, instrument uncertainty, and minimum detection concentration calculations are provided in SOP 708.

9.4 TPU FACTORS
As defined in SOP 708, calculate the one-sigma (1σ) Total Propagated Uncertainty (TPU) as follows:

9.4.1 Aqueous Samples: Require a 1σ preparation uncertainty factor of 0.110. This is based on one gross aliquot, one volumetric measurement, one ICP determination, one spike/carrier addition, three quantitative transfers, one pipetting and two reagent additions:

$$0.110 = \sqrt{.05^2 + .006^2 + .083^2 + .025^2 + .025^2 + .025^2 + .025^2 + .004^2 + .006^2 + .006^2}$$

9.4.2 Solid Samples: Require a 1σ preparation uncertainty factor of 0.071. This is based on one gross aliquot, one mass measurement, one spike/carrier addition, and three quantitative transfers:

$$0.071 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2 + 0.025^2 + .025^2}$$

9.4.3 Instrument Uncertainty (IU):

The IU is 0.054. This is based on the in-house preparation of calibration standards, counting reproducibility, counting efficiency, and dead time estimates:

$$0.054 = \sqrt{0.05^2 + 0.01^2 + 0.015^2 + 0.01^2}$$

10. QUALITY CONTROL

Per Paragon protocol, spikes are added before the sample receives any chemical treatment. Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.1 A blank, prepared in one liter of DI water for aqueous samples, must be analyzed with each batch of 20 or fewer field samples (i.e., at a five percent frequency). No matrix is used for blanks used in soil batches - muffle an empty 100mL beaker.

10.2 One blank spike (LCS), prepared in one liter of DI water for aqueous samples, and a Whatman™ filter paper for solid samples, must be analyzed with each batch of 20 or fewer field samples (i.e., at a 5 percent frequency). The spiking level for LCSs should be at least 4-10 times the requested MDA, or 100dpm, whichever is larger.

10.3 For solid samples, at least one matrix spike (MS) should be prepared for each batch of 20 samples (i.e., at a 5 percent frequency). If there is more than one type of solid matrix in the batch, an additional MS should be prepared for each type of matrix present. The spiking level should be at least 4-10 times the expected activity of the sample, or 100dpm, whichever is larger.

10.4 Duplicate sample analyses will be performed at a minimum frequency of ten percent. If there is insufficient sample volume for this frequency of sample duplicates, LCS duplicates may serve as a measure of batch reproducibility.

11. DEVIATIONS FROM METHOD

11.1 This SOP meets the requirements of EPA Method 903.1 for water samples. In addition to describing a procedure for aqueous samples, this SOP describes a procedure for determining ^{226}Ra and its progeny in soil, which the laboratory employs at a client's request. Also, this SOP provides procedures for determining the chemical yield as an addition to EPA Method 903.1. This measurement increases the accuracy of the method.

11.2 Only 1.0mL of barium carrier, instead of 2.0mL, is added to aqueous samples. The lesser amount of carrier facilitates dissolution of the precipitate in EDTA. Since Ba yield is determined by ICP, this amount is more than sufficient for $Ba(Ra)SO_4$ precipitation and Ba chemical recovery measurement.

11.3 25mL of EDTA is used to dissolve the $Ba(Ra)SO_4$ precipitate. This volume ensures a complete dissolution of the precipitate in a normal sample. For difficult matrices, up to 35mL may be used to dissolve the precipitate.

11.4 A 40mL VOA vial is used for sample storage and transfer instead of a radon bubbler. There is essentially no difference in the function of these two pieces of apparatus. VOA vials are more cost effective and easier to store, so a larger number of samples may be stored at once.

11.5 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the lab's internally derived acceptance criteria.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Safety glasses, lab coats and gloves should be worn in the laboratory at all times.

12.1.2 Use care when handling mineral acids (e.g., HNO_3, H_2SO_4). Work only in a fume hood with adequate ventilation and wear appropriate eye, face, and body protection.

12.1.3 Radon is an odorless, colorless gas. Care should be taken when handling samples where there is a possibility of radon buildup in the container (e.g., purging samples in VOA vials prior to in-growth). Work in a well ventilated area, preferably a fume hood.

12.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

12.2 WASTE DISPOSAL

12.2.1 Four Satellite Accumulation Area (SAA) containers are available for disposal of samples after the results are reported. (One each for radioactive and non-radioactive aqueous samples and solid samples.)

12.2.2 Other process waste, as indicated in Section 8, may be discarded into the PAR waste water treatment facility.

13. REFERENCES

13.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, Method 903.1, Radium-226-Radon Emanation Technique.

13.2 HASL-300, Environmental Measurements Laboratory Procedure Manual, Method Ra-03, 27th Ed., Rev. Feb. 1992.

13.3 Standard Methods for the Evaluation of Water and Wastewater, Method 7500-Ra C., 18th Edition, 1992.

13.4 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.5 Analysis of Ra-226 in Soils by Alpha Scintillation Without Chemical Separation (EPA 903.1m); Burns, Freda, Gallegos, Workman; RRMC, 2003, \\PARAGON\VOL1\ATI\OPRTNS\RAD\Meth_Dev\RaEmSol\ABSTRACT.DOC.

13.6 FMC Method Blank Contamination Trial; PA work order 0422022; Kellogg; 3/22/05, \\2ksvr2\2ksvr2_vol1\InstRawData\Rad\In-House wo\2004\Ra\0422022_FMC_MB.PDF.

13.7 Radium-226 in soils by Rn emanation: EDTA vs. HNO_3; PA work order 0416017; Freda; 5/3/04, \\2ksvr2\2ksvr2_vol1\InstRawData\Rad\In-House wo\2004\Ra\0416017_EDTAvsHNO3.PDF.

DOCUMENT REVISION HISTORY

4/10/06: Calibration frequency reduced from every 20 analyses to annually with the adoption of CCVs every 20 analyses. Plateau calibration procedure described. Soil digestate changed from EDTA to HNO_3. LIMS Program Specification directive added to 'Responsibilities' Section. Added DOCUMENT REVISION HISTORY.

9/11/06: Added comment to INTERFERENCES describing corrective action for solid digestates that precipitate in the bubble apparatus.

8/31/07: Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Section 7.1. Removed activity and MDC calculations from Section 9 and referenced Paragon SOP 708 instead. Added statements to Section 10 that per Paragon protocol, spikes are added before the sample receives any chemical treatment, and acceptance limits for quality control parameters may vary per client specifications, consult applicable LIMS program specification.

Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Must Discard 30 Days from _____ (date printed)

Ammended 9/27/07 (Section 8.1): Hold for 24hrs (not 16) after pH adjustment (consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57) DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 784 REVISION 0

TITLE: DETERMINATION OF RADIUM-228 PER EPA METHOD 904.0 – DRINKING WATER COMPLIANCE

FORMS: 631 (use most current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 10/5/06

QUALITY ASSURANCE MANAGER _____ DATE 10/5/06

LABORATORY MANAGER _____ DATE 10-5-06

HISTORY: New, Rev0, 10/5/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references -- EPA Method 904.0 -- describe the measurement of radium-228 in drinking waters. This technique is devised so that the beta activity from actinium-228, which is produced by the decay of radium-228, can be determined and related to the activity concentration of radium-228 present in the sample.

To quantify actinium-228 and thereby determine radium-228, the efficiency of the beta counter for measuring the very short half-lived actinium-228 (average beta energy of 0.404MeV), is to be calibrated with a beta source of comparable average beta energy such as Sr-89 (average beta energy of 0.589MeV).

If desired, the determination of radium-226 may be conducted on the purified radium solution prior to barium sulfate precipitation determination of the chemical yield. Methods 903.1, 903.0, and their equivalent methods in SW-846, HASL, or Standard Methods, are compatible with this approach.

2. SUMMARY

2.1 The radium isotopes in a water sample are collected by co-precipitation of barium and lead sulfate and purified by re-precipitation out of a basic EDTA solution. After a 36-hour period to allow for the ingrowth of actinium-228, lead is removed as PbS, actinium is carried on yttrium (Y) as the hydroxide and mounted as the oxalate, and quickly beta counted (~6 hours) to minimize decay of the short-lived Ac-228.

2.2 If radium-226 according to EPA Method 903.0 or 903.1 is requested, the supernatant containing radium following separation of the Y/Ac is taken into SOP 712 or 783, as appropriate.

3. RESPONSIBILITIES

3.1 **It is the responsibility of the preparation chemist and instrument analyst to perform this method in strict accordance with this SOP and to complete all documentation required for review.**

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 The **preparation chemist** shall notify the Instrument Lab Gas-Flow Proportional Counter analyst in advance of the number of samples arriving and the expected delivery date and time. This allows the analyst to schedule adequate instrument time to analyze the short-lived Ac-228 analyte.

3.4 It is the responsibility of the instrument analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715, as well as the LIMS program specifications related to the client, project, and test method being performed.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the **preparation or analysis** of the samples. Any discrepancies must be noted and corrective action taken and documented.

3.6 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

4. INTERFERENCES

4.1 As indicated in EPA Method 904.0, performance studies show that the presence of strontium/yttrium-90 in a water sample will lend a positive bias to the measured radium-228 activity.

4.2 Excess barium in the sample may interfere with an accurate chemical yield determination.

4.3 The presence of significant quantities of dissolved constituents that may form insoluble sulfate precipitates interferes with the proper separation of radium and the subsequent quantification of Ra-228. In this case, reduced sample volumes may be required to minimize the matrix interference effects.

4.4 The presence of sediments in the preserved sample is a significant interference to this method. Drinking water protocols indicate that the entire sample should be analyzed so that the dose estimates to the consumer are representative of the actual water that is consumed. Consequently, the analysis of sedimented water samples may result in a significant bias to the analytical results, and these results may not be representative of the dose received by the consumer.

4.5 The presence of significant quantities (>500mg) of suspended solids in a sample may interfere with collection of the barium sulfate precipitate, which may result in a low chemical yield in the analytical process.

5. DEVIATIONS FROM THE METHOD

Chemical yields in this method are performed at Paragon Analytics by ICP analysis of the Ba and Y carriers, rather than by the gravimetric determination described in EPA 904.0. This avoids potential biases in the yield determinations presented by interfering constituents and the observed inconsistencies in the hydration factor of the dried yttrium oxalate precipitate.

6. APPARATUS AND MATERIALS

6.1 Stirring hot plate

6.2 Magnetic stir bars

6.3 Centrifuge

6.4 Centrifuge tubes, polypropylene, Falcon™, 50mL, Do Not Substitute

6.5 Counting planchets, stainless steel, flat, 2”

NOTE: Prior to use, the planchets are soaked in diluted Radiacwash™ for approximately three hours, drained, rinsed with deionized water, transferred to a metal pan, and placed in the drying oven until dry.

6.6 Funnels, plastic

6.7 Graduated cylinders, 100mL and 1 or 2L

6.8 Pyrex™ beakers, or equivalent, 2L

6.9 Forceps

6.10 Specimen cups, with lids, polypropylene, 150mL

6.11 Specimen cups, polypropylene, 250mL

6.12 Eppendorf™ pipettors, or equivalent

6.13 Test tubes, polypropylene, **with polyethylene caps**, disposable, 15mL

6.14 Parafilm™

6.15 Desiccator

6.16 Vortex mixer

6.17 Hot water bath

6.18 Transfer pipets, disposable

6.19 Whatman™ #42 filter paper, ashless, 90mm diameter

6.20 Qualitative filter paper, fluted

6.21 Volumetric flask, 1L

6.22 Analytical balance, Mettler™ AE 200, or equivalent

6.23 **pH paper, wide range**

7. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) of less than 50ppm, shall be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

7.1 Deionized (DI) water, **obtained from the laboratory's DI water system**

7.2 Acetic acid, 17.4M, Glacial CH_3COOH, reagent grade, concentrated
TLV = 10ppm (TWA); Irritant

7.3 Ammonium hydroxide, 15M, NH_4OH, reagent grade, concentrated
TLV = 25ppm (TWA for NH_3)

7.4 Ammonium oxalate, 5%: Dissolve 25g $(NH_4)_2C_2O_4 \cdot H_2O$ in about 400mL of hot DI water. When cool, dilute to 500mL with DI water.

7.5 Ammonium sulfate, 200mg/mL: Dissolve 200g $(NH_4)_2SO_4$ in DI water and dilute to 1000mL.

7.6 Ammonium sulfide, 2%: Dilute 10mL $(NH_4)_2S$ (20-24%) to 100mL with DI water.

7.7 Standardized Barium Carrier, 16mg/mL (27mg/mL $BaSO_4$ yield)

7.7.1 PREPARATION: Place a 1000mL Class A volumetric flask on a stir plate, add a stir bar and ~500mL of DI water. Add 28.5g $BaCl_2 \cdot 2H_2O$ and stir until completely dissolved, then add 5mL 16M HNO_3. Remove stir bar, rinsing with DI water, and dilute to 1000mL with DI water. Transfer to a clean, labeled 1L poly container. Document the

preparation of this carrier in the Reagent Prep Logbook and Paragon's Standards and Solutions Database.
TLV = 0.5mg Ba/m^3 = 0.06ppm (TWA). Irritant

7.7.2 STANDARDIZATION OF Ba CARRIER BY ICP ANALYSIS: Prepare in triplicate a 1000-fold dilution of the Ba carrier using the ICP solution described in Section 7.10 below. Submit to the Metals Lab for analysis. Average the results and record in the reagent prep logbook.

7.8 Citric acid, 1M: Dissolve 210.14g of $C_6H_8O_7 \cdot H_2O$ in DI water and dilute to 1000mL.

7.9 EDTA basic reagent, 0.25M: Dissolve 80g NaOH in ~3L of DI water. Slowly add 372g of (ethylenedinitrilo)tetraacetic acid, disodium salt, dihydrate - EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$), while stirring. After the salt is in solution dilute to 4L. If necessary, adjust the pH to ≥10 using a minimal volume of 10M NaOH.

7.10 ICP diluting solution (1% HNO_3 / 5% HCl). Carefully add 10mL of concentrated HNO_3 and 50mL of concentrated HCl to 940mL of DI water. Mix thoroughly.
TLV = 2ppm for conc. HNO_3 (TWA), and 5ppm for conc. HCl (ceiling). Both irritants, corrosive

7.11 Lead carrier, 15mg/mL: Dissolve 23.98g $Pb(NO_3)_2$ in DI water. Add 5mL 16M HNO_3 and dilute to 1000mL with DI water.
TLV = 0.05mg/m^3 (=0.004ppm)

7.12 Lead carrier, 1.5mg/mL: Dilute 10mL lead carrier (15mg/mL) to 100mL with DI water.
TLV = 0.05mg/m^3 (=0.004ppm)

7.13 Methyl orange indicator solution: Dissolve 0.100g methyl orange powder in 100mL of DI water.

7.14 Nitric acid reagent concentrated (16M HNO_3)
TLV = 2ppm (TWA). Irritant, corrosive

7.15 Nitric acid, 6M: Slowly and carefully add 375mL of concentrated nitric acid while stirring to 625mL of DI water.
TLV=2ppm (TWA). Irritant, corrosive

7.16 Nitric acid, 1M: Add 63mL of concentrated nitric acid while stirring to 937mL DI water.
TLV = 2ppm (TWA). Irritant, corrosive

7.17 Sodium hydroxide, 18M: Place about 500mL of DI water in a beaker in a cold water bath. Very slowly and carefully dissolve 720g of NaOH; work in the hood. **The solution will boil if the NaOH is added too quickly.** After the solution is cool, dilute to 1L with DI water. Store in a plastic container.
TLV = 2mg/m^3 = 1.2ppm (ceiling). Irritant

7.18 Sodium hydroxide, 10M: Follow the same procedure as above, but use 400g of NaOH instead. Store in a plastic container.
TLV = 2mg/m^3 = 1.2ppm (ceiling). Irritant

7.19 Strontium Carrier, 20mg/mL: Dissolve 48.3g $Sr(NO_3)_2$ in DI water. Add 1mL 16M HNO_3, then dilute to 1000mL with DI water.

7.20 Sulfuric acid, 18N, H_2SO_4: Very carefully and gradually, add 500mL of reagent grade concentrated sulfuric acid, while stirring, to 500mL DI water. **The solution will boil if the reagent is added too quickly.**
TLV = 1mg/m^3 (=0.25ppm) (TWA). Irritant

7.21 Sulfuric acid, 0.1N H_2SO_4: Add 5.6mL of 18N H_2SO_4 to ~900mL of DI water. Mix well and dilute to 1L with DI water. Alternately, add 120mL of 18N H_2SO_4 to ~2L of DI water, mix well and dilute to 22L.
TLV = 1mg/m^3 (=0.25ppm) (TWA). Irritant

7.22 Yttrium carrier, 9mg /mL: Add 11.43g Y_2O_3 to a Class A volumetric flask (1L), and add 100mL DI water. Heat to boiling and, while stirring with a magnetic stirring hot plate, add small portions of conc. HNO_3. (About 50mL may be necessary to dissolve the Y_2O_3. Small additions of deionized water also may be needed to replace the water lost by evaporation). After total dissolution, add 40mL conc. HNO_3 and dilute to 1000mL with DI water (1mL = 9mg/mLY^{+3}).

STANDARDIZATION: In triplicate, take 0.5mL of the Yttrium carrier solution and dilute 20-fold with DI water. Determine the concentration by ICP analysis.

7.23 Strontium-yttrium mixed carrier, 0.9mg Sr and 0.9mg Y / mL

7.23.1 Prepare Solutions A and B as indicated below:

Solution A: Dilute 20 mL of yttrium carrier to 100mL, using DI water.

Solution B: Dissolve 0.4384g. $Sr(NO_3)_2$ in DI water and dilute to 100mL.

7.23.2 Combine equal volumes of Solutions A and B; 1mL = 0.9mg Sr and 0.9mg Y.

7.24 Triton X-100™ non-ionic surfactant solution, VWR #3929-2, or equivalent

8. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 It is recommended that samples be preserved at the time of collection by adding enough 1M HNO_3 per liter of sample to bring the pH to 2 (15mL 1M HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of ~~16~~ 24 hours before analysis or transfer of the sample.

8.2 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

9. PROCEDURE

9.1 AQUEOUS SAMPLE PREPARATION

9.1.1 Verify and record (on Form 631) the pH of the sample according to SOP 733.

9.1.2 1.5L is a typical sample aliquot size for this method. However, this volume may need to be reduced if matrix interference is suspected. Use a graduated cylinder to measure the sample and pour into a clean, labeled 2L beaker. If less than 1.5L is used, record volume, then dilute to 1.5L with DI water.

9.1.3 Prepare quality control (QC) samples per Section 10, adding the appropriate amount of ^{228}Ra spiking solution to the samples that require it.

9.1.4 Place the beakers on stirring hot plates. Add a stir bar to each.

9.1.5 To each sample, add 8mL of 1M citric acid and 8-10 drops of methyl orange indicator. The solution should be red.

9.1.6 For all sample matrices, add 10mL of lead carrier (15mg/mL), 1mL of strontium carrier, 2mL Barium carrier, and 2mL of non-standardized yttrium carrier.

9.1.7 Prepare a Ba carrier reference solution by adding 2.0mL of standardized barium carrier to 1.5L of DI water.

9.1.8 Heat to incipient boiling and maintain at this temperature for 30min, while stirring.

9.1.9 Add 15M NH_4OH drop-wise until a definite yellow color is obtained; then add a few drops in excess.

9.1.10 Precipitate lead and barium sulfates by adding 18N H_2SO_4 drop-wise until the red color reappears; then add 0.4mL excess (~8 drops). Add 8mL 15M $(NH_4)_2SO_4$. Stir constantly and maintain temperature (approx. 90°C) for 30 minutes. If the indicator has been destroyed during digestion, add a few drops of methyl orange indicator.

9.1.11 Remove stir bars, rinsing with 0.1N sulfuric acid, and allow the solution to cool. Let precipitate settle for at least 4 hours, preferably overnight.

9.1.12 Aspirate supernatant. Transfer precipitate to a 50mL poly centrifuge tube, rinsing the last particles out of the beaker with 0.1N H_2SO_4. Centrifuge at 3,500 rpm for 10 minutes and discard the supernatant into the laboratory sink followed by plenty of cold tap water. **NOTE: For the remainder of this procedure, any reference to centrifuging means centrifuge at 3,500 rpm for 10 minutes.**

9.1.13 Wash the precipitate with 15mL 16N HNO_3, vortex, centrifuge, and discard the supernatant into the laboratory sink or into the back of a fume hood, followed with plenty of cold tap water. Repeat this washing a second time. At the analyst's discretion, additional washes may be performed to thoroughly remove interfering constituents.

9.1.14 Add 25mL EDTA basic reagent and vortex well. Heat in a hot-water bath for about 10min., stirring occasionally to aid in dissolution. If the precipitate does not dissolve after heating on the hot-water bath, add up to an additional 5.0mL of 10M NaOH dropwise, until the precipitate dissolves. If the precipitate persists, add up to four 5.0 mL increments of basic EDTA until the precipitate dissolves. If the sample re-precipitates while cooling, add a few drops of 10M NaOH to dissolve. Document the total volume of NaOH/EDTA solution used to dissolve the precipitate on the benchsheet. Vortex to mix the solution and take the aliquot for the initial ICP analysis. If solids persist, consult your Supervisor prior to filtering per SOP 712.

9.1.15 HOW TO TAKE INITIAL ICP ALIQUOT

9.1.15.1 Vortex the sample to mix thoroughly. Using a calibrated pipette, aliquot 0.1mL of sample into a clean, labeled test tube containing 9.9 or 10mL of DI water (record the volume of water used). Cover with Parafilm™, and invert several times or vortex to mix completely. With a calibrated pipette, aliquot 1.0mL of the diluted sample into another clean test tube labeled with the sample ID and "i" and containing 9.0mL of ICP diluting solution. Cover with a test tube cap

and mix well. Set aside until final ICP aliquot has been taken.

9.1.15.2 At this time, prepare an ICP "reference carrier" (RC) sample. Thoroughly mix the reference carrier solution (Section 9.1.7) on a stir plate. Add 1.0mL of the reference carrier solution to 9.0mL of ICP diluting solution, as stated above for samples. This RC sample will be submitted with the batch samples for ICP analysis to provide a reference concentration for the yield calculations.

9.1.16 Add 1mL of strontium-yttrium mixed carrier, and mix thoroughly. Add a few drops of 10M NaOH if any precipitate forms.

9.1.17 Add 1mL $(NH_4)_2SO_4$ and stir thoroughly. Add 17.4M acetic acid drop-wise until barium sulfate precipitates; then add 2mL excess. **Do not vortex.** Heat in a hot water bath (about 10min.) until precipitate settles. Centrifuge and discard supernatant into the Ba/Pb waste carboy, per Section 13.2 of this SOP.

9.1.18 Add 25mL EDTA basic reagent, vortex and heat in a hot-water bath until precipitate dissolves, (additional volume of EDTA reagent may be needed if the precipitate does not dissolve completely) then repeat steps 9.1.16 and 9.1.17. *Note the time of last barium sulfate precipitation on the benchsheet; this is T1, the beginning of the actinium-228 ingrowth time.*

9.1.19 Dissolve the precipitate with 25mL EDTA basic reagent. As before (i.e., Step 9.1.14), additional EDTA reagent may be required if the precipitate does not dissolve completely. Then add 1.0mL of standardized yttrium carrier and 1mL of lead carrier (1.5mg/mL). If $BaSO_4$ precipitates (a cloudy white solid), dissolve with a few drops of 10N NaOH. If $Y(OH)_3$ forms (a stringy, floating precipitate), dissolve with a few drops of 16M HNO_3.

NOTE: Prepare a reference carrier solution by adding 1.0mL of standardized yttrium carrier to a 50mL centrifuge tube. To this, add 25mL of 8M HNO_3 and dilute to 50mL with DI water.

Cap the polypropylene tubes and routinely store for **36 hours for ingrowth of Ac-228**.

9.1.20 After the 36-hour ingrowth period, add 0.3mL (about 6 drops) $(NH_4)_2S$ and vortex the samples. Add 0.5mL (about 10 drops) 10M NaOH, cap

and shake vigorously until lead sulfide precipitates. If precipitate fails to form, additional 10M NaOH may be added dropwise, with vigorous stirring, until the precipitate forms. After the precipitate forms, add 10 drops 10M NaOH in excess. Centrifuge and decant supernatant into a clean tube. Rinse the centrifuge tubes into the Ba/Pb waste carboy. Used centrifuge tubes may be soaked in Radiacwash™, rinsed in tap water and discarded in the sanitary trash.

9.1.21 In preparation to perform Step 9.1.24, place a bottle of 18M NaOH on a stir plate and mix thoroughly.

9.1.22 Add 1mL lead carrier (1.5mg/mL), 0.1mL (approx. 2 drops) $(NH_4)_2S$, and 3-4 drops of 10M NaOH, to repeat precipitation of lead sulfide as before. Centrifuge and filter supernatant through Whatman™ #42 filter paper, ashless, 90mm diameter, and into a clean tube. Precondition the filters with ~1mL of DI water. After the sample has passed through the filter, rinse twice with 1mL of DI water. Discard the filters into the filter lead waste. Rinse the funnels with 1mL of DI water, collecting the filtrate into the centrifuge tube.

9.1.23 **Due to the short half-life of actinium-228, the remainder of the prep should be completed in less than 4 hours. The Counting Lab should be notified in advance of incoming samples.**

9.1.24 Add 16mL of thoroughly mixed 18M NaOH to each sample. Cap and shake well and digest in a hot water bath for about 30min until yttrium hydroxide coagulates.

NOTE: Document time of yttrium hydroxide precipitation as T2 (time when samples come off steam bath); *this is the end of the actinium-228 ingrowth time and the beginning of actinium-228 decay time*.

9.1.25 Centrifuge and decant the supernatant into a 150mL poly specimen cup. *Save for barium yield determination (Section 9.1.26).*

9.1.26 Dissolve the precipitate with 2mL 6M HNO_3. Vortex, then heat in a hot water bath for about 5min. Add 3mL DI water and re-precipitate yttrium hydroxide with 6mL 10M NaOH. Vortex and heat in a hot water bath for about 10 min until precipitate coagulates. Centrifuge and add this supernatant to the supernatant produced in the previous Step in order to determine barium yield. Using a 100mL graduated cylinder, measure this combined supernatant and record the volume on the benchsheet.

9.1.27 FINAL ICP ANALYSIS. The aliquot for final ICP analysis must be taken from the combined supernatant collected. Follow the steps outlined in Section 9.1.15.1 to obtain the final ICP aliquot.

Upon the return of ICP sample fractions to the prep lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the PAR wastewater treatment facility (i.e., down the laboratory sink with plenty of cold tap water). The remaining Ba supernatant from above can be disposed of into the Ba/Pb waste carboy. The test tubes and centrifuge tubes may be soaked in Radiacwash™ and rinsed with tap water. Dispose of the centrifuge tubes and test tubes in the sanitary trash.

9.1.28 Dissolve the precipitate with 2mL 1M HNO_3, vortex, and heat in a hot water bath for 5min. Additional 1M HNO_3 may be added drop wise to achieve dissolution of the precipitate. If additional 1M HNO_3 is used, add proportionally increased volumes of DI water and 5% $(NH_4)_2C_2O_4 \cdot H_2O$ (Ammonium Oxalate) in the following Step.

9.1.29 Add 3mL of DI water and 2mL 5% $(NH_4)_2C_2O_4 \cdot H_2O$; heat about 10min to coagulate, centrifuge, and discard supernatant into the laboratory sink followed by plenty of cold tap water.

9.1.30 Rinse precipitate with 10mL of DI water. Centrifuge and discard supernatant into the laboratory sink.

9.1.31 Add 10mL of DI water, 6 drops 1M HNO_3 and 6 drops 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat and stir in a hot water bath for 5-6 min. **The time on the water bath should be monitored carefully, as this may significantly affect the chemical yields for the samples.** Centrifuge and discard supernatant into the laboratory sink.

9.1.32 Label a stainless steel planchet for each sample, and place planchets on a hot plate.

9.1.33 Add approximately 4mL of DI water to the centrifuge tubes and vortex until all of the precipitate is suspended. Working quickly to avoid the precipitate settling, remove the cap and rinse once with DI water; pour rinse into a planchet. Empty the contents of the centrifuge tube onto the planchet, rinse tube with DI water, add rinse to the planchet. The sample should be evenly distributed on the planchet. Allow solid to settle. Dry on a hot plate at setting 2 or 3. Submit planchets to the Counting Lab immediately for analysis. Used centrifuge tubes may be soaked in Radiacwash™, rinsed in tap water, and discarded in the

sanitary trash.

9.1.34 After counting, place each planchet in a labeled 150mL poly cup and add approximately 10mL of 8M HNO_3 to dissolve the yttrium oxalate precipitate.

9.1.35 Thoroughly rinse the planchets with 8M HNO_3 into the poly cups. After rinsing, the planchets can be disposed of in the sanitary trash.

9.1.36 The dissolved sample and rinse is brought up to 50mL with DI water.

9.1.37 Remove a 0.5mL aliquot from each sample, including the reference carrier from the note after Step 9.1.19, into a 15mL test tube containing 9.5mL of ICP diluting solution, to bring the total volume to 10mL. The samples are then capped, shaken, and brought to the Metals Lab for yttrium analysis by ICP.

Upon the return of ICP sample fractions to the prep lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the PAR wastewater treatment facility (i.e., down the laboratory sink with plenty of cold tap water). The test tubes may be soaked in Radiacwash™, rinsed with tap water, and disposed of in the sanitary trash.

9.2 PREPARATION OF CALIBRATION STANDARDS

9.2.1 Label and tare weigh 5 stainless steel 2-inch diameter flat planchets.

9.2.2 Spike between 1,000 and 10,000dpm of NIST-traceable Sr-89 directly onto each planchet.

NOTE: If the standard matrix is HCl, the standard must be converted to a nitric matrix during planchetting to avoid corroding the planchet. This can be accomplished by adding ~5mL 16N HNO_3 to the planchet along with the spiking solution.

9.2.3 Add 0.5mL of Sr carrier (approximately 10mg).

9.2.4 Dry on a hot plate set at "2".

9.2.5 Weigh on an analytical balance. Record the mass on the benchsheet.

9.2.6 Submit to the Counting Lab with all necessary documentation.

9.2.7 The calibration should be verified with the preparation and analysis of four method blanks and four ^{228}Ra LCSs, spiked at approximately

500dpm, performed per this SOP.

10. QUALITY CONTROL

NOTE: For solid matrices, the blank and LCS are prepared using a qualitative filter paper, instead of the 1500mL DI water used for aqueous QC.

10.1 One method blank, prepared with 1500mL of DI water, is prepared for each batch of twenty or fewer samples. To be acceptable, the method blank activity shall be less than the MDA (or, if higher, less than the contract required MDC). Samples associated with an elevated method blank are acceptable if the sample activity is greater than five times the blank activity.

10.2 One LCS, prepared with 1500mL of DI water for aqueous samples is prepared for each batch of twenty or fewer samples. The LCS activity should fall within the general range of 5-10 times the requested detection limit (default = 1pCi/L). The LCS sample accuracy (measured activity/added activity) will fall within currently established control limits, as described in the LIMS program specifications.

10.3 A duplicate is prepared at a frequency of one per ten or fewer samples. The duplicate sample DER will be within the established control limits, as described in the LIMS program specifications. Some clients may require use of RPD as a measure of precision. The duplicate sample RPD will be within specified control limits. Duplicate samples with activity levels less than 5 times the MDC will not be assessed using RPD.

10.4 The overall chemical yield, calculated as the product of the barium and yttrium yields, should be 40-110%. The individual barium and yttrium yield should also fall within these limits.

10.5 Batches for which the associated QC samples do not meet established criteria may need to be rerun. A non-conformance report (NCR, SOP 928) should be filled out, the Radiochemistry Technical Manager notified, and appropriate corrective action implemented and documented.

11. CALCULATIONS

11.1 Calculate the radium-228 concentration, Act, in pCi/L or pCi/g as follows:

$$Act = \frac{(SCPM - BKGCPM)(Ac * T_3/60)}{F * E * V * Y_T * D * (1 - e^{(-AcT_1)}) * (e^{(-AcT_2)}) * (1 - e^{(-AcT_3/60)})}$$

where:

Act = sample activity (pCi/L, pCi/g)

SCPM = gross sample beta count rate (cpm)

BKGCPM = background beta count rate (cpm)

Ac = decay constant for actinium-228 = ln2 / 6.15 hours = 0.113075 h^{-1}

F = activity conversion factor from dpm (for pCi = 2.22, for Bq = 60)

E = actinium-228 detection efficiency (cpm/dpm)

V = sample aliquot (L, g)

Y_T = total chemical yield, see Section 11.8

D = decay correction for radium-228 = $e^{(-RaT4)}$

T_4 = time elapsed between sample collection (or reference date) and actinium separation T_1 (days)

Ra = decay constant for radium-228 = ln2 / 2100 days = 0.00033004 d^{-1}

T_1 = elapsed time (hours) between the start of the actinium ingrowth (T_0) and the start of actinium decay (T_1) = (T_1 - T_0)

T_2 = elapsed time (hours) between the start of the actinium decay (T_1) and the start of the sample count (T_2) = (T_2 - T_1)

T_3 = duration of sample count (min)

11.2 Calculate the one sigma associated counting uncertainty, CU, in pCi/L or pCi/g as follows:

$$Unc = \frac{\sqrt{(SCPM/T_3) + (BKGCPM/BT)}(Ac * T_3/60)}{F * E * V * Y_T * D * (1 - e^{(-AcT_1)}) * (e^{(-AcT_2)}) * (1 - e^{(-AcT_3/60)})}$$

where:

BT = background count time

11.3 Calculate the one-sigma total propagated uncertainty (TPU), in pCi/L or pCi/g as follows:

$$TPU = \sqrt{CU^2 + (IU^2 * Act) + (PU^2 * Act)}$$

The instrument uncertainty, IU, can be found in SOP 743.

The prep uncertainty, PU, is 0.1374. This is based on SOP 743 guidelines for one gross aliquotting, four quantitative transfers, three volumetric measurements, and two ICP determinations:

$$0.1374 = \sqrt{0.05^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.025^2 + 0.006^2 + 0.006^2 + 0.006^2 + 0.083^2 + 0.083^2}$$

11.4 Calculate the one sigma minimum detectable concentration, MDC, in pCi/L or pCi/g as follows:

$$MDC = \frac{(4.65 * \sqrt{(BKGCPM/T_3)} + 2.71)(Ac * T_3/60)}{F * E * V * Y_T * D * (1 - e^{(-AcT_1)}) * (e^{(-AcT_2)}) * (1 - e^{(-AcT_3/60)})}$$

11.5 The detection efficiency, E, is calculated as follows:

$$E = \frac{(StCPM - BKGCPM)}{StDPM}$$

11.6 Calculate the barium chemical recovery for aqueous samples, Ba, as a percentage, as follows:

$$Ba_i = V_i * ICP_i * DF$$

$$Ba_f = V_f * ICP_f * DF$$

$$Ba_{RC} = V_{RC} * ICP_{RC} * DF$$

$$Ba = \frac{Ba_f}{X} * 100$$

where:

Ba_i = barium recovery from initial ICP aliquot (µg)

V_i = final dilution volume when taking initial ICP (mL)

ICP_i = initial barium concentration measured by ICP (µg/mL)

DF = dilution factor

Ba_f = barium recovery from final ICP aliquot (µg)

V_f = final dilution volume when taking final ICP (mL)

ICP_f = final barium concentration measured by ICP (µg/ml)

Ba_{RC} = barium recovery from RC aliquot (µg)

V_{RC} = RC final volume (mL)

ICP_{RC} = RC barium concentration measured by ICP (µg/mL)

X = either Ba_i or Ba_{RC}, whichever is greater

11.7 Calculate the yttrium chemical recovery for aqueous samples, Y, as a percentage, as follows:

$$Y_f = V_f * ICP_y * DF$$

$$Y_{RC} = V_{RC} * ICP_{yRC} * DF$$

$$Y = \frac{Y_f}{Y_{RC}} * 100$$

where:

Y_f = yttrium recovery from final ICP aliquot (µg)

ICP_y = final yttrium concentration measured by ICP (µg/mL)

Y_{RC} = yttrium recovery from RC aliquot (µg)

ICP_{yRC} = RC yttrium concentration measured by ICP (µg/mL)

11.8 Calculate the total chemical yield, Y_T, as a percentage, as follows:

$$Y_T = Ba * Y * 100$$

For chemical yields above 100%, assume a quantitative recovery and use 100% in the yield calculation. This avoids a low bias in the final analytical results.

11.9 Calculate the actual volume, V_A, of sample analyzed (accounting for volumes of sample removed) as follows:

$$V_A = V * \frac{V_i - V_{ICP}}{V_i}$$

where:

V_{ICP} = initial aliquot taken for ICP (mL)

12. DEVIATIONS FROM METHOD

EPA Method 904.0 addresses drinking water samples. There is no official holding time for analyses in the 900 series. This procedure is substantially compliant with Method 904.0.

12.1 This SOP provides procedures for determining the chemical yield by ICP as an addition to EPA Method 904.0. This measurement increases the accuracy of the method.

12.2 25mL of EDTA is used to dissolve the $Ba(Ra)SO_4$ precipitate. This volume

ensures a complete dissolution of the precipitate in a normal sample.

12.3 Where EPA drinking water methodologies are required by the client, the LCS recovery acceptance criteria shall be ±20%, irrespective of Paragon's internally derived acceptance criteria.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 SAFETY AND HAZARDS

13.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

13.1.2 Safety glasses, and lab coats must be worn in the radiochemistry prep labs at all times.

13.1.3 Gloves, safety glasses, and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

13.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 14.2 below.

13.1.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

13.1.6 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

13.2 WASTE DISPOSAL

The analytical process effluent has been determined to not be hazardous in other than corrosivity except the Ba and Pb containing supernatants. These supernatants must be segregated into the Ba and Pb waste containers supplied by the Waste Disposal Coordinator.

14. REFERENCES

14.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, Method 904.0, Radium-228 Drinking Water Method, Page. 49.

14.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

14.3 PAR SOP 743 "Estimating Total Propagated Uncertainties for Radiometric

Analyses".

DOCUMENT REVISION HISTORY

10/5/06: This SOP has been developed to meet drinking water requirements, and to facilitate compliance with State of Colorado certification requirements for Method 904.0.

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Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Not Applicable - remove from next iteration of SOP. DAS 10/18/07

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 785 REVISION 4

TITLE: TOTAL ACTIVITY IN ENVIRONMENTAL MATRICES

FORMS: 631 use current iteration

APPROVED BY:

TECHNICAL MANAGER Renee Vallejos DATE 7/21/08
QUALITY ASSURANCE MANAGER Dib Schantz DATE 7/20/08
LABORATORY MANAGER [signature] DATE 7/21/08

HISTORY: NEW, Rev0, 3/12/03; Rev1, 12/3/03; Rev2, 5/17/04; Rev3, 8/16/06; Rev4, 7/18/08.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the method used to determine the total activity of non-volatile radionuclides in solid or liquid matrices. The total activity is determined via liquid scintillation counting (LSC) with the approximate window setting from channel 50 to channel 999. Total activity matrix spikes and laboratory control samples (LCSs) are prepared with Tc-99 (a pure beta-emitter). Total activity of non-volatile beta-emitting radionuclides is achieved by adjustment of the analytical region of interest.

2. SUMMARY

2.1 WATERS

Water samples are routinely analyzed on a "total" or "unfiltered" basis (i.e., unless specifically requested by the client, water samples are not filtered prior to preparation). An aliquot of water is evaporated in a liquid scintillation vial, taken to near dryness, and re-dissolved in dilute nitric acid. Ultima Gold AB™ cocktail is added and total activity determined via liquid scintillation counting (LSC).

2.2 LEACHATES OR DIGESTATES

Following preparation, sample leachates or digestates are determined as described in Section 2.1 above for waters.

2.3 NON-AQUEOUS OR MIXED PHASE LIQUIDS

Non-aqueous liquids are analyzed and reported on an 'as received' basis. They may be treated as waters as long as the physical or chemical characteristics of the sample are amenable to safe evaporation with the eventual addition of nitric acid. Questionable cases should be addressed to the Radiochemistry Manager, Project Manager, or Health and Safety Manager prior to initiation of analysis.

2.4 SOILS AND NON-SOIL SOLIDS (hereafter referred to as "solids")

Solids are analyzed on a 'dry weight' basis. Samples are prepared as stated in SOP 702 - Gross Alpha and Gross Beta in Environmental Matrices, with the

exception that Tc-99 is used for the total activity matrix spike and LCS.

2.5 AIR FILTERS
Air Filters are processed in a manner similar to solids except they need not be weighed and the units are reported on a default basis as "per filter."

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 The prepared scintillation vials are prone to building up pressure and rupturing in storage. It is the responsibility of the instrument analyst to dispose of the scintillation vials as soon as is practical after review and verification of the data, preferably within 60 days after preparation.

3.5 It is the responsibility of all personnel who work with samples utilizing this method to note any anomalous or out-of-control events associated with the preparation and analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 Radionuclides that are volatile during evaporation in nitric acid will not be dependably measured. This method is not applicable to the determination of H-3 or C-14. Other problematic nuclides include radioisotopes of iodine, cesium, and polonium.

4.2 Samples should be evaporated slowly and at low temperatures in order to avoid splattering.

4.3 Sample solutions in a beaker should be slowly evaporated to ***near*** dryness (≤5mL). Avoid evaporating the sample to complete or hard dryness, which could lead to analyte loss resulting from poorly soluble residues in the beaker, as well as volatilization of the Tc-99 spiking analyte.

4.4 Sample solutions in a liquid scintillation vial should be slowly evaporated just to dryness. This will require close observation as the sample approaches dryness. Avoid evaporating the sample to hard dryness, which could lead to analyte loss resulting from the volatilization of the Tc-99 spiking analyte.

4.5 The routine solids leaching procedure may not address radioactive constituents bound in the solid matrix of the sample. More aggressive digestion procedures may be necessary if a total dissolution of the sample is required (see SOP 721).

4.6 Non-aqueous liquid, non-soil solids, and samples with high organic content may not be amenable to this procedure.

4.7 The scintillation vial is an optical surface. Any markings or material on the outside of the scintillation vial will interfere with the detection of scintillation. These should be removed prior to analysis by wiping the vial with a lint-free lab wipe and alcohol. All labeling must be done on the cap of the vial.

4.8 The quench indicating parameter (QIP) (usually H-number) should be monitored. Variations in quench that could correspond to greater than 10% relative bias in the efficiency should be addressed either by the use of a quench curve or the method of standard additions.

4.8.1 The presence of visible coloration in the final sample will act as an ‘inner filter’. This effect, known as ‘color quenching’ is an interference to the detection of the scintillation.

4.8.2 The presence of particulate contamination in the final sample may interfere with the detection of the scintillation. This effect is known as ‘physical quenching’.

4.8.3 The presence of chemical contaminants in the sample may inhibit scintillation. This effect is known as ‘chemical quenching’.

5. APPARATUS AND MATERIALS

5.1 Narrow-range pH paper (0-2.5 pH)

5.2 Eppendorf™ pipettors or equivalent, and pipet tips

5.3 Centrifuge

5.4 Centrifuge tubes, 50mL

5.5 Kimwipes™

5.6 Glass liquid scintillation vials, 20mL

5.7 Polypropylene cups, 250mL

5.8 Top loading balance, 0.1g sensitivity

5.9 Analytical balance, 0.0001g sensitivity

5.10 Fluted filter paper, VWR Grade 313, or equivalent

5.11 Plastic funnels

5.12 Hot plate

5.13 Steam bath

5.14 Wash bottles

5.15 Graduated cylinders

5.16 Desiccator

5.17 Transfer pipettes, ~3mL, plastic, disposable

5.18 Beakers, 500 and 1000mL

5.19 Vortex mixer

6. REAGENTS

NOTE: Threshold Limit Value (TLV) and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Deionized (DI) water

6.2 Methanol, reagent grade

6.3 Ultima Gold AB™ liquid scintillation cocktail

6.4 Tc-99 spiking solution, NIST traceable (source is different than that used for calibration)

6.5 Nitric acid, concentrated (16M), ACS grade

TLV = 2 ppm (TWA). Irritant, corrosive.

6.6 Nitric acid, 8M: Carefully add 500mL concentrated nitric acid to 500mL DI water.

TLV = 2 ppm (TWA). Irritant, corrosive.

6.7 Nitric acid, 2M: Carefully add 125mL concentrated nitric acid to 500mL DI water, and bring to a final volume of 1.0L with DI water.

TLV = 2 ppm (TWA). Irritant, corrosive.

6.8 Nitric acid, 1M: Carefully add 62.5mL concentrated nitric acid to 500mL DI water, and bring to a final volume of 1.0L with DI water.

TLV = 2 ppm (TWA). Irritant, corrosive.

6.9 Nitromethane, reagent grade.

TLV = 20 ppm (TWA). Extremely hazardous, highly reactive, highly flammable, flash-back hazard, carcinogen.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough HNO_3 to bring the pH to less than 2. The volume of nitric acid should be minimized to avoid significant dilution of the sample. If samples are to be collected without preservation, they should be brought to the laboratory within 5 days then preserved, with a minimum volume of concentrated HNO_3, to a pH less than 2. After preservation, the samples should be held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.2 The container should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 PROCEDURE FOR WATERS

8.1.1 Verify with pH paper that the sample has been properly preserved to a pH <2. Record the pH on the sample condition form (Form 631). Record all appropriate information such as pH, unusual appearance, sedimentation, etc., on the sample condition form.

NOTE: If the pH is $\geq$ 2, acidify to pH <2 with conc. HNO_3. Record the acid addition and the final pH on sample condition form. The date and time of acidification must be noted. Return the sample to storage for at least 24 hours before repeating Step 8.1.1.

8.1.2 Prepare quality control (QC) samples per Section 10.

8.1.3 For default detection limits of 1000 pCi/L, a 10mL sample is required. In this case, aliquot 10mL of sample directly to a liquid scintillation vial and proceed to Step 8.1.7. If a sample aliquot larger than 20mL is required, proceed to Step 8.1.4.

8.1.4 If a sample aliquot of greater than 20mL is required, transfer an aliquot of water to a clean, labeled beaker.

8.1.5 Place the samples on a hot plate and evaporate until approximately 5mL of sample remains. Transfer the sample to a liquid scintillation

vial with a transfer pipette.

8.1.6 Rinse the beaker three times with 5mL 1M HNO_3 and transfer each rinse to the vial.

8.1.7 Evaporate the samples just to dryness on a hot plate over low heat (approximate setting of 3). Allow the samples to cool before proceeding.

8.1.8 Add 2mL 2M HNO_3 to each vial. If necessary, re-dissolve the sample residue over low heat with the caps placed loosely on the vials.

8.1.9 Allow the samples to cool. Add 18mL Ultima Gold AB™ cocktail to each vial, cap tightly, and shake thoroughly to homogenize. Wipe the outside of each vial with methanol in ensure a clean optical surface.

8.1.10 Deliver the samples to the Counting Lab with the necessary documents. Place the racks in the liquid scintillation counter and allow at least 3 hours for samples to "dark adapt" prior to counting. The Counting Lab will analyze and dispose of the scintillation vials, within 60 days, in the manner described in SOP 704.

8.2 PROCEDURE FOR SOLIDS

8.2.1 Solid samples are routinely ground before taking an aliquot for analysis. See SOP 721 for soil preparation procedure. Analysis is routinely reported on a dry-weight basis.

NOTE: In such cases where the client requests gross alpha/beta analysis and total activity analysis, sample preparation as described in SOP 702 may be used. The digestate prepared in SOP 702 may be used for both analyses, although an additional total activity matrix spike and LCS are prepared.

8.2.2 Weigh 3g of solid sample to the nearest 0.0001g into a labeled 50mL centrifuge tube.

8.2.3 Prepare QC samples per Section 10.

8.2.4 Slowly add 8M HNO_3 to yield a total volume of 30mL. Be sure to account for the volume of spiking solutions (i.e., the LCS would receive only 29mL of nitric acid if it already contained 1mL of spiking solution). Some samples may react vigorously with the acid; it may be necessary to add the acid in small increments.

8.2.5 Mix to homogenize the solid and acid solution.

8.2.6 Heat the samples on a steam bath with caps on loosely for one hour. Allow samples to cool, then mix by vortexing.

8.2.7 Centrifuge at approximately 3500 rpm for 10 minutes and filter the supernatant using VWR Grade 313 fluted paper, or equivalent, into a new, labeled centrifuge tube.

8.2.8 Transfer 5mL of the sample leachate obtained in the previous step to a clean, labeled liquid scintillation vial.

8.2.9 Evaporate the samples just to dryness on a hot plate over low heat (approximate setting of 3). Allow the samples to cool before proceeding.

8.2.10 Add 2mL 2M HNO_3 to each vial. If necessary, re-dissolve the sample residue over low heat on a hot plate with the caps placed loosely on the vials.

8.2.11 Allow the samples to cool. Add 18mL Ultima Gold AB™ cocktail to each vial, cap tightly, and shake thoroughly to homogenize. Wipe the outside of each vial with methanol to ensure a clean optical surface.

8.2.12 Deliver the samples to the Counting Lab with the necessary documents. Place the racks in the liquid scintillation counter and allow at least 3 hours for samples to "dark adapt" prior to counting. The Counting Lab will analyze and dispose of the scintillation vials, within 60 days, in the manner described in SOP 704.

9. PREPARATION OF CALIBRATION VIALS (FOR QUENCH CURVE)

Twelve spike and twelve blank vials are prepared with increasing volumes of nitromethane for calibration.

9.1 Blank calibration vial preparation: Add 2mL of 2M HNO_3 to each of twelve blank vials, labeled BLK1-BLK12. Blank vial 1 does not receive nitromethane. Nitromethane is added to each subsequent vial in 30 µL increments (i.e., BLK2 receives 30µL; BLK3 receives 60µL and so on, up to BLK12, which receives 330µL of nitromethane). Add 18mL Ultima Gold AB™ liquid scintillation cocktail to each vial. Cap tightly and shake each vial to homogenize. Wipe the outside of each vial with methanol to ensure a clean optical surface.

9.2 Spike calibration vial preparation: Add a known volume of Tc-99 standard (consult with the liquid scintillation counter primary operator for appropriate spike activities to be used) to each of twelve blank spike vials, labeled S1-S12. Then add an appropriate amount of 2M HNO_3 to each vial to bring the total volume to 2mL. Spike vial 1 does not receive nitromethane. Nitromethane is added to each subsequent vial in 30µL increments (i.e., S2 receives 30µL; S3 receives 60µL and so forth, up to S12, which receives 330µL of nitromethane). Add 18mL of Ultima Gold AB™ liquid scintillation cocktail to bring the final volume of acid + standard + cocktail of each vial to 20mL. Cap tightly and shake each vial to homogenize. Wipe the outside of each vial with methanol to ensure a

clean optical surface.

9.3 Deliver the quench curve vials to the counting lab with the necessary documents. Place the racks in the liquid scintillation counter and allow at least 3 hours for samples to "dark adapt" prior to counting. The counting lab will analyze and ultimately dispose of the scintillation vials in the manner described in SOP 704.

10. QUALITY CONTROL

Acceptance criteria for QC samples may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.1 **Calibration blanks** will be run at a frequency of three per batch. Calibration blanks are prepared directly in the scintillation vials and consist of 2mL 2M HNO_3, and 18mL Ultima Gold AB™ liquid scintillation cocktail, each quenched with approximately 50µL nitromethane. The count data from the calibration blanks will be used to adjust the background quench curve for batch-specific background corrections.

10.2 **Method blanks** will be run at a frequency of five percent (i.e., one per 20 field samples), with a minimum of one per batch. Method blanks for water consist of deionized (DI) water and match the largest sample volume used. Nitric acid is added to the method blank, as it is to the samples, prior to evaporation. Method blanks for solids consist of 30mL of 8N nitric acid.

10.3 **Duplicate** (or replicate) samples will be run at a frequency of ten percent, with a minimum of one per batch. Client requested duplicate analyses shall be run as required and may count as the QC replicates for that batch.

10.4 **Laboratory Control Samples** (LCSs) will be run at a frequency of five percent, with a minimum of one per batch. The spiking levels are determined according to specific data quality objectives for the work being performed, but will generally be 5-10 times the required minimum detectable concentration (MDC) for the respective analyte, or at an activity level roughly equivalent to levels expected to be observed in the samples. The volume for the water LCS is as large as the largest sample volume. The water LCS consists of deionized water and the appropriate volume of spiking solution. The LCS for solids consists of the spike volume brought up to 30mL with 8N nitric acid.

10.5 **Matrix Spike** (MS) will be run at a frequency of five percent with a minimum of one per batch. The spiking levels are generally the same as that used for the LCS. The volume for the water MS is as large as the sample volume of the spike sample. The water MS consists of the sample and the appropriate volume of spike solution. The MS for solids consists of 3g of the solid sample and the spike volume brought up to 30mL with 8N nitric acid.

11. CALCULATIONS

As defined in SOP 743, the following 1σ preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU):

11.1 Water samples require a preparation uncertainty factor of 0.0505. This factor is based on one gross aliquoting (sample homogeneity), one volumetric measurement, one quantitative transfer, and one pipetting. See the following equation:

$$0.0505 = \sqrt{0.05^2 + 0.006^2 + 0.004^2}$$

11.2 Soil samples require a preparation uncertainty factor of 0.0566. This factor is based on one gross aliquoting (sample homogeneity), one mass measurement, one volumetric measurement, two pipetting, and one quantitative transfer. See the following equation:

$$0.0566 = \sqrt{0.05^2 + 0.003^2 + 0.006^2 + 0.004^2 + 0.004^2 + 0.025^2}$$

These two preparation uncertainty factors are substantially equivalent and to simplify analytical reporting, the larger of the two preparation uncertainties calculated above, 0.0566, will be used for both soil and water matrices.

Additional information pertaining to calculations for radioanalytical results can be found in PAR SOP 708.

12. SAFETY HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.1.2 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.2 below.

12.1.3 The building is equipped with a safety shower, eyewash station, fire extinguisher and fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

12.1.4 Safety glasses, lab coats and gloves should be worn in the laboratory at all times.

12.1.5 Use care when handling strong acids (e.g., HNO3, HCl, etc.). Work only in a fume hood with adequate ventilation and wear appropriate eye, face, and body protection. Care should be taken when diluting

acids. Always add acids to water, NOT water to acid.

12.1.6 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at a minimum with: (1) the compound name, (2) NFPA Health, Flammability and Reactivity ratings, and (3) expiration date.

12.2 WASTE DISPOSAL

12.2.1 The liquid effluent from the solid procedure has been determined to not be hazardous other than corrosivity. This material may be discharged into the lab wastewater treatment facility. Here the solution will be neutralized prior to discharge and the activity will be monitored to ensure compliance with Colorado Rules and Regulations, pertaining to Radiation Control Part 4, regarding discharges to sanitary sewers.

12.2.2 Solids and filtered residues should be accumulated in the appropriate container in the designated satellite accumulation area to await further disposal, per consultation with the Waste Disposal Coordinator.

13. REFERENCES

13.1 This is a proprietary SOP developed by Paragon Analytics.

13.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

8/16/06: LIMS program specification language augmented. Standard aliquot sizes reduced to more closely match the Paragon standard MDCs; consequently, the volume reduction, quantitative transfer to the scintillation vial, and the associated TPU factor was changed. Other clerical changes made. DOCUMENT REVISION HISTORY added.

7/18/08: Various clerical changes made. Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Sections 7.1 and 8.1.1. Removed calculations from this SOP and referenced SOP 708 instead. Added QC limits comments as introduction to Section 10.

Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 786 REVISION 5

TITLE: **GROSS ALPHA IN WATER BY COPRECIPITATION METHOD -- SM 7110C**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07
QUALITY ASSURANCE MANAGER _____ DATE 9/3/07
LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, 7/15/97; Rev1, 11/2/00; Rev2, 4/26/02; Rev3, 8/27/03; Rev4, 9/11/06; Rev5, 8/31/07.

1.0 SCOPE AND APPLICATION

This SOP describes the procedure used to analyze water samples with high dissolved solids content for gross alpha activity by coprecipitation according to Standard Methods for the Analysis of Water and Wastewater, Method 7110C.

2.0 SUMMARY

An aliquot of water is acidified with sulfuric acid and boiled vigorously for 10 minutes to outgas carbon dioxide and ^{222}Radon from the sample. Barium carrier is added to precipitate barium sulfate and the sample is digested while warming to 50°C for 30 minutes. Iron carrier is then added and the sample is neutralized with ammonium hydroxide and is heated and stirred for another 30 minutes to coprecipitate other alpha emitters with iron hydroxide carrier. The precipitate is filtered, dried and counted for alpha activity.

3.0 RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data

involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4.0 INTERFERENCES

4.1 Alpha-emitting radionuclides are coprecipitated on barium sulfate and iron hydroxide, thereby separating the alpha-emitting radionuclides from other sample dissolved solids. The combined precipitates are mounted and counted for alpha activity. Relatively large samples can be analyzed so that sensitivity is improved and counting time is minimized.

NOTE: Polonium is not dependably measured using this method. Thus, other methodologies should be used if the contribution by these nuclides to gross alpha activity is required

4.2 Suspended solids should be removed by filtration prior to chemical separation. Small quantities of suspended solids may be accommodated by this method provided that the range of the attenuation curve is not exceeded.

4.3 Soluble ions that coprecipitate and add to the mixed barium sulfate and iron hydroxide precipitate weights result in reduced sample capacity and elevated detection limits. Small quantities of excess coprecipitated solids may be accommodated by this method provided that the range of the attenuation curve is not exceeded.

4.4 Iron hydroxide precipitates collected on membrane filters without a holding agent may flake when dried and can be easily lost from the filter. Approximately 5mg of paper pulp fiber are added to the sample to help stabilize the iron hydroxide precipitate on the filter. The use of glass fiber filters will prevent loss of precipitate because the rough surface of the filters help to secure the precipitate.

4.5 Minimize filtration time to prevent more air from being drawn through the filter than necessary if counting the same day is planned. Likewise, allow at least 3 hours for decay of radon progeny before beginning the count.

4.6 A significant positive bias for low level samples (less than 5pCi/L) was found in laboratory tests.

5.0 APPARATUS AND MATERIALS

5.1 stirring hot plate

5.2 stir bars

5.3 Eppendorf® pipettors or equivalent, with disposable pipet tips

5.4 beakers, Pyrex® or similar, 1.5 or 2L

5.5 fiber filters, glass, Gelman® Type A/E filter membranes, Millipore® Type AP, or Whatman® Type 934-AH or other equivalent, 0.45µm pore size , 47mm diameter

5.6 planchets, stainless steel, 5cm diameter

6.0 REAGENTS

NOTE: TLV and other hazard information may also be given here. Any chemical with a Threshold Limit Value (TLV) below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that a substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Deionized water, from the laboratory deionized water system.

6.2 Ammonium hydroxide, 6N. Dilute 400mL reagent grade NH_4OH to 1L with deionized water.
TLV= 25ppm for NH_3. Irritant.

6.3 Barium carrier, 5mg Ba^{+2}/mL. Dissolve 4.4g $BaCl_2 \cdot 2H_2O$ in 500mL DI water.
TLV = 0.06ppm (TWA). Irritant.

6.4 Bromocresol purple. Dissolve 0.2121g of the water-soluble reagent and 29.6988g NaOH in 500mL DI water.

6.5 Iron carrier, 5mg Fe^{+3}/mL. Dissolve 12.1g $FeCl_3 \cdot 6H_2O$ in 200mL DI water, containing 2mL 16N Nitric acid. Dilute to 500mL.
TLV = 0.15ppm, irritant

6.6 Nitric acid, concentrated, 16N.
TLV = 2ppm (TWA), irritant, corrosive

6.7 Sulfuric acid, 1N. Dilute 56mL of 18N H_2SO_4 to 1L with DI water.
TLV = 0.25ppm, irritant, corrosive

6.8 Paper pulp/water mixture. Place 1g of paper pulp in a plastic container and dilute to 1L. Add 5 drops of diluted detergent. Stir vigorously for 3 hours before using. This mixture should be stirring when an aliquot is taken.

6.9 Diluted detergent, 1:4. Dilute any commercial water-soluble detergent or wetting agent with DI water.

6.10 NIST-traceable ^{241}Americium standard solutions: One source for calibration, and a second source for laboratory control samples (LCSs).

7.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15mL 1N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days and then preserved and held in the original container for a minimum of 24hrs before analysis or transfer of the sample.

7.2 The container should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

8.0 PROCEDURE

8.1 PROCEDURE FOR SAMPLES

8.1.1 Use a measured aliquot of water sample. If the available sample volume is less than 500mL, or if a decreased aliquot size is required due to suspected coprecipitation of dissolved solids, dilute a reduced aliquot to 500mL with distilled water. No dilution is necessary for aliquot sizes greater than 500mL.

8.1.2 Prepare quality control (QC) samples per Section 10.

8.1.3 Add 5 drops of the diluted detergent.

8.1.4 Place the sample on a magnetic stirrer/hot plate and, while stirring, gently add 20mL of 1N sulfuric acid and boil for 10 minutes to flush carbon dioxide (from carbonates and bicarbonates) and radon from the sample.

8.1.5 Lower the hot plate temperature to below sample boiling, continue stirring, and add 1mL of barium carrier solution. Continue stirring for 30 minutes.

8.1.6 Add 1mL of bromocresol purple indicator solution, 1mL of iron carrier and 5mL of paper pulp/water reagent (aliquot taken while the paper pulp mixture is stirring). You may cut the end off of the pipet tip to facilitate pipetting the paper pulp if necessary.

8.1.7 Continue stirring and add 6M NH_4OH drop wise to the sample until there is a distinct color change (yellow to purple). Continue warming and stirring for 30 minutes.

8.1.8 Filter the sample through a glass fiber filter, rinsing all precipitate from the beaker to the filter. Wash the precipitate with 25mL of DI water.

8.1.9 Dry the filter in the drying oven and allow a minimum of 3 hours for the collected radon progeny to decay.

8.1.10 Three filter blanks, consisting of a glass fiber filter mounted on a flat planchet, are processed with the samples and used to determine the contribution to background and in determining the background correction to be applied to samples.

8.1.11 Count the filters for alpha activity on a calibrated low background gas flow proportional counter (GFPC).

8.1.12 Store samples in a desiccator if they are to be recounted at a later date. The Instrument Lab will ultimately dispose of the filters in the manner described in SOP 724.

8.2 PREPARATION OF CALIBRATION STANDARDS

8.2.1 Add at least 100pCi of NIST-traceable standard alpha-emitter (^{241}Am or other, as appropriate to meet DQOs), to a series of 500mL portions of DI water in separate beakers.

Add varying amounts of barium and iron carrier solutions (hold the volume of Fe carrier equal to that of the volume of Ba carrier), to produce final precipitate weights varying from 10-110mg.

Add 2.5mL conc. HNO_3 to each beaker and process according to the method.

Determine the background and decay corrected counting efficiency (cpm/dpm) for the alpha-emitter of each standard by taking these known additions through the procedure.

Prepare a curve of at least six standards to determine counting efficiency as a function of residue mass.

Plot mass of residue vs. measured efficiency to establish alpha attenuation correction factors for this method.

8.2.2 The normal mass-corrected efficiency is in the form of::

$$e * b * m^{a(x-x_0)}$$

where:

e = the individual zero-mass detector efficiency

x = the residual mass on the planchet in mg

x_0 = the average residual mass of the efficiency planchets

The mass attenuation curve used for gross alpha by co-precipitation is unable to incorporate a zero-mass point since a precipitate is necessary to the method. To facilitate reporting, in this case e equals the individual mid-mass detector efficiency and x_0 equals the mid-mass in mg.

9.0 CALCULATIONS

9.1 Total Propagated Uncertainty (TPU) is reported at the one sigma level.

9.2 The Prep uncertainty is 0.0564, based on one gross aliquoting, one quantitative transfer, one pipetting, one mass measurement and one volumetric measurement:

$$0.0564 = \sqrt{0.05^2 + 0.025^2 + 0.004^2 + 0.003^2 + 0.006^2}$$

9.3 Instrument uncertainty is assumed to be equivalent to that specified in SOP 708.

10.0 QUALITY CONTROL

Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames); consult applicable LIMS program specification.

10.1 One Laboratory Control Sample (LCS) is processed with each set of 20 or fewer samples. This is done by aliquoting 500mL of DI water made acidic to a pH less than 2 with concentrated nitric acid. The LCS is spiked with approximately 100dpm of ^{241}Am.

10.2 One Blank is processed with each set of 20 or fewer samples. This is done by aliquoting 500mL of DI water made acidic to a pH less than 2 with concentrated nitric acid.

10.3 One duplicate sample is prepared for each batch of ten samples.

10.4 One matrix spike analysis is performed per 20 samples. Matrix spikes are spiked at 5-10 times expected activity.

NOTE: Spikes are added *before* the sample receives any chemical treatment.

11.0 DEVIATIONS FROM METHOD

There are no significant deviations from Standard Method 7110C.

12.0 SAFETY HAZARDS AND WASTE

12.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.2 Gloves, safety glasses, and lab coats must be worn during the sample preparation part of this procedure.

12.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g. solvents and acids).

13.0 REFERENCES

13.1 "Coprecipitation Method for Gross Alpha Radioactivity in Drinking Water" (PROPOSED), Method 7110C, Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.

13.2 "Radiochemical Determination of Gross Alpha Activity in Drinking Water by Coprecipitation", Method 00-02, Eastern Environmental Radiation Facility Radiochemistry Procedures Manual, US-EPA 520/5-84-006, Montgomery, AL, 1984.

13.3 "Gross Radium Alpha Screening Procedure", Method 900.1, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, US-EPA 600/4-80-032, Cincinnati, OH, 1980.

13.4 Paragon SOP 708, "Calculations for Radioanalytical Results".

13.5 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

DOCUMENT REVISION HISTORY

9/11/06: No technical changes. Augmented LIMS program specification language (RESPONSIBILITIES). Added DOCUMENT REVISION HISTORY section. Other minor clerical corrections.

8/31/07: Updated sample hold in original container from 16 to 24hrs when pH adjusted, for consistency with updated CFR metals requirement (Federal Register, 3/26/07, Volume 72, Number 57), Section 7.1. Removed activity calculations and referenced SOP 708, Section 9. Added Notes to Section 10 that acceptance limits for quality control parameters may vary per client specifications, consult applicable LIMS program specification; also spikes are added *before* the sample receives any chemical treatment.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 791 REVISION 3

TITLE: PREPARATION OF SILICA GEL SAMPLES FOR TRITIUM ANALYSIS

FORMS: 302, 311

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/6/07
QUALITY ASSURANCE MANAGER _____ DATE 8/14/07
LABORATORY MANAGER _____ DATE 8/15/07

HISTORY: Rev0, 11/02/01; Rev1, 4/07/03; Rev2, 10/7/03; Re-released w/o revision 11/30/04 and 3/15/05 (format updated); Rev3, 8/12/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the preparation of silica gel matrices for quantitative measurement of tritium by liquid scintillation analysis. This SOP was written specifically for the ESH-17 group at Los Alamos National Laboratory (LANL), but may be applicable to silica gel samples from other clients and sites.

2. SUMMARY

The contents of silica gel filter cartridges used to monitor environmental airborne tritium, are heated in a traditional distillation apparatus to capture the trapped water. The distillate is then analyzed by liquid scintillation counting (LSC, SOP 704) to quantify the tritium extracted from the sample. Water removal efficiencies are monitored by measuring the amount of water extracted from the sample and comparing this value to the field measurement of the corresponding pre-loaded and post-loaded silica gel weights.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst performing the method to notify the Instrument Lab Gas-Flow Proportional Counter analyst in advance of the number of samples arriving and the expected delivery date and time. This allows the analyst to schedule adequate instrument time to analyze the short-lived Ac-228 analyte.

3.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715

as well as the LIMS program specification related to the client, project, and test method being performed.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 This method addresses the preparation of silica gel that has been loaded with ambient water vapor. The presence of other volatile organic compounds has been shown to cause elevated luminescence in the sample/LSC cocktail mixture, which may interfere with the subsequent analysis by liquid scintillation counting. For this reason, silica gel samples are always counted in the LS6000. This instrument provides a lumex correction.

4.2 The target nuclide in this analysis is an isotope of hydrogen (^{3}H), usually bound to a water molecule. Addition of water, acid or any other materials containing significant quantities of hydrogen, and possibly tritium, can significantly alter the hydrogen and tritium concentrations in the sample and could potentially compromise sample integrity.

4.3 All glassware used for this procedure must be cleaned per Paragon SOP 720, using Radiacwash™ or similar detergent, triple-rinsed with DI water, and thoroughly dried in a 100-110°C oven. Distillation flasks should be thoroughly cleaned with aqua regia, as needed, to remove buildup of visible residues in the flasks.

4.4 When determining water removal efficiencies, the mass of water extracted is compared to the mass of water loaded onto the silica gel. In some cases, moisture native to the silica gel, which is not part of the ambient water vapor loaded onto the gel, may be co-distilled and interfere with the accurate determination of distillation efficiency.

4.5 When used for liquid scintillation counting, the scintillation vial is an optical surface. Therefore, any markings or material on the outside of the scintillation vial will interfere with the detection of scintillation using the LSC instrument. All

markings and materials must be removed prior to analysis using alcohol and a lint-free lab wipe. ***All labeling must be done on the cap of the vial.***

4.6 The presence of visible discoloration in the distillate will act as an 'inner filter' in the sample/cocktail mixture. This effect, known as 'color quenching', is an interference to the detection of the scintillation. The quench indicating parameter or 'QIP' (usually H-number), should be monitored, and variations in quench that could correspond to a greater than 10% relative bias in efficiency (+/-15 H#'s), should be addressed by using standard additions to determine a sample specific efficiency. The correct procedure for performing standard additions is detailed in Paragon SOP 704.

4.7 The presence of particulate contaminant in the final distillate may interfere with the detection of the scintillation. This effect is known as 'physical quenching'. The symptoms, control limits, and corrective actions for physical quenching are identical to those discussed in Section 4.6 above.

4.8 The presence of chemical contaminants in the final distillate may inhibit scintillation. This effect is known as 'chemical quenching'. The symptoms, control limits, and corrective actions pertaining to chemical scintillation are identical to those mentioned in Section 4.6 above.

4.9 The presence of volatile beta- (or alpha-) emitting materials (e.g., low boiling organics, etc.), which could co-distill with water, are a positive interference to this method. The sample spectrum is monitored for evidence of higher energy species in the distillate (especially ^{14}C). When counts above the established control limits are observed in the higher energy analysis region, these counts could bias the tritium results, and a Non-Conformance Report (NCR; Form 313), must be initiated. If the tritium results are below the calculated MDC for that sample, or if the sample contains sufficient tritium such that the potential bias is not significant, a Quality Assurance Summary Sheet (QASS; Form 302) and appropriate narrative comments are sufficient.

5. APPARATUS AND MATERIALS

5.1 Scintillation vials, low-potassium glass, 20mL

5.2 VOA vials, 40mL

5.3 Glass bottle, amber, 125mL

5.4 Condenser, Pyrex™, #8946-24 or equivalent, 24/40 ground glass joints

5.5 Distillation neck, Pyrex™, #8946-24 or equivalent, 24/40 ground glass joints

5.6 Flask, round-bottom, Pyrex™ or equivalent, 250mL, 24/40 ground glass neck

5.7 Drying tube, polyethylene with desiccant

5.8 Heating mantle assembly, Lancor™, #01023 or equivalent, fits 250mL flasks

5.9 Variable output transformer, Staco™, #3PN1010 or equivalent

5.10 Infrared Thermometer, Raynger ST #267249, or equivalent

5.11 Small funnel

5.12 Pipette and disposable pipet tips, fixed, 1mL

5.13 Pipettor, adjustable, 1-5mL

5.14 Re-pipette dispenser and disposable pipet tips, adjustable, 1-20mL

5.15 Transfer pipettes, disposable, glass

5.16 Rigid tubing for vacuum, attached to condenser outlet

5.17 Specimen cups, plastic, disposable, with lid

5.18 Analytical balance, 0.0001g sensitivity

6. REAGENTS

6.1 Deionized (DI) water, obtainable from the laboratory's DI water system

6.2 Anhydrous calcium sulfate ($CaSO_4$), or indicating Drierite™

6.3 Liquid scintillation cocktail, Ultima-Gold™ LLT or equivalent brand (e.g., Packard)

6.4 Hydrochloric acid (HC1), 12N, concentrated. TLV = 5 ppm (ceiling). Irritant, corrosive

6.5 Nitric acid (HNO_3), 16N, concentrated. TLV = 2 ppm (TWA). Irritant, corrosive

6.6 Tritium-free water: Water from a deep well or other reagent water (e.g., distilled or deionized), that shows activity indistinguishable from the method background. At the time of publication of this SOP, an independent source of tritium-free water has not been located. As long as this remains the case, each analytical batch will be prepared with laboratory deionized water.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Environmental tritium is collected in a silica gel cartridge. The silica gel can be removed from the cartridge in the field and transferred to a separate container for shipment to the lab, or the loaded cartridge may be sent directly to the lab.

7.2 Tritium samples should not be chemically preserved.

7.3 Keep all sample containers tightly closed. If samples are to be stored for an extended period of time, refrigeration or freezing is recommended to prevent biological growth in the sample.

7.4 At the current time, there is no regulatory holding time for tritium preparation and analysis. Many sampling and analysis plans, however, apply a default holding

time of 180 days from collection for this analysis. If samples are analyzed more than 180 days after collection, this fact should be noted in the case narrative.

8. SILICA GEL DISTILLATION PROCEDURE

8.1 Note the number of functional distillation apparatti available, and gather the appropriate number of collection vessels to be used. The processing of the Quality Control (QC) samples described in Section 9 of this SOP, must also be provided for. Use a 20mL scintillation vial as the collection vessel for these QC samples.

8.2 Consult the moisture loading data provided by the client to determine which type of collection vessel should be used for each sample. For samples with less than 18mL of water loaded onto the silica gel, a 20mL scintillation vial may be used. For samples with greater than 18mL of water loaded, use a 40mL VOA vial. If the moisture loading data indicates that more than 35mL of water is loaded onto the silica gel, use a 125mL amber glass bottle as the collection vessel.

8.3 Label the cap of each collection vessel with a field or QC sample ID. Obtain a tare weight for each collection vessel with cap, using an analytical balance on which a daily calibration verification check has been performed (SOP 305). Record this capped empty collection vessel tare weight on the benchsheet.

8.4 Assuming that the silica gel has already been removed from the sampling cartridge, remove one silica gel sample per remaining available distillation apparatus from the sample storage area. Transfer the entire contents of each sample container into a labeled round bottom flask.

NOTE: If the entire sample does not fit into the flask, **stop immediately**. Tightly cover the flask and sample container with Parafilm, and notify the supervisor and project manager immediately, to receive directions on how to proceed.

8.5 If not already assembled, assemble the distillation apparatti. The heating mantle should be controlled with a variable output transformer. The round bottom flask should fit snugly in the mantle. The neck of the flask and the condenser should be supported with a ring-stand or similar apparatus. The round bottom flask should be fitted securely onto the condenser. The collection vessel (Step 8.1), should be placed snugly under the bottom of the condenser, and should be supported in a small disposable cup or similar apparatus to prevent spillage.

8.6 Fit a flask, containing sample, onto each distillation apparatus. Make sure that the ground glass joints fit tightly together.

8.7 Turn the heating mantle power on. The variable output transformer should be set to approximately 80%.

8.8 Allow the silica gel (or QC sample) to heat for a minimum of two hours. After two hours, use an infrared thermometer to check the surface temperature of the round bottom flask. *The each day of use check (SOP 210) must be performed before using the infrared thermometer.*

Take great care in aiming the thermometer to ensure an accurate reading of the flask below the level of the gel. Be sure not to measure the mantle or other apparatus. If the temperature reads below 200°C, additional heating time is required. Continue heating the sample, checking the temperature approximately every thirty minutes.

NOTE: The infrared thermometer is verified in-house, annually, per SOP 923. General procedures for operating the infrared thermometer are given in SOP 210.

8.9 When the temperature of the flask exceeds 200°C, the distillation is complete. Remove the collection vessel and cap tightly. Be sure that the collection vial is labeled properly with the sample ID number.

8.10 Weigh the vial containing the collected distillate and record this mass on the benchsheet. For field samples, this mass is used to determine the net weight of water recovered, for comparison with the moisture loading data provided by the client. If the water recovery is less than 90% of the expected value, continue heating the sample until the net weight of the distillate remains constant (i.e., ±2%) over a 60 minute interval. ***Do not turn the heating mantle off until this criterion is achieved.*** A QASS should be written for each sample that required additional distillation, to describe the situation and the corrective action taken.

8.11 Once the heating mantles are turned off, allow the silica gel to cool for approximately 60 minutes. When the flask is cool enough to handle, discard the gel into the sanitary trash.

8.12 Use a previously calibrated pipettor (SOP 321), to aliquot 5.0mL of distillate from the collection vial into a labeled, 20mL, glass scintillation vial. Record the aliquot of sample distillate used on the benchsheet.

8.13 If less than 5.0mL of distillate is available, tare a scintillation vial on an analytical balance, transfer the available distillate, Record the transferred distillate on the benchsheet and bring the distillate to the standard mass of 5.0 grams with tritium-free water. This brings the reduced sample volume to a standard counting geometry volume. If the distillate was collected in a 20mL glass scintillation vial, this same vial may be used for the actual analysis, without transferring the sample to a new vial.

8.14 Dispense 15.0mL Ultima Gold LLT™ scintillation cocktail into each scintillation vial, cap, and shake well.

8.15 Clean the outside of the scintillation vials with a lint-free wipe and alcohol to remove dust, smudges, and fingerprints.

8.16 Place the vials in a scintillation counting rack, and deliver the vials and benchsheet to the Instrument Lab for counting.

9. QUALITY CONTROL

9.1 CALIBRATIONS

9.1.1 Re-pipettor calibration: The re-pipette dispenser is checked monthly by dispensing a 10mL aliquot of scintillation cocktail into a 10mL graduated cylinder. The volume dispensed should be 10mL +/- 0.1mL. If not, adjust the dispenser and re-check. Record the calibration check in the pipette calibration logbook (Form. When scintillation cocktail is dispensed in Step 8.14 of this SOP, it is delivered as two 7.5mL aliquots.

9.1.2 Efficiency calibration: Single point efficiency calibrations should be performed in the same counting geometry as the samples, typically 5.0mL sample in 15.0mL cocktail. The specific calibration sequence is detailed in SOP 704.

9.1.3 Background calibration (calibration blanks): Unless the client specifically requests otherwise, the instrument background rate will be determined by preparing seven calibration blanks in the same counting geometry as the samples (i.e., 5mL of DI water with 15mL of Ultima Gold™ LLT scintillation cocktail added will be used). The calibration blanks will be counted under identical parameters as the samples, and the mean gross count rate will be used as the instrument background count rate for this method. This approach should be noted in the case narrative, and all pertinent raw data and calculations should be provided in the data package report. If requested by the client, the instrument background rate may be determined using the background calibration procedure described in SOP 704.

9.2 QC SAMPLE PREPARATION

9.2.1 Quality control samples are processed and results calculated in the same manner as the associated field samples.

9.2.2 Method Blank. One Method Blank is prepared per each batch of 20 or fewer samples. The method blank is prepared by distilling 10mL of DI water (distill 20mL of DI water if a laboratory control sample duplicate

is prepared for the sample set; this provides for volume consistency amongst the QC samples), without silica gel, as described in Section 8.

9.2.3 Blank Spike (also known as the Laboratory Control Sample, LCS). Prepare one Blank Spike (LCS) per batch of 20 or fewer samples. If there is insufficient field sample to prepare a client sample duplicate per Section 9.2.3 below, the laboratory control sample can be prepared in duplicate (i.e., create an LCSD).

Dilute approximately 2000 pCi ^{3}H with tritium-free water to a final volume of 10.0mL to prepare an LCS. If both an LCS and LCSD are to be prepared, dilute approximately 4000 pCi ^{3}H with tritium-free water to a final volume of 20.0mL.

Distill and prepare as described in Section 8.

9.2.4 Sample duplicates are prepared at a minimum frequency of two per batch of 20 samples or 10%, whichever is greater. The sample duplicate is prepared by aliquotting a second 5.0mL portion from the same distillate obtained for the sample (the total amount of sample distillate should exceed 10.3mL in order to accommodate the duplicate as well). If the volume of sample distillate is limited, note in a QASS and prepare an LCSD (as described in Section 9.2.2) instead.

10. CALCULATIONS

10.1 The sample activity, TPU, and minimum detection concentration calculations are provided in SOP 708, Calculations for Radioanalytical Results.

10.2 The tritium Prep Uncertainty, as shown below, is 0.007 based on one pipetting and one reagent addition:

$$0.007 = \sqrt{(0.004^2 + 0.006^2)}$$

11. DEVIATIONS FROM METHOD

This procedure is compliant with Method H-02, of the Eastern Environmental Radiation Facility (EERF) Procedures Manual.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 Renew the anhydrous $CaSO_4$ desiccant approximately every analytical run, or as needed. Remove the drying tube and replace the spent $CaSO_4$ with fresh anhydrous $CaSO_4$.

12.1.2 Read the MSDSs prior to preparing standards or using any solvents or reagents.

12.1.3 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

12.1.4 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents) or when handling materials or equipment potentially contaminated with chemicals (e.g., samples).

12.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at a minimum with compound name; NFPA Health, Flammability, and Reactivity ratings; and date.

12.1.6 Care should be taken when working with the heating mantles and boiling water to prevent thermal burns.

12.1.7 Silica gel, when dry, can be a skin and respiratory irritant. All handling of the silica gel should be done inside a fume hood.

12.2 WASTE DISPOSAL

12.2.1 All empty radionuclide standard solutions are disposed of by rinsing the standard container a minimum of three times using tap water. The container must be surveyed prior to release for disposal. Please note that all labels and markings must be defaced or removed prior to disposal.

12.2.2 The tritium analytical process effluent from this method has been determined to not be hazardous in any way. Consequently, this material may be discharged into the Paragon wastewater treatment facility (i.e., down the drain with plenty of tap water). The solution will be neutralized prior to discharge, and the radionuclide concentration will be monitored to ensure compliance with Colorado Rules and Regulations, Radiation Control, Part 4.

12.2.3 Silica gel is non-hazardous and, after distillation, may be disposed of in the sanitary trash. The original sample containers may also be placed in the sanitary trash after rinsing the container and removing the client ID label and any other identifying marks.

12.2.4 Check with waste management staff for proper disposal of scintillation cocktail.

12.2.5 Vials of sample/cocktail mixture may be accumulated (intact) in a container provided by Waste Management Staff.

13. REFERENCES

Eastern Environmental Radiation Facility (EERF) Manual, Method H-02; June, 1984.

DOCUMENT REVISION HISTORY

8/12/07: Calculations were removed and reference to SOP 708 -- Calculations for Radioanalytical Results was made instead. Added DOCUMENT REVISION HISTORY and Forms.

Paragon Analytics

QUALITY ASSURANCE SUMMARY SHEET

PAR W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

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TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

FORM 302r6.doc (4/22/04)

Paragon Analytics

PIPETTE CALIBRATION VERIFICATION LOG

Balance ID_____

Date	Analyst	Pipet ID Number	Nominal Volume (mL)	Observed Wt. (g)	Pipet Setting	Comment

PIPETTE TOLERANCE: ±1.0 % (regardless of volume dispensed)

Reviewed by _____ Date: _____

FORM 311r6.frm (9/10/2002)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 792 REVISION 0

TITLE: **DETERMINATION OF TOTAL ALPHA-EMITTING RADIUM ISOTOPES IN ENVIRONMENTAL SAMPLES BY ALPHA SPECTROSCOPY**

FORMS: **631**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 9/4/07

QUALITY ASSURANCE MANAGER _____ DATE 9/3/07

LABORATORY MANAGER _____ DATE 9-4-07

HISTORY: Rev0, was DRAFT, first published 8/31/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the measurement of total soluble alpha emitting isotopes of radium, namely Ra-223, Ra-224, and Ra-226, in environmental samples.

2. SUMMARY

2.1 SAMPLE PREPARATION (MINERALIZATION / CONCENTRATION / DISSOLUTION)

2.1.1 **Aqueous Samples:** Barium-133 tracer is equilibrated with an aliquot of the sample. Aqueous samples are concentrated using cation exchange. The column eluate is taken to dryness and is redissolved in 0.095M HNO_3. Radium is separated from the concentrated sample as summarized in Section 2.2 below.

2.1.2 **Solid Samples:** A representative sub sample of the sample is dried and ground. Barium-133 is equilibrated in 1 gram of the ground sample. The sample may be muffled if significant organic material (e.g., humic soils or oily solids) is present. The sample is digested on a steam bath in concentrated HCL, HNO_3, and HF acids. The sample is taken to dryness and redissolved in concentrated HNO_3 and DI water. The sample is concentrated using cation exchange resin. The column eluate is taken to dryness and is redissolved in 0.095M HNO_3. Radium is separated from the concentrated sample as summarized in Section 2.2 below.

2.2 SEPARATION, PURIFICATION, AND MOUNTING OF THE RADIUM

Radium is separated from the nitric acid digestate/concentrate using Eichrom LN-Resin. The radium is co-precipitated with $BaSO_4$ and mounted onto a

polypropylene filter. The filter is mounted onto a planchet and submitted for alpha spectroscopy analysis, as described in SOP 714. To quantify Ra-224 directly, the alpha counting must start within 24 hours of barium sulfate precipitation. After alpha counting the filter is counted by gamma spectrometry to determine the Ba-133 concentration to establish the chemical recovery of the sample. The radiometric results are corrected for chemical yield on a sample-by-sample basis.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful completion of a proficiency evaluation test.

3.2 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715, and the applicable LIMS program specification.

3.3 In the event that Ra-224 analysis is required , it is the responsibility of the technician performing this separation method to coordinate the delivery of samples with the instrument analyst to ensure that sufficient detector capacity is immediately available.

3.4 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon’s standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who perform this procedure to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 The presence of significant native barium in the sample may cause interference by producing excessive precipitate in the final preparation steps. This will lead to degradation of spectral quality due to mass-attenuation of the alpha particle kinetic energy. In this case, a split of the separated (Ra + Ba) sample must be performed prior to micro-precipitation, in order to limit the total mass of $Ba(Ra)SO_4$ deposited on the filter.

4.2 Samples that contain very high concentrations of cation concentrations can overwhelm the capacity of the cation exchange column. This will cause a low chemical and radiometric recovery in the samples.

4.3 Samples that contain a significant concentration of sulfates may sequester the radium and barium as $Ba(Ra)SO_4$, making these analytes unavailable to the separation technique. This may result in a either a low chemical yield, with otherwise acceptable results, or an overall low bias in the final results.

5. APPARATUS AND MATERIALS

5.1 Disposable ion exchange columns: 15mL resin volume with attachable funnel to receive 2 L bottle. (Environmental Express part numbers R10204 and R10304 or equivalent.)

5.2 Disposable Bio-rad column (catalog #731-1553) or equivalent, with funnel.

5.3 Analytical balance with 0.0001g resolution, Mettler AE200 or equivalent.

5.4 Pipet tips

5.5 Graduated cylinder, 1L

5.6 50 mL polypropylene centrifuge tubes

5.7 2 L disposable plastic bottles

5.8 Repipettor, Eppendorf model 4780 or equivalent

5.9 pH paper

5.10 Eppendorf pipets or equivalent, variable volumes

5.11 Specimen cups, 250mL, or equivalent

5.12 Specimen cups 100mL or equivalent

5.13 Tongue depressors

5.14 Test tubes, 15mL, disposable, with caps

5.15 Beaker, 50, 100, 400, and 500mL

5.16 Plastic stir rods

5.17 Polypropylene filter, 0.1 micron, 25mm

5.18 Polysulfone funnel

5.19 Heat lamp

5.20 Desiccator

5.21 Metal wire, bent into a loop

5.22 Hot Water Bath, (90-100 °C)

5.23 Vacuum apparatus

5.24 Vacuum desiccator

5.25 0.45µ membrane filter

5.26 Stir bars, plastic

5.27 Erlenmeyer flask, 250mL

5.28 Blast burner, or equivalent

5.29 Tongs

5.30 Transfer pipets, plastic

5.31 Funnel, plastic, to fit in the Bio-rad column

5.32 Filter paper, Whatman 41

6. REAGENTS

NOTE: TLV and other hazard information may also be given here. Any chemical with a TLV below 50 ppm must be worked with in a laboratory fume hood. The absence of this information does not mean that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Deionized (DI) water, ASTM Type II.

6.2 NIST traceable ^{133}Ba spiking solution. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.3 NIST traceable ^{226}Ra spiking solution. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.4 Hydrofluoric acid (HF), 48.0-51.0 %, conc. TLV = 3 ppm (ceiling). Irritant, burns, bone, teeth, fluorosis.

6.5 Nitric acid, concentrated (16M). ACS grade. TLV = 2 ppm (TWA). Irritant, corrosive

6.6 Nitric acid, 8M: Cautiously add 500mL of concentrated nitric acid to 400mL of DI water. Dilute to 1 L. See 6.5 for TLV.

6.7 Nitric acid, 0.1M: Cautiously add 6.3mL of concentrated nitric acid to 900mL of DI water. Dilute to 1 L. See 6.5 for TLV.

6.8 Nitric acid, 0.095M: Cautiously add 6.0mL of concentrated nitric acid to 900mL of DI water. Dilute to 1 L using a class A 1 L volumetric flask. See 6.5 for TLV.

6.9 Hydrochloric acid, concentrated (12M). ACS grade. TLV = 5 ppm for conc. HCl (ceiling). Irritant, corrosive.

6.10 ICP Solution; 5% HNO_3/2.5% HCL for diluting solutions to be analyzed by ICP. Carefully add 50mL of concentrated HNO_3 and 25mL of concentrated HCL to 925mL of DI water. Mix thoroughly. See 6.5 and 6.9 for TLVs.

6.11 Cation exchange resin, AG50x8 (Eichrom or equivalent).

6.12 LN resin, Eichrom (particle size 50-100µm).

6.13 Silica sand, reagent grade.

6.14 Barium chloride, dihydrate ($BaCl_2 \bullet 2H_2O$), reagent grade. TLV = 0.5 mg/m^3 (TWA) as Barium.

6.15 Barium carrier, 0.75mg/mL: Dissolve 338 mg of barium chloride, dihydrate, in 200 mL DI water and dilute to 250 mL with DI water. See 6.14 for TLV.

6.16 Glacial Acetic Acid (CH_3COOH_2), 17.4N, concentrated: 99.8%, ACS reagent grade. TLV = 10 ppm (TWA). Irritant.

6.17 Acetic acid, 1:1: Add 500mL of glacial acetic acid to 400 mL DI water and dilute to 1 L. Shake to mix before use. See 6.16 for TLV.

6.18 Sodium sulfate, anhydrous, reagent grade.

6.19 Sodium sulfate, 20%: Dissolve 100g of anhydrous sodium sulfate in 460mL of DI water at room temperature with stirring and filter through 0.45µm filter. Collect filtrate and discard residue on the filter.

6.20 Sodium sulfate, 70%: Add 45mL of concentrated sulfuric acid slowly with continuous stirring to 180mL of water in a 500mL beaker. Add 104g of anhydrous sodium sulfate. Cover the beaker and stir until completely dissolved. See 6.21 for sulfuric acid TLV.

6.21 Sulfuric acid, concentrated (36M). ACS grade. TLV = 1 mg/m^3 (= 0.25 ppm)

(TWA). Irritant. Strong mists are considered a suspected human carcinogen.

6.22 Seeding suspension: Place 11.3mg of barium chloride, dihydrate, 10mL of the 70% sodium sulfate solution in a 250 mL Erlenmeyer flask. Evaporate the solution carefully over high heat (e.g. a blast burner) while swirling the solution continuously to prevent bumping until the barium sulfate has dissolved. Increase the heating and continue until most of the excess sulfuric acid has been expelled and a fusion is obtained. Cool the flask and add a solution of 50mL of 20% sodium sulfate solution and 25mL of DI water. Swirl to mix. **To be prepared fresh weekly.** (Old seeding suspension may cause a degradation of the alpha peak resolution. In old suspensions, recrystallization of the barium sulfate may occur that is significant enough to cause the original extremely finely divided barium sulfate to become more granular, which in turn sets the lattice for the precipitation.) See 6.14 and 6.20 for TLVs.

6.23 Methanol, reagent grade. TLV = 200 ppm.

6.24 Amyl acetate, reagent grade. TLV = 100 ppm as n-Amyl acetate.

6.25 Collodion, reagent grade.

6.26 Thin film solution: Add 1:1 ration of amyl acetate and collodion together. Mix well. Prepare fresh weekly. See 6.24 for TLV.

7. PROCEDURE

7.1 SOLID SAMPLES

7.1.1 Verify and record (on Form 631) the condition of the sample.

7.1.2 Weigh 1 gram of dried, pulverized soil into a permanently labeled 50 or 100mL glass beaker. Typical aliquot size is 1.0g but may be adjusted due to MDA or matrix interference considerations. Record the sample weight and beaker number on the benchsheet.

NOTE: If the samples do not require muffling (little to no organic material), aliquot into a 250mL specimen cup.

7.1.3 Prepare QC samples by placing an ashless filter paper in a permanently labeled 50 or 100mL glass beaker. If no muffling is required do not add filter paper, label a 250mL specimen cup instead.

NOTE: Spiking and tracing activity levels for solids, and in some cases liquids, may need to be significantly adjusted to allow for possible splitting of the prepared sample, before micro-precipitation. This may be necessary in samples with elevated native barium concentrations.

Unless otherwise directed, spike the LCS with 10-50 dpm of Ra-226. Activity levels may be adjusted after consulting with the alpha spectroscopist, and with approval from the Department Manager. Add spikes *before* chemically treating sample.

7.1.4 Add 1,000-5,000dpm of Ba-133 to all the samples. Activity levels may be adjusted after consulting with the gamma spectroscopist, and with approval from the department manager.

7.1.5 If muffling is not required proceed to Section 7.1.8, also adding 25mL of concentrated nitric acid. Otherwise proceed to Step 7.1.6.

7.1.6 Dry the beakers on a hotplate set at 2. Cover beakers with a watch glass and muffle at approximately 600˚C for at least 4 hours.

7.1.7 After muffling, allow the beaker to cool and transfer to a 250mL specimen cup with 25mL of concentrated nitric acid. Scraping with a plastic spatula may be necessary to remove all of the soil from the beaker.

7.1.8 Add 25mL of concentrated HCl and 25mL of concentrated HF. Cover the sample with a 100mL specimen cup and heat for 4 hours on a steambath.

7.1.9 Remove the 100mL specimen cup and take the sample to dryness. The 100mL specimen cups may be rinsed off with tap water and disposed of in the sanitary trash.

7.1.10 Once samples are dry, redissolve the residue in 10 mL of concentrated nitric acid and approximately 100mL of DI water. Leave on the steambath for 15 minutes to aid in the dissolution of the sample. Remove from steambath.

7.1.11 Remove a known aliquot for ICP analysis. Bring the sample to a known volume with DI water. Using the graduations on the specimen cup to determine the sample volume is acceptable. Record this volume on the bench sheet. Pipette 0.1mL, into a disposable test tube. Add 9.9mL ICP solution. Submit to the metals department for Ba analysis by ICP.

7.1.12 Proceed to Section 7.3 for concentration by cation exchange.

7.2 PROCEDURE FOR AQUEOUS SAMPLES

7.2.1 If, based on the expectation of matrix interferences, an ICP analysis of the native Ba concentration is indicated, perform Step 7.1.11 before proceeding.

7.2.2 Verify and record the pH of the sample on a liquid sample condition form per SOP 733.

7.2.3 Measure an aliquot in a graduated cylinder and place the aliquot in a labeled disposable 2 L bottle. Record the volume in mL on the benchsheet. Typical sample volume is 1 L. If sample volume is less than 1 L, note the volume on the benchsheet.

7.2.4 Prepare a blank and an LCS by aliquotting 1 L of DI water for both and tranfering to a labeled 2 L disposable bottle.

7.2.5 NOTE: Spiking and tracing activity levels for solids, and in some cases liquids, may need to be significantly adjusted to allow for possible splitting of the prepared sample, before micro-precipitation. This may be necessary in samples with elevated native barium concentrations.

Unless otherwise directed, spike the LCS with 10-50 dpm of Ra-226. Activity levels may be adjusted after consulting with the alpha spectroscopist, and with approval from the Department Manager.

7.2.6 Add 1,000-5,000 dpm of Ba-133 to each sample.

7.2.7 Proceed to Section 7.3 for concentration by cation exchange.

7.3 CONCENTRATION BY CATION EXCHANGE

7.3.1 Precondition a disposable ion exchange column by adding 1-2mL of methanol, just enough to pass through the frit at the orifice of the column, which is hydrophobic. Transfer cation exchange resin to the stem of the column as a slurry with DI water to at least the 7 cm mark. Place a layer of glass beads (approximately 1 cm) on top of the resin bed to hold the resin in place. Attach the funnel to the column (make certain that the column and funnel fit tightly), and precondition the column with 50mL of 0.1M HNO_3. Discard the conditioning solution into the Paragon wastewater treatment facility (down the laboratory sink followed by plenty of tap water).

7.3.2 Pass the sample through the column at a rate of about 1-2 mL/min. This is accomplished by inverting the 2 L bottle into the funnel that is attached to the top of the cation exchange column. Secure the 2 L bottle to a laboratory stand or support with a rubber band. The sample will feed automatically through the column. For solid samples pour the entire sample directly into the funnel.

7.3.3 After the sample has completely passed through the resin, rinse the column with 30 mL of 0.1M HNO_3.

7.3.4 Discard the feed and rinse solutions into the Paragon wastewater treatment facility (down the laboratory sink followed by plenty of tap water).

7.3.5 Elute Ra, Ba, and other cations with 100 mL of 8M HNO_3. Collect the solution in a labeled 250mL specimen cup and take to dryness on a steambath.

7.3.6 The used resin from the column is collected in a wide mouth jar labeled "Resin Waste" for disposal. When the container is full contact the Waste Management Officer for disposal instructions.

7.3.7 Dissolve the residue from Step 7.3.5 with 10mL of 0.095M HNO_3. If necessary, cover with a 100 mL specimen cup and heat on the steambath to aid in dissolution.

7.3.8 Proceed to Section 7.4 for purification by LN resin.

7.4 PURIFICATION BY LN RESIN

7.4.1 Prepare LN resin column: Use a Bio-rad column (catalog #731-1553) or equivalent and transfer the LN resin to the column as a slurry with DI water. Add resin up to approximately the 1.6 mark on the column. Place a layer of clean silica sand on top of resin bed to hold resin in place. Attach a funnel to the column.

7.4.2 Precondition the LN resin column by passing 5mL of 0.095M HNO_3 through the column.

7.4.3 Place a clean, labeled 250 mL specimen cup underneath each column.

NOTE: The following Steps 7.4.3 to 7.5.18 should be carried out without a break and as quickly as possible. Where ICP determination of native Ba concentrations is required, ensure that the ICP results are available and reviewed before proceeding.

7.4.4 Transfer the sample solution to the funnel of the column. Collect the eluate for Ra and Ba.

7.4.5 Rinse the 250mL specimen cup with 5mL of 0.095M HNO_3 and add to the column after the feed has passed through. Collect the eluate for Ra and Ba.

7.4.6 Rinse the column with 5mL of 0.095M HNO_3 and collect the eluate for Ra and Ba.

7.4.7 Repeat Step 7.4.5.

7.4.8 Place the specimen cups containing the Ra and Ba fraction on a steambath and evaporate to about 10mL. Cool solution to room temperature.

7.4.9 Transfer the solution to a 50mL centrifuge tube, rinsing the specimen cup with approximately 5mL of DI water.

NOTE: Where a gravimetric split of the sample may be necessary due to elevated native Ba concentrations, record the tare weight of any 50mL centrifuge tubes that will be used for splitting samples, before transferring the samples into the tubes.

7.4.10 For those reasons discussed in the "Interferences" section, the total mass of barium in the sample, including Ba carrier added, should not exceed 0.1mg. The following steps should be followed for soils, and potentially for waters, in which native Ba is suspected and for which ICP Ba analyses have been performed.

7.4.10.1 Carefully review of the native Ba concentrations, determined by ICP. Calculate a sample fraction, to be used in the micro-precipitation of the sample, that does not contain more than 0.1mg native barium.

7.4.10.2 Gravimetrically transfer the appropriate aliquot of the sample, as calculated in Section 7.4.10.1, to a clean, tared 50mL centrifuge tube.

7.4.10.3 When the entire fraction for analysis contains more than 0.05 mg native Ba, skip Section 7.5.1 and proceed directly to Step 7.5.2. If the entire fraction for analysis contains less than 0.05mg native Ba, proceed to Section 7.5.1.

7.5 MICROPRECIPITATION OF RADIUM AND BARIUM

7.5.1 Add 0.1mL of Ba carrier.

7.5.2 Add 6mL of 20% sodium sulfate solution. Immediately add 4 drops of 1:1 acetic acid solution and gently mix.

7.5.3 Add 0.1mL of seeding suspension, cap the sample and mix the solution gently.

7.5.4 Place the tube in an ice-water bath for at least 30 minutes.

7.5.5 Place a 25mm 0.1µ polypropylene filter on a filter apparatus with a polysulfone funnel.

7.5.6 Add approximately 5mL of methanol to the filter, applying vacuum and ensuring there is no leak along the sides. Add approximately 5mL of DI water to the filter.

7.5.7 Just as the DI water is about to pass all the way through, transfer the solution from Step 7.5.4 into the funnel.

7.5.8 Rinse the sample tube with 5mL of DI water and transfer into the funnel.

7.5.9 Rinse the sides of the funnel thoroughly with DI water.

7.5.10 Rinse the funnel with approximately 5mL of methanol.

7.5.11 Remove filter and attach to a stainless steel planchet using double sided tape.

7.5.12 Dry the filter under a heat lamp.

7.5.13 Place the filter into a desiccator and apply vacuum for 20 minutes. After 20 minutes, close the valve to the desiccator first, followed by the closer of the vacuum valve. At the desiccator, disconnect the hose that connects the desiccator to the vacuum line. Slowly open the desiccator valve in such a manner as to release the vacuum in the desiccator very slowly.

7.6 PREPARATION OF "THIN-FILM" COVERING TO PROTECT ALPHA DETECTORS

7.6.1 Add approximately 250mL of DI water to a 400mL beaker.

7.6.2 Place a metal wire loop into the DI water; making sure the entire loop is covered by the DI water. Bend the arm of the wire loop over the beaker to hold the loop in place.

7.6.3 Place 1 drop of the Thin film solution into the beaker. Allow 30 seconds for the thin film to cure, then remove and allow to dry.

7.6.4 Once dry, place thin film over the planchet. Push the wire loop down below the planchet to seal the thin film to the rim of the planchet and to break off the excess film material. If necessary, smooth the excess

under the planchet.

7.6.5 Repeat Steps 7.6.1 through 7.6.4 above until all samples have thin films placed over them.

7.6.6 Arrange the planchets in a petri dish and label the petri dish with the analyte, sample ID's and batch number. Submit the prepared samples and the updated benchsheet to the Counting Lab. Relinquish the samples to the Counting Lab in the ICOC. The Counting Lab will analyze and ultimately dispose of the planchet and disk in the manner described in SOP 714.

8. CALIBRATION

8.1 Prepare a set of three calibration samples by adding approximately 5,000 dpm Ba-133 and approximately 10,000 dpm Ra-226 activity to a labeled, empty 250mL specimen cup.

8.2 Take to dryness on a steambath.

8.3 Redissolve the residue in 10mL of 0.095M HNO_3.

8.4 Proceed to Section 7.4 and continue until Step 7.6.6.

9. CALCULATIONS

TPU FACTORS. As defined in SOP 708, the following one-sigma preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty:

9.1 Water samples require a preparation uncertainty factor of 0.0752. This factor is based on one gross aliquoting (sample homogeneity), one volumetric measurement, one tracer addition, and four quantitative transfers. See the following equation:

$$0.0752 = \sqrt{.05^2 + .006^2 + .025^2 + .025^2 + .025^2 + .025^2 + .025^2}$$

9.2 Soil samples require a preparation uncertainty factor of 0.0792. This factor is based on one gross aliquoting (sample homogeneity), two mass measurements, one tracer addition, and five quantitative transfers. See the following equation:

$$0.0792 = \sqrt{.05^2 + .003^2 + .003^2 + .025^2 + .025^2 + .025^2 + .025^2 + .025^2 + .025^2}$$

9.3 In practice, these values are substantially equivalent. For simplification in reporting, the larger factor of 0.0792 may be used for both matrices.

10. QUALITY CONTROL

Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.1 A blank and laboratory control sample (blank spike, LCS) is run for each batch. Both are run at a 5% minimum frequency. Each is taken through the entire procedure as specified for the matrix.

10.2 The LCS (blank spike) is spiked with 10 - 50 dpm of Ra-226 standard solution using a calibrated pipet.

10.3 DI water is used as the matrix for the blank and blank spike of water samples. If soil samples are to be muffled, an ashless filter is used for the blank and blank spike. If soil samples do not need muffling, an empty 250mL specimen cup is used for the blank and blank spike.

10.4 Sample duplicates are run at a 10% minimum frequency. If enough sample is not provided to do duplicates, an LCS duplicate is prepared and analyzed.

11. DEVIATIONS

This method is adopted from the ASTM Draft Method, "Standard Test Method for Alpha-Emitting Radium Isotopes in Water". Paragon has adapted this method to accommodate soils and solids, including the ICP determination of native Ba to prevent mass-attenuation in analysis by alpha spectrometry.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids). TLVs may be found in the reference cited in Section 13.2 below.

12.2 Read the appropriate MSDSs before preparing standards or using any reagents.

12.3 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

12.4 Gloves, safety glasses and lab coats must be worn when working with any chemicals (e.g. standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals. Use care when handling strong acids (e.g. HNO_3, HCl, etc.). When diluting strong acids, always add acids to water, not water to acids.

12.5 All non-original containers used to hold reagents (e.g. wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) the date.

13. REFERENCES

13.1 ASTM Draft Method, "Standard Test Method for Alpha-Emitting Radium Isotopes in Water". 11/22/04.

13.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

Paragon Analytics

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 799 REVISION 3

TITLE: DETERMINATION OF RADON-222 IN WATER SAMPLES BY LIQUID SCINTILLATION COUNTING - SM METHOD 7500-Rn B AND ASTM METHOD D5072-92

FORMS: 631

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/31/06

QUALITY ASSURANCE MANAGER _____ DATE 8/31/06

LABORATORY MANAGER _____ DATE 8-31-06

HISTORY: Rev0, 3/14/00; Rev1, 4/26/02; Rev2, 9/22/03; Rev3, 9/1/06.

1. SCOPE AND APPLICATION

The methods specified are for Rn-222 (radon) in drinking water. This procedure has been developed for the analysis of radon in drinking water, groundwater and surface-water. Applications of this analytical procedure to matrices other than drinking water have not been studied; use caution in analyzing any such samples.

The Minimum Detectable Concentration (MDC) is estimated at <50pCi/L for a 50 minute count time assuming ~6cpm background (optimized counting window), ~3cpm/dpm efficiency, and 2-4 days decay between sampling and analysis.

This procedure is substantially compliant with Standard Methods for the Evaluation of Water and Wastewater Method 7500-Rn B and ASTM Method D5072-92.

2. SUMMARY

The sample is carefully transferred from a zero headspace 40mL VOA vial to a scintillation vial containing water-immiscible mineral-oil cocktail, taking precautions to minimize losses of Rn-222 in the water sample. The vial is capped and shaken. Radon partitions selectively into the mineral-oil scintillation cocktail. The sample is dark-adapted, and the short-lived Radon daughters are allowed to come to equilibrium. The samples are then counted in a Liquid Scintillation Counter (LSC) using a region of the energy spectrum optimal for radon alpha particles. Results are reported as pCi/L and decay corrected to the time and date of collection.

3. RESPONSIBILITIES

3.1 In the event that a sample containing headspace is received by the lab, it is the responsibility of the analyst to immediately notify the Project Manager (PM) for instructions.

3.2 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 and also in any LIMS program specification related to the client, project, and test method being performed.

3.3 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.4 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review or in the performance of precision and accuracy tests, or by other suitable means.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 There are no known chemical interferences from species found in drinking water or from the dilute concentration of acid that may be present in the calibration standards.

4.2 Uranium, radium, or other radioactive elements may cause a positive bias, if present in quantities significantly greater than the radon. Thorium-228 or Uranium-235 daughters (Thorium-227 and shorter-lived progeny) in the samples will lead to the presence of Radon-220 or Radon-219 in the sample. The half-lives of these species is such that partitioning into the cocktail is minimal, thus interference with the Radon-222 measurement is routinely minimal.

4.3 Diffusion of radon is affected by temperature and pressure. Let samples equilibrate to room temperature before processing.

4.4 Some cocktails are quenched by atmospheric oxygen after opening. This effect has not been noted for the mineral-oil-based cocktail.

4.5 Precision and accuracy of the method are affected by the background in the energy window used for analysis. This procedure provides for optimization of the counting window to minimize the background in the measurement.

4.6 Radon has an affinity for some plastics used in sample containers. Use only glass sample containers or glass scintillation vials with Teflon or foil-lined caps.

5. APPARATUS AND MATERIALS

5.1 Pipettor, Precision® mechanical pipette, or syringe, 10mL. Calibration of pipette must be verified (SOP 321) before use.

5.2 Pipette tips, modified by cutting approximately 5mm from the tip to minimize turbulence during the sample transfer.

5.3 Scintillation cocktail dispenser, or pipette adjusted to deliver 10mL. Calibration of pipette must be verified (SOP 321) before use.

5.4 Scintillation vials, borosilicate glass, 23mL, with Teflon or foil-lined caps.

5.5 KimwipeS®

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that a substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.2 Scintillation cocktail, Dupont water-immiscible *High Efficiency Mineral Oil Cocktail*®, or other commercial equivalent

6.3 Water, radon-free demineralized or equivalent

6.4 Methanol, reagent grade. TLV = 200 ppm.

6.5 Radium-226 standard solutions, NIST-traceable, one source for calibration and a second source for check standards.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLD TIME

7.2 Sampling is the sole responsibility of the client. Guidance from the laboratory, however, is appropriate to help assure the integrity of results. The recommended sampling procedure is summarized in Appendix A of this SOP, and should be provided to clients requesting this test.

7.3 Radon-222 has a 3.823 day half-life. The USEPA has established a holding time of 4 days for this analysis. Sample analysis must be completed counting within 4 days of collection.

7.4 Sampling schedules must be pre-arranged and approved by the laboratory to ensure that adequate capacity is available to meet the hold time restriction of 4 days.

7.5 Samples are routinely collected from a non-aerated water source (distribution system or well, etc.) that has been allowed to flow for sufficient time so that the sample is representative of the water being sampled.

7.6 The time, date and time zone for sample collection must be accurately recorded and used for decay correction of sample results. Transport samples by overnight delivery to the laboratory in a cooler or other suitable insulated package to avoid large temperature changes and out-gassing of radon. Samples should be stored in a cooler.

8. PROCEDURE

8.2 PREPARATION OF CALIBRATION STANDARDS

8.2.1 Prepare an appropriate volume of radium-226 in water standard so that the final activity will deliver adequate response such that 10,000 net counts can be gathered in the analysis window within a reasonable count period.

8.2.2 Transfer 10mL diluted standard into a scintillation vial, to which 10mL of mineral oil cocktail has been added. Prepare at least three standards and three backgrounds using distilled or deionized water.

8.2.3 Set standards and background samples aside for ~25 days (99% ingrowth) to allow radon progeny to attain secular equilibrium with radium-226.

8.2.4 Determine optimal analytical window as outlined in Section 8.3 below.

8.2.5 After the ingrowth period, let the sample dark adapt for 3 hours and count for 50 minutes or other appropriate time period, ensuring that 10,000 net counts are gathered for each standard.

8.2.6 From pooled results, calculate a system calibration factor which reflects the system response in net cpm per dpm Rn-222, using the equation in Step 9.1.

8.3 SELECTING THE OPTIMAL WINDOW

8.3.1 Count a radon standard for 5 minutes or sufficient time to acquire several thousand counts or more in the alpha region, and generate a sample spectrum.

8.3.2 For greater clarity, use a log scale for the channel number or energy axis, if possible. The alpha activity region of interest (ROI) will be

obvious as one or two large peaks at the higher end of the energy spectrum. The lower peak is the doublet of radon-222 and polonium-218 and the higher peak is that of polonium-214. The optimal window is formed by extending the region by approximately 10 channels on each side of the alpha peaks. Use this window for subsequent calibration and analysis. The calibration factor (see 9.1) should be at least 6cpm/pCi with the background not exceeding 6cpm.

8.3.3 For counters not having a spectrum display, set the window initially wide-open and count for sufficient time to obtain several thousand counts. Adjust the energy window to a width of 5% of full scale at the upper end of the scale (95 to 100%) and determine the count rate in the region. Repeat counts at successively lower regions using the same 5% interval (90 to 95, 85 to 90, 80 to 85, etc.). Plot the count rate versus the midpoint of each interval and choose a ROI, which will be evident by one or two prominent peaks in the upper half of the energy scale. Background should be 6cpm or less and the conversion factor should be approximately 6cpm/pCi.

8.4 PREPARATION OF CALIBRATION BLANKS

Two pre-prepared calibration blanks are supplied in the instrument lab and are counted as the first and last samples in each count batch. The calibration blanks consist of 10mL mineral-oil-based cocktail mixed with 10mL of Rn-free water, and are prepared analogous to samples at a time separate from the preparation of a given batch. The calibration blanks are to be prepared from the same batch of cocktail as is used for samples and must be re-established for each new lot number of cocktail used. The average of the two calibration blanks (or a running mean of the calibration blanks if the test is run frequently enough that a representative population of calibration blanks may be assembled), is used in calculations to provide the value for background corrections.

8.5 PREPARATION OF SAMPLES

8.5.1 Include the following samples in each quality control (QC) batch (see Secion 10): the first three samples in each batch are a) Reagent Blank-1, b) LCS-1 (see Section 10.3 for preparation of the LCS), and c) Method Blank-1 (see Section 10.2 for preparation of the method blank), in that order. Up to 20 field samples then follow. The last three samples in each batch are the x) Method Blank-2, y) LCS-1-D1, and z) Reagent Blank-2, in that order.

8.5.2 Pre-label one scintillation vial (lid only) for each sample, replicate (see Section 10.4), and method blank to be analyzed.

8.5.3 Do not take the pH of the samples, they are assumed to be neutral. However, a sample condition form (Form 631) should still be used to note any abnormalities.

8.5.4 Using a calibrated repipettor, transfer 10mL of mineral-oil-based cocktail to each scintillation vial to be used for analysis.

8.5.5 If any bubbles are noted in any of the original sample vials available for each sample, note the discrepancy on the sample condition form (Form 631) and do not use the vial for analysis. If more than one vial contains bubbles, note the discrepancy on the benchsheet and only aliquot one sample. If all vials contain bubbles, aliquot the two with the smallest bubbles, note the discrepancy, and notify the PM regarding the discrepancy.

NOTE: Work carefully while performing sample transfers. Radon gas can be easily lost while sample vials are open and during the transfer process. Minimize the time that vials are open by removing the VOA vial cap one sample at a time and working quickly during sample transfer.

8.5.6 Prepare the first method blank as the first sample by transferring 10mL of radon-free distilled water to a VOA vial. Tightly cap the vial. Record the date and time of this preparation on the benchsheet.

8.5.7 Using a calibrated pipettor with a modified 10mL pipette tip (see 5.2), carefully withdraw a 10mL aliquot from the VOA vial for each sample. Avoid radon loss by taking extra care to avoid drawing bubbles into the pipette and by withdrawing slowly enough to minimize turbulence in the pipette tip. Also, avoid disturbing any sediment in the vial, so as not to transfer it to the scintillation vial. Carefully and quickly pipette the liquid under the surface of the mineral-oil cocktail to minimize radon losses during transfer. Cap the vial tightly immediately following completion of the transfer. If any problems are encountered during the transfer, discard the first sample and continue aliquotting using the backup vial.

8.5.8 Shake the samples for at least 30 seconds to facilitate extraction of the radon into the mineral oil.

8.5.9 Wipe the surface of each vial with a Kimwipe® and methanol to remove any residues on the surface of the vial.

8.5.10 Immediately submit the samples to the instrumentation lab for analysis.

8.5.11 Sample analysis must be completed within the 4-day hold-time. Count samples for a period of time that will allow achievement of the requested detection limits. The counting lab will ultimately dispose of the scintillation vials in the manner described in SOP 704.

9. CALCULATIONS

9.1 SYSTEM CALIBRATION FACTOR

$$EFF = \frac{S - B}{C \times V}$$

where:

EFF = efficiency, cpm/dpm.

S = average standard gross count rate, cpm.

B = average background gross count rate, cpm.

C = concentration of radium-226 standard, dpm/g, decay corrected to count date.

V = volume of standard used, g

9.2 TPU and MDC:

$$ACT = \frac{S - B}{CF \times D \times V \times 2.22}$$

$$CU = \frac{1.96 \times \sqrt{\frac{S}{T_S} + \frac{B}{T_B}}}{CF \times D \times V \times 2.22}$$

$$TPU = \sqrt{(CU)^2 + (ACT \times PU)^2 + (ACT \times IU)^2}$$

$$MDC = \frac{4.65 \times \sqrt{\frac{B}{T_S}} + \frac{2.71}{T_S}}{CF \times D \times V \times 2.22}$$

$$D = e^{-\lambda t}$$

$$l = ln2 / 3.823 \text{ days}$$

$$PU = 0.008 = \sqrt{0.006^2 + 0.006^2}$$

where:

ACT = Rn-222 activity in pCi/L decay corrected to the time and date of sampling.

CU = Counting uncertainty at the 2 sigma level, pCi/L.

TPU = Total Propagated Uncertainty (See SOP 743), pCi/L

MDC = Minimum Detectable Concentration, pCi/L.

V = volume of aliquot, L.

D = Decay correction factor from Sample collection to midpoint of count.

T_S = Sample count duration, min.

T_B = Background count duration, min.

t = elapsed time between time and date of collection and the midpoint of sample count, days.

PU = 0.008, based on one volumetric measurement and one repipetting of reagent, per SOP 743

IU = 0.056, based on a calibration with an in-house prepared calibration standard, per SOP 743

9.3 DATA REPORTING AND EVALUATION

9.3.1 The LCS sample consists of Rn-222 supported by Ra-226. For purposes of LCS and blank calculations, the sample date is entered as the start of the sample count.

9.3.2 All samples are decay corrected to the point of collection.

9.3.3 For consistency purposes, all times will be noted in Mountain time.

9.3.4 The LCS-Duplicate is used to evaluate precision.

9.3.5 Method blanks are batch QC samples and are used to evaluate the acceptability of data in a given QC batch. Reagent blanks are not QC samples, rather are used to calculate the background count rate for purposes of sample calculations.

9.3.6 Results are reported to the client for each replicate of the field sample. This data is not evaluated as a duplicate. Such evaluation is left to the client. It is important to note that failure to replicate may be indicative of problematic sampling in the field.

10. QUALITY CONTROL

10.2 Two method blanks are prepared for each batch of samples. The method blank consists of 10mL cocktail and 10mL of radon-free deionized water and is prepared as are samples.

10.3 Two pre-prepared calibration check standards (LCS) are supplied in the instrument lab and are counted as the second and next-to-last samples in each count batch. The calibration check samples consist of 10mL mineral-oil-based cocktail mixed with 10mL of Ra-226 standard solution at concentrations in the range of 5-50,000pCi/L, prepared analogous to samples. The calibration check samples are to be prepared from the same batch of cocktail as is used for samples and must be re-established for each new batch of cocktail used. These standards are allowed to come to secular equilibrium prior to use. The calibration samples are measured and evaluated against appropriate control limits for each batch of samples analyzed. These are reported as LCS1 and LCS1-D1 in association with sample results.

10.4 Sample replicates are run at 100% frequency, where sample volume is available. Due to limited sample availability, replicate results are reported and appropriately qualified. Repreparation of samples is generally not possible when replicate criteria are not met.

11. DEVIATIONS FROM METHOD

11.2 This procedure references ASTM Method D5072-92. The transfer is conducted with a pipette instead of the syringe noted in the method. This is consistent with Method 7500-Rn B, below.

11.3 This procedure references Standard Methods for the Evaluation of Water and Wastewater Method 7500-Rn B. The sample volume used is 10mL sample + 10mL of cocktail. This reflects the volumes used in USEPA Round Robin Testing. QC requirements prescribed in the SOP are comparable to those outlined in the Method, but have been modified to provide consistency with more procedures in place for liquid scintillation counting at Paragon.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.2 SAFETY AND HAZARDS

12.2.1 Read the appropriate MSDSs before preparing standards or using any reagents.

12.2.2 Safety glasses and lab coats must be worn in the radiochemistry prep labs at all times.

12.2.3 Gloves, safety glasses, and a lab coat must be worn when working with any chemicals (e.g., standards, solvents, reagents, or samples) or when handling materials potentially contaminated with chemicals.

12.2.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in laboratory fume hood (e.g., solvents and acids).

12.2.5 All non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with: 1) the compound name, 2) NFPA Health, Flammability and Reactivity ratings, and 3) date.

12.2.6 Care should be taken when diluting acids. Always add acids to water, NOT water to acid.

12.3 WASTE DISPOSAL
Wastes that are "corrosive only", are disposed of by discharging into the Paragon wastewater treatment facility. These materials that are "corrosive only" (i.e., have no hazardous components or characteristics other than corrosivity) may be neutralized in the waste treatment facility.

13. REFERENCES

13.2 "Method 7500-Rn B. Liquid Scintillation Method"; Standard Methods for Analysis of Water and Wastewater, Edition 18.

13.3 ASTM Standard Method D5072-92, Vol. 11.01, May 1992.

13.4 "Two Test Procedures for Radon in Drinking Water"; Whittaker, E.L., J.D. Akridge & Giovino, ES, USEPA Las Vegas, NV, 1987.

DOCUMENT REVISION HISTORY

9/1/06: LIMS program specifications referenced. DOCUMENT REVISION HISTORY section added. Form attached. Other clerical changes.

APPENDIX A

Recommended Sampling Procedure for Rn-222 by Liquid Scintillation

SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sampling is the sole responsibility of the client. This or other equivalent sampling procedures should be followed carefully to ensure the integrity of sample results. The following information is based on the procedure provided in the 18th Edition of Standard Methods for the Evaluation of Water and Wastewater, Method 7500-Rn B.

Sampling schedules must be pre-arranged and approved by the laboratory to ensure adequate capacity is available to meet hold time requirement of analysis within 4 days of collection.
Samples are routinely collected from a non-aerated water source that has been allowed to flow for sufficient time so that a representative water sample is taken. The following procedure is designed to minimize the loss of radon from the sample during collection.

Equipment Needed:

Faucet connector or universal faucet adapter (where sample is being drawn from well or distribution system)

Plastic tubing for connector or adapter

VOA vials, borosilicate glass, 40mL, with Teflon-lined septum closure

Sample storage and shipping containers, insulated

Chain of Custody (COC) forms

Procedure

1. Place a clean 40mL VOA vial (with Teflon-lined septum closure) in a 300- to 600mL beaker, or other suitable container; attach delivery tube to faucet, and start the flow. Make sure that the delivery tube does not let bubbles enter the sample.
2. Fill the 40mL VOA vial to prevent its floating, then fill beaker until the vial is submerged.
3. Place the tip of the delivery tube about two thirds of the way into the vial and fill until approximately two or more vial volumes (50 to 100mL) have been displaced.
4. Carefully remove vial by hand or with a pair of 25cm (10in.) tweezers and cap the vial with a Teflon or foil-lined cap. Cap sample vials underwater, if possible.
5. Invert sample and check for air bubbles. If any bubbles are present, discard sample and repeat sampling procedure.
6. Sample results will be reported decay corrected to the date and time of collection, assuming the presence of unsupported Rn-222 activity in the samples. On the COC, note the date and exact time of sampling for each vial to the nearest minute. Include a reference to time zone (e.g., EDT or PST). The collection time is converted to Mountain Time (where appropriate) at the point of receipt to ensure that accurate decay corrections are performed for the samples.
7. Ensure that the sample is properly, clearly and unambiguously labeled. Append a fraction ID to the field sample ID for each of the three vials collected per sample (i.e., XXXXXX (1), XXXXXX (2) and XXXXXX (3)).
8. Repeat Steps 1-7 of this procedure two times to collect three vials for each sample.
9. Pack the samples on ice (4$\pm$2 °C) and ship overnight to the laboratory for analysis.

Paragon Analytics.

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	COLOR	REMARKS

Form 631r4a.doc (7/21/06)

Paragon Analytics.

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	TEXTURE	REMARKS

Form 631r4b.doc (7/21/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 806 REVISION 13

TITLE: **DIGESTION OF WATERS, SOILS AND WASTES FOR METALS ANALYSIS -- METHODS SW3005A, SW3010A, SW3050B, EPA 200.2, AND CLP SOW ILM03.0 & ILM04.0**

FORMS: **805, 824** **(use current iteration)**

APPROVED BY:

TECHNICAL MANAGER Roy French DATE 11/5/07

QUALITY ASSURANCE MANAGER Deb Schantz DATE 11/4/07

LABORATORY MANAGER K Neal DATE 11/5/07

HISTORY: Rev0, 3/22/93; Rev1, PCN # 87, 1/18/94; Rev2, 4/9/96; Rev3, 11/18/96; Rev4, 10/07/99; Rev5, 3/07/01; Rev6, 11/10/01; Rev7, 3/02/02; Rev8, 4/29/02; Rev9, 12/04/02; Rev10, 4/23/04; Rev11, 1/31/05; Rev12, 7/26/05 and 3/13/06; Rev13, 11/4/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- Methods SW3005A, SW3010A, SW3050B, EPA 200.2, CLP SOW ILM03.0 and CLP SOW ILM04.0 – describe the digestion and preparation of liquid and solid samples prior to total or dissolved metals analysis.

2. SUMMARY OF METHOD

The purpose of these procedures is to extract metals from the native matrix and hold them in a form that is suitable for analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS). The extraction is accomplished by refluxing the acidified sample at a suitable temperature for a period of time or until the sample is reduced to a desired volume.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the workorder file indicates that the data are complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 In sample preparation, contamination is of prime concern. The work area, including bench top and fume hood should be periodically cleaned in order to eliminate environmental contamination.

4.2 The analyst should be cautioned that these digestion procedures might not be sufficiently vigorous to release all metals from complexed forms.

4.3 Waste samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method SW3050B is applicable to a given waste.

4.4 Chemical interferences are matrix dependent and cannot be documented prior to analysis. Interferences are discussed in the analytical SOPs.

5. APPARATUS AND MATERIALS

5.1 Hot plate or Steam bath, capable of maintaining a constant temperature of 95°C$\pm$5°C.

5.2 Beakers and lids, polypropylene, disposable, 100mL and 200mL capacity

5.3 Watch glasses (or equivalent), ribbed and non-ribbed

5.4 Balance, top loading, able to read to 0.1g

5.5 Membrane filter paper, cellulose acetate, 0.45µm, Corning, #431220 or equivalent

5.6 Glass fiber filter paper, 0.7µm, Whatman™ #1441 150 or equivalent

5.7 Buchner funnel and flask, or similar filtration device

5.8 Volumetric flasks of suitable size and accuracy

5.9 Volumetric pipets of suitable size and accuracy

5.10 Scissors

5.11 Autosampler tubes, polypropylene, 14mL

5.12 Ion exchange columns, disposable, graduated to 10cm (Environmental Express #R10204) or equivalent

6. REAGENTS

NOTE: Only trace metals grade acids may be used. Lot # must be verified by the Metals Department prior to the analysis of samples with any new acids. Each lot of acids must be certified (no metals detected at or above the RL).

6.1 Hydrochloric acid (HCl), concentrated, trace metals grade, JT Baker #9530-33 or equivalent. Also a diluted (1:1) hydrochloric acid solution.

6.2 Nitric acid (HNO_3), concentrated, trace metals grade, JT Baker #9598-34 or equivalent. Also a diluted (1:1) nitric acid solution.

6.3 Reagent water, deionized, obtained from Paragon's DI water system.

6.4 Hydrogen Peroxide (H_2O_2), 30%, Malinckrodt #5240 or equivalent.

6.5 Cation exchange resin, analytical grade, 50W x 8 (Eichrom or equivalent).

6.6 SPIKING SOLUTIONS
Prepared from purchased certified individual elemental standards or analyte mixes. ***Records of vendor-supplied certificates of analysis must be maintained by the Department.*** Undiluted stock solutions may be retained until the manufacturer's expiration date (at least one year), replaced sooner if degradation occurs. Diluted stock solutions may also be retained until the manufacturer's expiration date (at least one year), replaced sooner if degradation occurs.

All spiking solutions are prepared, documented, and stored in accordance with Paragon SOP 300. All spiking solutions are to be contained in fresh (previously unused) polypropylene bottles.

6.6.1 Spike Solution Z:

Element	*Concentration (µg/mL)*
Al, Ba, As, Se, Tl, Si	100
Fe, B, Mo	50
Sb, Co, Mn, Ni, V, Zn	25
Ti, Sn, Li, Sr, Pb	25
Be, Cd	2.5
Cr	10
Cu	12.5

6.6.2 Cation Spike Solution: Contains 2,000 µg/mL Ca, Mg, K, Na.

6.6.3 C Spike: Contains 10 µg/mL Ag.

6.6.4 CLPP-Spike-1:

Element	*Concentration* (µg/mL)
Al, Ba	2000
Fe	1000
Co, Mn, Ni, V, Zn	500
Cu	250
Cr	200
Ag, Be	50

6.6.5 CLPP-Spike-4:

Element	*Concentration* (µg/mL)
Sb	100
Cd, Tl	50
As	40
Pb	20
Se	10

6.6.6 Non-TAL Spike:

Element	*Concentration* (µg/mL)
Si	200
B, Mo	100
Li, Sr, Sn, Ti	50

NOTE: CLPP-Spike-1 & CLPP-Spike-4 are mixes prepared and purchased from a vendor. All other spiking solutions listed are prepared from commercially purchased single element stock standards.

6.6.7 Be Filter Spike:

Element	Concentration (ug/mL)
Be	1.0

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples for total or potentially dissolved metals analyses are collected in plastic or glass containers and must be chemically preserved with nitric acid to

pH<2. Typically, a 1L sample is collected. Samples for dissolved metals analyses should be filtered in the field prior to chemical preservation. Analysis of the sample cannot begin until it has been acidified for at least 24hrs.

7.3 Solid samples are collected in plastic or glass containers. Solid samples are not chemically preserved.

7.4 All samples, liquid or solid, should be maintained at 4±2°C. All samples, liquid or solid, must be prepared and analyzed within 180 days of collection.

8. PROCEDURE

8.1 METHOD SW3005A, 200.2 - DISSOLVED METALS PREPARATION (ICP-AES and ICP-MS)

8.1.1 Samples to be analyzed for dissolved (soluble) metals are to be filtered through a 0.45µm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid.

- If the samples have been filtered prior to entering the lab, check that the pH of the sample(s) is <2 and that there are no visible solids or precipitates in the sample container. If the pH of a sample if found to be >2, then concentrated nitric acid (trace metals grade) must be added and the sample held for a minimum of 24 hours until verified to be pH<2 (Form 824).
- Record on the LIMS tracking sheet that the samples were received filtered and preserved.
- If solids or precipitates are noticed in a sample that is filtered and preserved, consult Project Manager before continuing with the sample preparation.
- The samples are now ready for digestion (see Section 8.3, Method SW3005A).

8.1.2 If the samples have not been filtered or preserved before entering the lab, then they need to be filtered through a 0.45µm filter and preserved with concentrated nitric acid to a pH<2.

8.1.3 Prepare a blank, blank spike (Laboratory Control Sample, LCS) and sample duplicate and carry them through the preceding filtration and preservation Steps at a frequency of at least 1 per 20 samples of like matrix (see Section 9.0).

8.1.4 Aliquot about 100mL of filtered and preserved samples into properly labeled disposable beakers.

8.1.5 All steps must by recorded in the metals digestion logbook (Form 805)

and any pertinent comments regarding the samples recorded on the LIMS tracking sheet to be included with the workorder file.

8.1.6 The samples are now ready for digestion (see Section 8.3, Method SW3005A).

8.2 FINAL VOLUME ADJUSTMENT

8.2.1 Final volumes for the digestion procedures described in Sections 8.3 through 8.8 are adjusted by bringing the digestion beaker containing the digestate to a predetermined weight by adding reagent (double-deionized) water after the digestion is completed.

8.2.2 The predetermined weight for water samples is the total weight of the empty digestion beaker plus the weight of the desired final volume of digestate, recorded to the nearest 0.01 grams. The predetermined weight for soil samples is the total weight of the empty digestion beaker plus the weight of the soil aliquot plus the weight of the desired final volume of digestate, recorded to the nearest 0.01 grams.

8.2.3 The weight of the final volume of digestate depends on the acid content of the digestate. Hence, each digestion method results in digestates with slightly different densities because the acid concentrations are different.

8.2.4 The weight of the final volume of digestate for the digestion procedures described in Sections 8.3 through 8.8 has been determined by digesting method blanks and weighing the digestates after bringing to volume in a volumetric flask (see below, further details provided in Appendix A).

SOP Section	Method	Final Volume (mL)	Weight of Digestate (g)
8.3	SW3005A	50	51.18
8.4	SW3010 A	50	52.39
8.5	EPA 200.2	50	50.38
8.6	SW3050B	100	105.11
8.7	CLP Water	100	100.83
8.8	CLP Soil	200	206.95

8.2.5 If digestates are to be brought to a final volume not given above, the weight of the desired final volume of digestate should be determined by digesting a method blank and weighing the digestate after bringing to volume in the appropriate volumetric flask.

8.2.6 The empty weight of the disposable polypropylene beakers used for a

digestion must be determined prior to performing the digestion. The empty beaker weight for each lot of beakers is determined by weighing 10 beakers and calculating the average. The empty beaker weight data for each lot is recorded in the beaker weight logbook.

8.2.7 The formula used for the calculation of the predetermined weight is given below:

$$P = B + D + S$$

where:

P = Predetermined weight (Section 8.2.1 to 8.2.5)

B = Empty beaker weight (Section 8.2.6)

D = Weight of final volume of digestate (Sections 8.2.4 and 8.2.5)

S = Weight of soil aliquot (S = 0 for water samples)

8.2.8 The predetermined weight, empty beaker weight, weight of the final volume of digestate and the beaker Lot number are recorded on the digestion benchsheet (Form 805).

8.3 METHOD SW3005A - TOTAL RECOVERABLE METALS DIGESTION OF WATERS FOR ICP-AES AND ICP-MS ANALYSIS

8.3.1 For each sample in the batch, use a test strip to verify that the solution pH is <2. Record the measured pH on the benchsheet. If the pH of a sample is >2, then concentrated nitric acid (trace metals grade) must be added and the sample held for a minimum of 24hrs until verified to be pH<2 (Form 824).

8.3.2 Transfer a 50mL aliquot of preserved (pH<2), well-mixed sample to a beaker.

8.3.3 Add 1.0mL of concentrated nitric acid and 2.5mL of concentrated hydrochloric acid.

NOTE: When analyzing for Vanadium using ICP-MS, the 2.5mL of concentrated HCl is not used. Instead, a total of 4mLs of concentrated nitric is used to avoid interferences.

8.3.4 Cover the beaker with a ribbed watch glass and heat at 95±5°C ***without boiling*** until the volume has been reduced to about 10mL.

8.3.5 Remove the beaker from the heat and allow to cool.

8.3.6 Wash down the beaker walls and the watch glass with reagent water.

8.3.7 Filter the sample only if necessary.

8.3.8 Adjust the final volume to 50mL with reagent water (adjust to the predetermined weight as described in Section 8.2).

8.3.9 Prepare quality control (QC) samples as discussed in Section 9.0.

8.3.10 The metals digestion logbook (Form 805) is to be completed in full for each digestion batch of 20 or fewer samples.

8.4 METHOD SW3010A - TOTAL METALS DIGESTION OF WATERS FOR ICP-AES AND ICP-MS ANALYSIS

8.4.1 For each sample in the batch use a test strip to verify that the solution pH is <2. Record the measured pH on the benchsheet. If the pH of a sample is >2, then concentrated nitric acid (trace metals grade) must be added and the sample held for a minimum of 24hrs until verified to be pH<2 (Form 824).

8.4.2 Transfer a 50mL aliquot of preserved (pH<2), well mixed sample to a beaker.

8.4.3 Add 1.5mL of concentrated nitric acid and cover the beaker with a ribbed watch glass.

8.4.4 Heat the sample ***without boiling*** until the volume has been reduced to a low volume (about 5mL), ***making sure the sample doesn't go to dryness.***

8.4.5 Cool the sample and add another 1.5mL of concentrated nitric acid.

8.4.6 Heat the sample briefly until the volume has been reduced to a low volume (about 5mL), ***making sure the sample doesn't go to dryness***. If necessary, continue to repeat the addition of 1.5mL of concentrated nitric acid and heating until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).

8.4.7 Cool the sample and add 5mL of 1:1 Hydrochloric Acid. Heat the sample for about 15 minutes.

8.4.8 Cool the sample and wash down the beaker walls and watch glass with reagent water.

8.4.9 Filter the digestate only if necessary.

8.4.10 Adjust the final volume to 50mL with reagent water (adjust to the predetermined weight as described in Section 8.2).

8.4.11 This procedure is used for the digestion of TCLP extracts, initially using a 5mL sample aliquot of filtered TCLP leachate and following the steps stated above. The 50mL final volume results in a 1/10 dilution for TCLP leachates during the digestion procedure.

8.4.12 Prepare quality control (QC) samples as discussed in Section 9.0.

8.4.13 The metals digestion logbook (Form 805) is to be completed in full for each digestion batch of 20 of fewer samples.

8.5 METHOD 200.2 - TOTAL RECOVERABLE METALS DIGESTION OF WATERS FOR ICP-AES AND ICP-MS ANALYSIS

8.5.1 For each sample in the batch use a test strip to verify that the solution pH is <2. Record the measured pH on the benchsheet. If the pH of a sample is >2, then concentrated nitric acid (trace metals grade) must be added and the sample held for a minimum of 24hrs until verified to pH<2 (Form 824).

8.5.2 Transfer a 50mL aliquot of preserved (pH<2), well mixed sample to a beaker.

8.5.3 Add 2mL of 1:1 Nitric Acid and 1mL of 1:1 Hydrochloric Acid.

8.5.4 Cover the beaker with a ribbed watch glass and heat until the volume has been reduced to about 20mL.

8.5.5 Replace the ribbed watch glass with a non-ribbed watch glass and reflux the sample for about 30 minutes.

8.5.6 Cool and adjust the final volume to 50mL with reagent water (adjust to the predetermined target weight as described in Section 8.2).

8.5.7 Prepare quality control (QC) samples as discussed in Section 9.0.

8.5.8 The metals digestion logbook (Form 805) is to be completed in full for each digestion batch of twenty or fewer samples.

8.6 METHOD SW3050B - TOTAL DIGESTION OF WASTES, SEDIMENTS, SLUDGES, AND SOILS FOR ICP-AES AND ICP-MS ANALYSIS

8.6.1 Mix the sample by stirring with a disposable wooden spatula in order to obtain a representative aliquot. The aliquot should have a similar particle size distribution as the bulk sample (visually). For very heterogeneous or unusual matrices, consult the Department Manager and Project Manager. Document if special processing was required prior to taking an aliquot in the comments section of Form 805. Also,

record on the digestion benchsheet the texture (coarse, medium, fine) and color of the sample.

8.6.2 Weigh a 1-1.5g sample aliquot into a 200mL disposable polypropylene beaker. Record the aliquot size to 0.01g on the digestion benchsheet.

8.6.3 Add 10mL of 1:1 Nitric Acid, mix the slurry and cover with a ribbed watch glass.

8.6.4 Heat the sample to 95±5°C and reflux for 10 to 15 minutes without boiling.

8.6.5 Cool the sample and add 5mL of concentrated nitric acid. Replace the watch glass and reflux for about 30 minutes. If brown fumes are generated indicating oxidation of the sample by nitric acid, then repeat this Step (addition of nitric acid) until no brown fumes are given off. Heat sample at 95±5°C without boiling until the solution evaporates to approximately 5mL or if necessary continue heating at 95±5°C without boiling for a total of about 2hrs. The maximum two hours may be necessary for example if the sample matrix is not readily reduced. Maintain a covering of solution over the bottom of the vessel at all times.

8.6.6 Cool the sample and add 2mL of reagent water and 3mL of 30% hydrogen peroxide. Care must be taken to avoid loss of sample due to excessive effervescence.

8.6.7 Heat the sample until the effervescence subsides.

8.6.8 Cool the sample and continue to add 30% hydrogen peroxide in 1mL aliquots (up to 10mL) with heating until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than 10mL of 30% hydrogen peroxide. Continue heating without boiling at 95±5°C until the volume is reduced to approximately 5mL or if necessary continue heating at 95±5°C for a total of about two hours. The maximum two hours may be necessary for example if the sample matrix is not readily reduced. Maintain a covering of solution over the bottom of the beaker at all times.

8.6.9 Cool and add 10mL conc. HCl. Cover with watch glass.

8.6.10 Heat the sample for about 15 minutes at 95±5°C

8.6.11 Cool and bring to 100mL final volume with reagent water (adjust to the predetermined weight as described in Section 8.2).

8.6.12 Mix well and allow solids to settle. Filter the sample only if necessary.

8.6.13 Prepare quality control (QC) samples as discussed in Section 9.0.

8.6.14 The metals digestion logbook (Form 805) is to be completed in full for each digestion batch of 20 of fewer samples.

8.7 CLP ILM03.0 AND ILM04.0 - ACID DIGESTION FOR TOTAL METALS IN WATERS (ICP-AES AND ICP-MS)

8.7.1 For each sample in the batch use a test strip to verify that the solution pH is <2. Record the measured pH on the benchsheet. If the pH of a sample is >2, then concentrated nitric acid (trace metals grade) must be added and the sample held for a minimum of 24hrs until verified to be pH<2 (Form 824).

8.7.2 Shake the container and transfer 100mL of well-mixed sample to a 250mL beaker. The sample aliquot is measured gravimetrically (100±0.5g). Add 2mL of 1:1 nitric acid (trace metals grade) and 10mL 1:1 hydrochloric acid to the sample.

8.7.3 Cover with watch glass and heat on a steam bath for about 2 hours at 95±5°C or until sample volume is reduced to between 25 and 50mL, making certain sample does not boil.

8.7.4 Cool the sample and filter only if necessary.

8.7.5 Adjust sample volume to 100mL with reagent water (adjust to the predetermined target weight as described in Section 8.2).

8.7.6 Prepare quality control (QC) samples as discussed in Section 9.0.

8.7.7 The metals digestion logbook (Form 805) is to be completed in full for each digestion batch of 20 or fewer samples.

8.8 CLP ILM03.0 AND ILM04.0 - ACID DIGESTION FOR TOTAL METALS IN NON-AQUEOUS SAMPLES (ICP-AES AND ICP-MS)

8.8.1 Mix the sample by stirring with a disposable wooden spatula in order to obtain a representative aliquot. The aliquot should have a similar particle size distribution as the bulk sample (visually). For very heterogeneous or unusual matrices, consult the Department Manager and Project Manager. Document in the comments section of Form 805 if special processing prior to taking an aliquot was required. Record on the digestion benchsheets the texture (coarse, medium, fine) and color of the sample as well.

8.8.2 Weigh a 1-1.5g sample aliquot into a 200mL disposable polypropylene beaker. Record the aliquot size to 0.01g on the digestion benchsheet.

8.8.3 Add 10mL of 1:1 Nitric Acid, mix the slurry, and cover with a watch glass.

8.8.4 Heat the sample to 95±5°C and reflux for about 10 minutes without boiling.

8.8.5 Allow the sample to cool, add 5mL of concentrated nitric acid, replace the watch glass, and reflux for about 30 minutes. Maintain a covering solution over the bottom of the beaker and do not allow the volume to be reduced to less than 5mL.

8.8.6 Cool the sample and add 2mL of reagent water and 3mL of 30% hydrogen peroxide.

8.8.7 Heat the sample until effervescence subsides.

8.8.8 Cool the sample and continue to add 30% hydrogen peroxide in 1mL aliquots (up to 10mL) with heating until effervescence is minimal or until the general sample appearance is unchanged. Do not add more than 10mL of 30% hydrogen peroxide.

8.8.9 Add 5mL of 1:1 HCl and 10mL of reagent water; return the covered beaker to the hot plate and heat for an additional 10 minutes.

8.8.10 Cool the sample and filter only if necessary.

8.8.11 Dilute the sample to 100mL with reagent water.

8.8.12 The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5.0% (v/v) HNO_3. Dilute the digestate 1:1 (200mL final volume), to the predetermined weight with acidified water to maintain constant acid strength (as described in Section 8.2).

8.8.13 Prepare quality control (QC) samples as discussed in Section 9.0.

8.8.14 The metals digestion logbook (Form 805) is to be completed in full for each digestion batch of 20 or fewer samples.

8.9 SPECIAL DIGESTION OF AIR FILTERS FOR BERYLLIUM ANALYSIS

8.9.1 Rinse scissors with acetone and cut filters in half.

8.9.2 Place one half of filter in 100mL polypropylene beaker (archive the other half in case reanalysis is necessary).

8.9.3 Add 5mL conc. HNO_3 and 5mL conc. HCl.

8.9.4 Heat sample at 95±5°C until dry.

8.9.5 Remover beaker from heat and allow to cool.

8.9.6 Add 10mL of blank acid (5% HNO_3, 2.5% HCl) to beaker using a calibrated pipet.

8.9.7 Weigh beaker and record weight.

8.9.8 Heat sample at 95±5°C for about 15 minutes.

8.9.9 Remove beaker from heat and allow to cool.

8.9.10 Bring digestate to 10mL final volume gravimetrically by adding blank acid (5% HNO_3, 2.5% HCl) to bring beaker weight to the weight recorded in Step 8.9.7. Mix thoroughly.

8.9.11 Transfer the digestate from the 100mL beaker to a labeled 15mL polypropylene autosampler tube. Cap with parafilm.

8.9.12 Prepare quality control (QC) samples as discussed in Section 9.0.

8.9.13 Document information in the metals digestion logbook (Form 805) for each digestion batch of twenty or fewer samples.

8.10 SPECIAL CLEANUP PROCEDURE FOR ARSENIC AND SELENIUM ANALYSIS BY ICP-MS

The measurement of arsenic and selenium by ICP-MS is difficult in heavy matrices, mainly due to the presence of chloride and its associated interferences. To improve these measurements, the digestates are passed through a cation exchange column. This column should remove most calcium and sodium from the sample matrix and help reduce the Ca^{40} Cl^{35} interference on the monoisotopic As^{75} as well as reducing the suppression of signal usually seen with high concentrations of sodium.

8.10.1 Digestates to be analyzed for arsenic and/or selenium by ICP-MS should be diluted a minimum of ten-fold before being treated by the cation exchange column. This dilution is done to achieve a better match between sample matrix and standards and also to improve the effectiveness of the cation exchange column.

8.10.2 All digested samples and matrix quality control samples will be treated with the cation exchange procedure before analysis. In addition, the interference check standards (ICSA and ICSAB), which contain known

amounts of calcium and sodium plus analytes of interest, will be treated with the cation exchange procedure. These treated interference check standards should help demonstrate the effectiveness of the cation exchange procedure.

8.10.3 Create cation exchange columns that contain 4 to 5cm of resin. Fill an empty column (5.12) to between 8 and 10cm with slurry of ½ resin and ½ reagent water. This will yield a cation exchange column with a quantity of resin between 4 and 5cm.

8.10.4 Rinse each column with 10 to 20mL of reagent water.

8.10.5 Rinse each column with 10 to 20mL of the diluted digestate or interference check standard. Discard this volume to waste.

8.10.6 Pass at least 20mL of diluted digestate or interference check standard through the column and collect in a labeled, 100mL polypropylene container and cover. These solutions are now ready for analysis by ICP-MS.

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

A batch is defined as a group of twenty (20) or less field samples of like matrix that is associated with one unique set of batch QC samples that have been processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS) and matrix spike and duplicate (MS/MSD). All QC samples must be carried through all stages of the sample preparation and measurement steps.

9.2 MB

Also referred to as a laboratory reagent blank (LRB) or Preparation Blank (PB). The MB consists of an aliquot of reagent water (or TCLP fluid) that has been digested and prepared in the same manner as the associated samples, and is run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. See determinative SOP for acceptance limits.

9.3 LCS

Referred to as a laboratory fortified blank (LFB) in Method 200.2, also referred to as a Blank Spike (BS). The LCS consists of an aliquot of reagent water, TCLP fluid, or a certified, commercially prepared, spiked solid that is digested and prepared in the same manner as the associated samples. The LCS is analyzed to measure the accuracy of the method. Guidance regarding the identity and amount of spike solution to be used is presented below:

Procedure / Method	Spiking Solution Used	Amount of Spike Used	Final Vol. Digestate
SW3005A / Dissolved Metals - ICAP	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
200.7 / Dissolved Metals - ICAP	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
SW3005A / Total Recoverable Metals - ICAP	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
SW3010A / Total Metals - ICAP	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
200.2 / Total Recoverable Metals - ICAP (Waters)	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
SW3050 / Soils for ICAP	Spike Solution Z C Spike Cation Spike	2.0mL 0.50mL 2.0mL	100mL
CLP 4.0 / for Solid	Solid LCS	1.0g	200mL
CLP 4.0 / for Waters	Spike Solution Z C Spike Cation Spike	2.0mL 0.50mL 2.0mL	100mL
Be Filter	Be Filter Spike Solution	0.05mL	10mL

NOTE: A commercially prepared solid LCS standard with established control limits is used at the client's request.

See determinative SOP for manner of calculation and acceptance limits.

9.4 MS/MSD

Sometimes referred to as a laboratory fortified matrix (LFM) sample. MS/MSDs consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection. One MS/MSD are analyzed with each batch of 20 or fewer field samples (SW846 and CLP); one MS/MSD is analyzed with each batch of 10 or fewer field samples for EPA Method 200.7. For TCLP leachates, an MS/MSD

set are run for each fluid type present per batch of 20 samples or less. Guidance regarding the identity and amount of spike solution to be used is presented below:

Procedure / Method	Spiking Solution Used	Amount of Spike Used	Final Vol. Digestate
SW3005A / Total Recoverable Metals - ICAP	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
SW3010A / Total Metals - ICAP	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
200.2 / Total Recoverable Metals - ICAP (Waters)	Spike Solution Z C Spike Cation Spike	1.0mL 0.25mL 1.0mL	50mL
SW3050 / Soils for ICAP	Spike Solution Z C Spike Cation Spike	2.0mL 0.50mL 2.0mL	100mL
CLP 4.0 / for Solid	CLP-SPK-1 CLP-SPK-4	0.20mL 0.20mL	200mL
CPL 4.0 / for Waters	CLP-SPK-1 CLP-SPK -4	0.10mL 0.10mL	100mL

NOTE: Spikes may vary per client's request.

See determinative SOP for manner of calculation and acceptance limits.

9.5 LABORATORY DUPLICATE

The laboratory duplicate is analyzed as a measure of the precision of the analytical results generated. One duplicate is to be prepared per matrix for each sample batch. Quality control criteria for evaluating laboratory duplicates are presented in the analytical SOP.

10. DEVIATIONS FROM THE METHOD

This SOP meets the requirements of Methods SW3005A, SW3010A, SW3020A, SW3050B, EPA 200.2, CLP ILM03.0 and CLP ILM04.0. There are no known deviations from these methods.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) must be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The sample digestates shall be disposed of in the Aqueous Laboratory Waste.

11.2.2 Radioactive sample disposal - solid sample residues shall be disposed of in the Radioactive Soils & Solids container. Radioactive sample digestates shall be disposed of in the Radioactive Aqueous Lab Waste.

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. ***Please note that all labels and markings must be defaced prior to disposal.***

12. REFERENCES

12.1 USEPA SW-846, Test Methods For Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, December 1996.

12.2 USEPA 600/R-94/111, Methods for the Determination of Metals in Environmental Samples, May 1994.

12.3 USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis (Multi-Media, Multi-Concentration), ILM04.0.

DOCUMENT REVISION HISTORY

7/26/05: Added LIMS Program Specification directive in RESPONSIBILITIES.

4/10/06: Added DOCUMENT REVISION HISTORY.

11/4/07: Revamped Section 7. Added that sample must be acidified to pH<2 for a minimum of 24hrs before analysis may begin (Federal Register, 3/26/07, Volume 72, Number 57). Likewise changed '16' to 24hrs Sections 8.1.1; 8.3.1; 8.4.1; 8.5.1; 8.7.1. Also updated Form 824 and replaced logbook pages, trained analyst). Updated QC Section 9 to make it more consistent with PAR format (Definition of Batch 9.1; Blanks 9.2, etc.). Updated attached Forms.

Appendix A

The weight of the final volume of digestate for each digestion procedure was determined by digesting 5 method blanks and weighing the digestates after bringing to volume in a volumetric flask. The method blanks were placed in a variety of positions on the steam bath. Results for each digestion method are tabulated below.

Weight of digestate in grams.

	SW3050	***SW3005***	***SW3010A***	***EPA200.2***	***CLP H2O***	***CLP Soil***
	104.8	51.15	52.53	50.36	100.83	206.95
	104.72	51.18	52.32	50.49	100.86	206.83
	105.05	51.21	52.43	50.34	100.81	206.85
	105.2	51.18	52.39	50.35	100.88	207.05
	105.6	51.18	52.28	50.33	100.79	207.08
	105.38	51.21	52.36	50.38	100.83	206.98
	105.02	51.16	52.41	50.41	100.84	206.93
Ave Weight	105.11	51.18	52.39	50.38	100.83	206.95
%RSD	0.3	.04	.15	.11	.03	.05
Volume (mL)	100	50	50	50	100	200

METALS DIGESTION WORKSHEET

Paragon Analytics

Digestion Date _____ HCl Lot No. _____ Method: _____ Beaker Lot No. _____ Initial Prep _____ Final Prep _____

Digestion Batch _____ HNO_3 Lot No. _____ SOP/Rev: _____ Avg. Beaker Wt. (g) _____ Prep Start Time _____ Prep End Time _____

Water Bath Temp _____ °C Peroxide Lot No. _____ Balance(s): _____ Pipet(s): _____ Digestate Wt. (g) _____

Reviewed by / date _____

Form 805r17.xls (12/15/05)

QC Grp	Lab Sample ID	Instru-ment	Init Vol/Wt (mL / g)	Final Vol (mL)	Final Wt. (g)	pH	Texture	Before color	Before clarity	After color	After clarity	Comments, including metals list	LIMS QCA

ICP						Lab Sample ID		Init Vol/Wt. (mL / g)	Final Vol. (mL)	Final Wt. (g)
LCS						#2 D				
LCS 2						S				
ICP MS						DS				
LCS						#3 D				
LCS 2						S				
PB						DS				
#1 D						#4 D				
S						S				
DS						DS				

Spiking Information

QC	Amount

Paragon Analytics

Documentation of Acidification and/or Filtration of Water Samples in Metals Department

Sample ID	Initial Sample pH	Initial Sample Volume (mL)	Filtered through 0.45 µm ? (Y / N)	Volume HNO_3 Added (mL)	Lot # for Conc. HNO_3	Date HNO_3 Added	Time HNO_3 Added	Initials	Sample pH after 24 hrs	Initials	Comments

Reviewed by / date _____

Form 824r1.doc (8/1/07)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 807 REVISION 11

TITLE: **DETERMINATION OF METALS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY – METHOD EPA 200.7 (TRACE ICAP)**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER Steve Workman DATE 11/20/06

QUALITY ASSURANCE MANAGER Deb Graham DATE 11/20/06

LABORATORY MANAGER [signature] DATE 11-21-06

HISTORY: Rev1, 2/17/94; Rev2, 3/25/96; Rev3, 10/30/96; Rev4, 10/06/99; Rev5, 3/7/01; Rev6, 1/24/02; Rev7, 4/3/02; Rev8, 4/7/03; Rev9, 5/12/04; Rev10, 3/13/06; Rev11, 11/20/06.

re-released w/o revision 3/9/09 DAS

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references -- Method EPA 200.7 -- is used to determine the concentration of total or dissolved metals in aqueous samples. Analytes are viewed axially, providing detection limits for many analytes similar to those that may be achieved using Graphite Furnace Atomic Absorption (GFAA) analysis.

The following elements are routinely determined using this method:

Aluminum (Al)	Antimony (Sb)	Arsenic (As)	Barium (Ba)	Beryllium (Be)
Cadmium Cd)	Calcium (Ca)	Chromium (Cr)	Cobalt (Co)	Copper (Cu)
Iron (Fe)	Lead (Pb)	Lithium (Li)	Magnesium (Mg)	Manganese (Mn)
Molybdenum (Mo)	Nickel (Ni)	Phosphorous (P)	Potassium (K)	Selenium (Se)
Silicon (Si)	Silver (Ag)	Sodium (Na)	Strontium (Sr)	Thallium (Tl)
Tin (Sn)	Titanium (Ti)	Uranium (U)	Vanadium (V)	Zinc (Zn)

2. SUMMARY OF METHOD

Samples are digested and prepared prior to analysis in accordance with Method EPA 200.7, per SOP 806. Filtered liquid samples, liquid samples containing low solids, or leachates may also be analyzed by direct aspiration into the ICAP instrument (i.e., without prior digestion). A computer-controlled Inductively Coupled Argon Plasma (ICAP) Trace Analyzer is used to accomplish the analyses.

Samples or sample digestates are aspirated into the ICAP instrument, into a high temperature argon plasma stream. Radio frequencies are generated to induce excitation of the plasma stream that causes constituent elements contained in the sample to emit light at characteristic wavelengths. A grating spectrometer is used to disperse the resulting spectra. The light emissions are received by a photomultiplier tube, which in turn transmits a signal to the data acquisition system. The software of the data acquisition system interprets the signal by comparing it to a previously calibrated standard curve. The data are then further manipulated in the reporting process to incorporate such factors as dilution, etc.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 SPECTRAL INTERFERENCES

Potential spectral interferences include the following:

4.1.1 Overlap of a spectral line from another element at the analytical or background measurement wavelengths. Spectral overlap may be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element (see Section 8.8 for a description of this correction).

4.1.2 Unresolved overlap of molecular band spectra.

4.1.3 Background contribution from continuum or recombination phenomena.

4.1.4 Stray light from the line emission of high concentration elements. Background contribution and stray light may usually be compensated for by a background correction adjacent to the analyte line.

4.2 PHYSICAL INTERFERENCES

Effects associated with the sample nebulization and transport processes are considered physical interferences. Changes in viscosity and surface tension may cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the samples.

4.3 CHEMICAL INTERFERENCES

Molecular compound formation, ionization effects, and solute vaporization effects are chemical interferences. The most significant potential interference in the Trace ICAP instrument is ionization effects caused by varying levels of easily ionized elements in samples and standards. The ionization effects can be reduced by adding a constant amount of an easily ionized element (such as lithium) as an "ionization buffer" to all solutions. The lithium is added using a peristaltic pump that delivers a constant flow of lithium solution to the sample delivery tubing through a "T" connector.

5. APPARATUS AND MATERIALS

5.1 Autosampler: Thermo Jarrell Ash Model AS300 or equivalent

5.2 ICAP: An argon plasma trace analyzer (e.g., Thermo Jarrell Ash ICAP 61E Trace Analyzer), set to simultaneous operating conditions and containing the following:

- an axially mounted torch
- an R.F. (radio frequency) generator; set at 27.12MHz, 2kW (i.e., an inductively coupled argon plasma excitation source)
- holographic grating, 2400 grooves/nm, blazed at 500nm
- a 0.75m Rowland Circle spectrometer (polychromator) or equivalent, with a Paschen-Runge mount and capable of accepting up to 63 channels

- an automated instrument control and data acquisition system (i.e., personal computer or equivalent) capable of providing various (i.e., background, interelemental) corrections
- Thermospec™ version 6.20 or higher or ICAP Manager™ version 6.10 or higher software, or equivalent

5.3 Volumetric flasks, various sizes, of suitable precision and accuracy

5.4 Volumetric pipets, fixed or adjustable, verified per SOP 321

6. REAGENTS – Only trace metals grade solvents shall be used!!

6.1 Hydrochloric acid (HCl), concentrated, JT Baker #9530-33 or equivalent

6.2 Nitric acid (HNO_3), concentrated, JT Baker #9598-34 or equivalent

6.3 Reagent water, deionized (DI) water obtained from the laboratory's DI water system (SOP 319)

6.4 Liquid Argon, 99.99% pure

6.5 STANDARDS

6.5.1 All standard solutions are prepared, documented, and stored in accordance with Paragon SOP 300. All standard solutions are to be contained in fresh (previously unused) polypropylene bottles.

6.5.2 Detailed documentation of all standards associated with each ICAP acquisition (analytical sequence) is recorded in the Header Information of the ICAP software, and included with the associated raw data. This documentation includes the stock and intermediate standard identification numbers, dilutions performed to create the working standards, and the resulting concentrations of the working standards. (Further details pertaining to header information is provided in Section 8.4).

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are collected in plastic or glass containers, and must be chemically preserved with nitric acid to pH<2. Samples for dissolved metals analyses should be filtered in the field prior to chemical preservation. If samples are not preserved in the field, they may be acidified by the laboratory upon receipt, but must be held in their original container for a minimum of 16 hours before transfer or analysis of the sample.

7.3 Samples must be maintained at 4±2°C, and must be prepared and analyzed within 180 days of collection.

8. PROCEDURE

8.1 TYPICAL OPERATING CONDITIONS

Torch Gas:	High Flow
Auxiliary Gas:	Low
Nebulizer Gas:	25 PSI
RF Power:	1150 W
Pump Rate:	125 rpm
Sample Tubing:	Orange/Orange
Rinse Tubing:	Red/Red

8.2 The instrument is calibrated each day, by analyzing and processing multi-point calibration curves for each element quantitated. Second order (quadratic) calibration equations with at least 5 points are used to fit the calibration data and to determine concentration results.

8.3 The typical autosampler analytical sequence is listed below along with brief descriptions of each solution. Refer to attached quality control (QC) Table at end of SOP for performance criteria:

Autosampler Run Number	***Solution Name***	***Description***
1	Mix A	Reanalysis of the highest calibration standard for Mix A elements. Processed as a sample.
2	Mix B	Reanalysis of the highest calibration standard for Mix B elements. Processed as a sample.
3	Mix C	Reanalysis of the highest calibration standard for Mix C elements. Processed as a sample.
4	ICV	Initial Calibration Verification check standard for all elements (second source).
5	ICB	Initial Calibration Blank. Must be run following the multi-point calibration and before any samples are analyzed.
6	ICSA	Interference Check Solution A (contains high concentrations of Ca, Mg, Al, Fe).
7	ICSAB	Interference Check Solution B (contains high concentrations of Ca, Mg, Al, Fe and low concentrations of other elements).
8	CRI	Low concentration test solution containing analyte concentrations near the reporting limit; analysis of this solution is not described in Method 6010B. Run for informational purposes only, Paragon does not control on CRI recovery, unless required by client LIMS program specification.

Autosampler Run Number	*Solution Name*	*Description*
9	CCV	Continuing Calibration Verification check standard for all elements (second source).
10	CCB	Continuing Calibration Blank. Must follow CCV analyses.
11 thru 20	Samples	Additional analytical samples. Analytical samples include all samples analyzed on the instrument except ICV, ICB, CCV and CCB. The CRI, ICSA and ICSAB, along with all samples in the sequence and any dilutions, post-spikes (see Section 8.6.4), laboratory and matrix spikes, duplicates, serial dilutions and method/ preparation blanks, are all considered to be analytical samples. The sequence is closed out with the following solutions: CRI, ICSA, ICSAB (analyzed at the end of each analytical sequence, and every eight hours if the analytical sequence is longer than eight hours), followed by CCV, CCB.
21	CCV	Continuing Calibration Verification check standard for all elements (second source).
22	CCB	Continuing Calibration Blank, must follow CCV analyses.
Repeat (11 through 22); the sequence continues with CCV and CCB analyzed after every 10 analytical samples.		

8.4 After the analytical sequence is complete, a "header and summary" section is produced which includes:

- Standard information including standard identifications, expiration dates, elements and concentrations, and preparation procedures
- Acid lot numbers
- Pipet identification numbers
- Dilution information and preparation procedures
- Analytical spike information and preparation procedures
- Daily and monthly maintenance items performed. (Maintenance is further discussed in Section 8.10).
- Summary page with analytical sequence and elements of interest

8.5 At the completion of the sequence, the instrument is shut down as follows:

8.5.1 Disconnect pump tubing.

8.5.2 Lower "purge optics" gas flow to approximately 1L/min.

8.5.3 Exit the software.

8.6 PREPARATION AND EVALUATION OF QUALITY CONTROL (QC) SAMPLES

8.6.1 Calibration Blank (STD-Blank): An aliquot of reagent water is acidified in the same manner as the sample digestates. This calibration blank is used as a component in establishing the calibration curve and is also analyzed repeatedly throughout the analytical sequence as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB). To be acceptable, the calibration blank cannot contain any analyte above the analyte reporting limit (or as otherwise specified in the applicable LIMS program specification). Refer to Section 10.1 for further discussion.

8.6.2 Method Blank (MB): Referred to as a reagent blank in Method 200.7 (40 CFR). One MB is prepared per batch of 20 or less field samples. The method blank consists of an aliquot of reagent water that has been digested and prepared in the same manner as the associated samples. To be acceptable, the method blank cannot contain any analyte above the analyte reporting limit (or as otherwise specified in the applicable LIMS program specification). Method blank results are also acceptable if sample concentrations are greater than 10 times the concentration found in the method blank. Refer to Section 10.5 for further discussion.

8.6.3 Sample Duplicate: One sample duplicate is prepared per batch of 10 or less field samples. The control limit for duplicate precision is that the relative percent difference (RPD) must be ≤20%. RPD is calculated as shown below:

$$\text{RPD} = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

The results are flagged if duplicate precision is greater than 20% RPD. Refer to Section 10.6 for further discussion.

8.6.4 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): One MS and MSD are prepared per batch of 10 or less field samples. MS and MSD samples consist of additional aliquots of a particular field sample that are spiked, digested and prepared in the same manner as the associated samples.

Matrix spike samples are evaluated in terms of recovery, calculated as follows:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right) (100)$$

Matrix spike recovery is not evaluated if the analyte concentration in the unspiked sample is greater than 4 times the spike level. The quality control limit for matrix spike recovery is 70 to 130%. The control limit for MS/MSD precision is that the RPD must be ≤20%. RPD for the MS/MSD is calculated the same as for the Sample Duplicate (see Section 8.6.3 above). Results are flagged if MS/MSD recovery or precision results are outside control limits.

A post digestion spike analytical spike (i.e., sample aliquot is spiked after digestion) should be performed when matrix spike recovery is outside the control limit. If recovery of the post digestion analytical spike is not within 90-110%, the result is flagged indicating that matrix interference is suspected. Refer to Section 10.8 for further discussion.

8.6.5 Laboratory Control Sample (LCS): One laboratory control sample is prepared per batch of 20 or less field samples. The LCS is a water sample with known analyte concentrations that is digested and prepared in the same manner as the associated samples. LCSs are evaluated in terms of recovery (%R), calculated as follows:

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right) (100)$$

The control limits for LCS recovery are 85-115%. All samples associated with a failed LCS must be redigested and reanalyzed. Refer to Section 10.9 for further discussion.

8.6.6 Serial Dilution Sample: A 1:5 serial dilution of an additional sample digestate is prepared per 20 field samples of like matrix that are processed as a unit. If analyte concentrations are sufficiently high (at least 50X the instrument detection limit), the results of the dilution test should agree within ±10 % of the undiluted results. Sample analyte results failing this test should be flagged indicating the existence of matrix interferences. Refer to Section 10.10 for further discussion.

8.7 LINEAR RANGE

The element concentrations in the Mix A and Mix B High Standards define the upper end of the analytical range. Samples whose concentrations exceed the calibration range must be diluted to bring their concentrations within the known calibration range of the instrument.

8.8 INTERELEMENT SPECTRAL INTERFERENCE CORRECTIONS

Interelement spectral interferences are determined by analyzing a solution that contains a high concentration of a potentially interfering element and observing the "apparent" concentration arising from the solution in other element channels. Interelement interference correction factors are calculated from these observations. *For example*: a 500ppm Al solution produces an apparent Pb concentration of 0.15ppm. The interelement correction factor K is calculated as follows:

$$K = \frac{Apparent\ Conc.\ in\ ppm}{Conc.\ of\ Interfering\ element\ in\ ppm}$$

In this example, K = 0.15 / 500 = 0.00030.

The interelement correction factor K is the amount of interference produced by 1ppm of the interfering element on the element being interfered with. Interference correction factors are used by the ICAP software to calculate corrected concentrations using the following equations:

$$Corrected\,Conc.(ppm) = Uncorrected\,Conc.(ppm) - \left(K * Conc.of\ Interfering\,Element(ppm)\right)$$

High concentrations of elements (such as Fe and Al in solid digestates) are the most likely sources of significant spectral interferences. The ICSA and ICSAB are analyzed at the beginning and end of each analytical sequence to verify that the spectral interferences arising from Al, Fe, Ca, and Mg are being corrected properly.

An interelement interference study is conducted every six months by analyzing single element solutions of each analyte at high concentrations. The study is used to verify or update interelement interference correction factors. Because the instrument is a direct reading polychromator with fixed detectors, interelement interference correction factors usually remain quite constant.

8.9 In addition to the electronic run information provided by the instrument's output (analyst, date, time, sample ID, etc.), a hardcopy Run Log is maintained as an internal Departmental record of instrument throughput. Standard intensities for selected elements are noted as comments, these recordings are used to verify that operating conditions remain the same. If a variation or trend is noticed in intensity readings, the cause should be determined and corrected if necessary.

8.10 REGULAR MAINTENANCE ITEMS

The following items should be checked prior to each run to ensure the instrument is in good working order.

- check argon level; order more as needed
- check printer, paper supply and ribbon; replace as needed
- check filters on rear of instrument and vacuum monthly
- check water level in drain bottle and empty if necessary
- check pump tubing -- replace when necessary
- check that the previous day's work is properly recorded and processed

There is a section in the raw data header information where the Regular Maintenance items may be initialed as completed.

8.11 MAINTENANCE LOG

A maintenance logbook is used to record all information concerning instrument maintenance that is not covered by the daily and monthly maintenance items described previously. This logbook is used to document all repairs and the symptoms of the problems.

9. QUALITY CONTROL

9.1 Various quality control indicators are discussed in Sections 8.3 and 8.6.

9.2 A method detection limit (MDL) study consisting of the analysis of a minimum of seven replicate aliquots of target analytes at concentration levels 3-5 times the anticipated detection limit, shall be performed as needed, and at a minimum, annually.

9.3 Instrument detection limits (IDLs) reflect instrument capability and are determined per CLP protocol. These studies are performed quarterly.

10. METHOD MODIFICATIONS

10.1 Section 12.1.1 of EPA Method 200.7 (40 CFR) recommends that the results for calibration blanks "should be within 2 standard deviations of the meal *(sic)* value." The intent of this statement is most likely that calibration blanks should be within ±2 standard deviations of the 'mean' value. Paragon follows a different criteria for calibration blanks than the one recommended. Paragon's criteria require that the calibration blank results be less than the reporting limit (ICB, CCB).

Method 200.7 (40 CFR) does not define the data set to be used for determining the control limits. Paragon notes that several factors could significantly affect data used for calculation of control limits. Some examples include: different acid lot numbers; instrumentation changes (nebulizer, torch); the number of data points used; and the frequency of updating the control limits. A significant problem with the recommendation given in Section 12.1.1, is that a control limit of ±2 standard deviations of the mean value could allow blank results to be higher

than the reporting limit. Paragon's criteria for evaluating calibration blanks are clearly defined and allow for straightforward data review and validation.

10.2 Section 12.1.2 of EPA Method 200.7 (40 CFR) recommends that results for the interference check sample "should fall within the established control limits of 1.5 times the standard deviation of the mean value." A control limit of 1.5 times the standard deviation of the mean value shows that the interelement spectral interference correction routines are operating reproducibly, but this control limit does not provide assurance that the corrections are accurate. Paragon analyzes 2 interference check samples (named ICSA and ICSAB) rather than one interference check sample as described in Method 200.7 (40 CFR). These solutions are analyzed at the beginning, end, and periodically throughout an analytical sequence. The ICSA solution contains Ca, Mg, Al and Fe at the upper analytical range concentration and no other analytes. Ca, Mg, Al and Fe are the elements most likely to cause significant spectral interferences in environmental samples. The control limits used by Paragon for the ICSA results require that no analyte concentrations (other than Ca, Mg, Al and Fe) may exceed the absolute value of 2 times the reporting limit. The ICSAB solution contains Ca, Mg, Al and Fe at the upper analytical range concentration and the other analytes at low concentrations. The control limits used by Paragon for the ICSAB results requires all analyte recoveries to be within ±20% of the known concentrations. The analysis of the ICSA and ICSAB solutions verifies that the spectral interference correction routines are functioning at concentrations near the reporting limit and also at concentrations above the reporting limit. Paragon control limits for the ICSA and ICSAB solutions are clearly defined and allow for straightforward data review and validation.

10.3 Paragon analyzes a CRI solution at the beginning and end of each sequence. This CRI solution provides assurance that the instrument sensitivity is adequate to support the reporting limit. Method 200.7 (40 CFR) does not describe the analysis of a low level test solution as part of an analytical sequence.

10.4 Section 12.1.1 in EPA Method 200.7 (40 CFR) states: "Analyze and *(sic)* appropriate instrument check standard at a frequency of 10%". This is assumed to mean that an appropriate instrument check standard should be analyzed. The control limit given in Method 200.7 (40 CFR) is ±5% of the true value. This control limit has been found to be too stringent to allow for the routine analysis of samples with widely varying matrix constituents. Instrumental drift is caused by samples containing high levels of dissolved constituents, which perturb the nebulizer, and changes in ambient temperature. Paragon's control limit for CCVs is ±10% of the true value. The ±10% control limit is also given in EPA Method 200.7 (EPA 600). The ±10% control limit provides adequate assurance that instrumental drift has not significantly affected quantitation.

10.5 Section 11.1 of Method 200.7 (40 CFR) recommends, "reagent blanks should be

subtracted from all samples". No criteria are given in Method 200.7 (40 CFR) defining the maximum allowable analyte concentration in reagent blanks. Paragon does not subtract method blank results from samples. If reagent (method) blank results are either above the reporting limit or are greater than 1/10 the concentration found in samples, then all associated samples are re-digested and re-analyzed.

10.6 EPA Method 200.7 (40 CFR) does not describe the preparation and evaluation of duplicate samples. Paragon performs duplicate analyses at a frequency of 10% to provide a measure of the precision of the analytical results.

10.7 Method 200.7 (40 CFR) does not discuss the preparation and evaluation of digested matrix spike and matrix spike duplicate samples. Paragon prepares and analyzes matrix spike and matrix spike duplicate samples at a frequency of 10%.

10.8 Section 5.2.2 of Method 200.7 (40 CFR) recommends that a spike addition test should be performed whenever a new or unusual matrix is encountered. It is assumed that the spike addition is performed on a digested sample (i.e., a post digestion analytical spike) because it is discussed in the same section (5.2) as the serial dilution test. It is not likely that a commercial laboratory will be able to determine if a matrix is new or unusual. Therefore, Paragon uses matrix spike recovery results in each preparation batch to evaluate matrix interferences. The matrix spike recovery control limits (70-130%) are taken from Method 200.7 (EPA 600). If matrix spike recovery is outside the control limit, then a post digestion spike is prepared and analyzed. Paragon uses the 90-110% control limit for post digestion spike recovery recommended by Method 200.7 (40 CFR).

10.9 Method 200.7 (40 CFR) does not describe the preparation and evaluation of a digested laboratory control sample (LCS). Paragon analyzes a LCS with each sample batch to provide assurance that the digestion and analysis is in control. Paragon's LCS recovery limit is 85-115%, which is taken from Method 200.7 (EPA 600).

10.10 Section 5.2 of Method 200.7 (40 CFR) recommends that serial dilution results should agree within $\pm$5% of the original determination. The amount that the sample should be diluted for the test is not defined. The difference between undiluted and diluted results usually becomes larger as the level of dilution increases. A $\pm$5% criterion seems too stringent for samples with widely varying levels of constituents. Paragon flags data if the serial dilution (5 fold dilution) results do not agree within ±10% of the original determination. The ±10% criterion is also suggested by Method 200.7 (EPA 600).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire

extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) should be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The sample digestates shall be disposed of in the Aqueous Laboratory Waste.

11.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. ***Note that all labels and markings must be defaced prior to disposal.***

12. REFERENCES

12.1 EPA Method 200.7, 40 CFR, Appendix C to Part 136.

12.2 EPA Method 200.7, US EPA 600/R-94/111, Revision 4.4, May 1994.

12.3 Operator's Manual, ICAP Trace Analyzers.

DOCUMENT REVISION HISTORY

11/20/06: SOP was updated to apply to newly acquired second trace ICAP instrument as well. Abbreviation 'ICP' was updated to 'ICAP' throughout. Element list verified, updated and presented in tabular form, Section 1. LIMS program specification reference augmented, Section 3.3. Simplified standards discussion, Section 6.5, and included reference to information contained in software header. Reorganized Section 7 and added comment that if acidified by laboratory, sample must be held in

original container for at least 16hrs prior to processing. Typical Operating Conditions added, Section 8.1. QC information taken out of analytical sequence Table (Section 8.3); QC Table at end of SOP referenced instead. References to LIMS program specification requirements added to QC Table where appropriate, MDL Study information added to Table. DOCUMENT REVISION HISTORY Section added.

Analytical Method: EPA 200.7	**Parameter**: ICAP Metals		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration, using, at minimum, 4 standards and a blank	Daily	Correlation coefficient for all analytes >0.995	Correct problem and repeat initial calibration
Reanalysis of Mix-A, Mix-B and Mix C calibration standards as samples	Immediately after calibration	All analytes within ±5% of expected value	Correct problem then repeat initial calibration
ICV (Initial Calibration Verification) check standard (second source); at or below midpoint	Daily after initiation calibration	All analytes within ±5% of expected value	Correct problem then repeat initial calibration
ICB (Initial Calibration Blank)	Immediately following ICV	Absolute value of result for each analyte < reporting limit (or as specified in the applicable LIMS program specification)	Correct problem then re-analyze ICB
CCV (Continuing Calibration Verification) check standard; concentration of analytes must be different from the ICV	After every 10 samples and at the end of the analytical sequence	All analytes within ±10% of expected value Note: (where compliance samples are analyzed for regulatory reporting purposes, a ±5% CCV must be maintained).	Repeat calibration and reanalyze all samples since last successful CCV
CCB (Continuing Calibration Blank)	Immediately after every CCV	Absolute value of result for each analyte < reporting limit (or as specified in the applicable LIMS program specification)	Correct problem then analyze CCB and previous 10 samples
ICSA (Interference Check Solution A)	At the beginning and the end of an analytical run	All analytes within ±20% of expected value	Terminate analysis, correct problem, reanalyze ICSA, reanalyze all affected samples
ICSAB (Interference Check Solution B)	At the beginning and the end of an analytical run	All analytes within ±20% of expected value	Terminate analysis, correct problem, reanalyze ICSAB, reanalyze all affected samples
MB (Method blank)	One MB per batch of 20 or fewer field samples	Absolute value of result for each analyte < reporting limit (or as specified in the applicable LIMS program specification)	Correct problem then reprep and analyze MB and all samples processed with the associated MB

Analytical Method: EPA 200.7	**Parameter**: ICAP Metals		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
LCS (Laboratory Control Sample)	One LCS per batch of 20 or fewer field samples	Recovery limit 85-115% for each analyte	Correct problem then reanalyze. If still out, reprep and reanalyze the LCS and all samples in the affected batch
Sample Duplicate	One sample duplicate per batch of 10 or fewer field samples	For each analyte RPD ≤20%	Flag results if RPD >20%.
MS/MSD (Matrix Spike/Matrix Spike Duplicate)	One MS/MSD pair per batch of 10 or fewer field samples	Recovery limit 70-130% for each analyte, not calculated if analyte conc >4X the spike level. For each analyte RPD ≤20%	Flag results if MS/MSD recovery or precision results are outside control limits, perform post digestion analytical spike as applicable
Post Digestion Spike	Performed when MS/MSD recovery is outside ± 30% (unless analyte conc > 4X the spike level)	Recovery limit 90-110% for each analyte	Flag results if post spike recovery or precision results are outside control limits
Serial Dilution sample analysis	Performed on one sample per batch of 20 or fewer field samples, where analyte concentrations exceed 50X IDL	Results should agree within ±10% of undiluted results	Flag results if outside criteria
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level ≤ to that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and QA Managers (RL may be adjusted, if needed).

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 812 REVISION 14

TITLE: PREPARATION AND DETERMINATION OF MERCURY BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY -- METHODS SW7470A, SW7471A, EPA 245.1, ILMO3.0, ILMO4.0

FORM NUMBERS: 808, 824

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/13/07

QUALITY ASSURANCE MANAGER _____ DATE 8/11/07

LABORATORY MANAGER _____ DATE 8-13-07

HISTORY: Rev0, 3/18/93; Rev1, PCN #84, 1/17/94; Rev2, PCN #262, 9/26/94; Rev3, 1/13/95; Rev4, 3/31/96; Rev5, 5/7/97; Rev6, 3/1/99; Rev7, 3/7/01; Rev8, 3/2/02; Rev9, 3/28/03; Rev10, 2/25/04; Rev11, 2/1/05; Rev12, 7/26/05; Rev13, 4/10/06; Rev14, 8/11/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the digestion procedures and instrument analysis of all matrices for mercury.

2. SUMMARY

Waters and TCLP leachates analyzed by methods SW7470A, EPA 245.1, CLP ILMO3.0, CLP ILMO4.0 are digested using the same basic procedure. A weighed portion of sample is digested using acids, potassium permanganate and potassium persulfate for liquid samples and soil CLP samples. Aqua regia and potassium permanganate are used for digesting SW7471A soil samples. After digestion, and the addition of hydroxlyamine sulfate, the digestate is analyzed using a cold vapor mercury atomic absorption spectrometer (CVAA). The mercury (Hg) is reduced to the elemental state by the addition of stannous chloride. The mercury vapor passes through a cell in the light path of an atomic absorption lamp that emits light at 253.7nm. The 253.7nm light is absorbed in proportion to the concentration of Hg atoms in the cell. The absorbance is measured as a function of mercury concentration by running a series of standards with each batch of samples. The typical reporting limits for this method are 0.0002mg/L and 0.0006mg/Kg.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Analysts must demonstrate the capability to generate and interpret acceptable

results utilizing these methods. This demonstration may come in the form of Supervisory/training review, performance of precision and accuracy tests, or the successful analysis of an unknown proficiency test sample.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20mg/L or 20mg/kg of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

4.2 Copper has also been reported to interfere, however, copper concentrations as high as 10mg/L or 10mg/kg had no effect on recovery of mercury from spiked samples.

4.3 Samples that contain relatively high amounts of chlorides or oxidizable organic material require additional permanganate (as much as 25mL in a 100mL final volume) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25mL).

4.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.5 Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if performed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as total Kjeldahl nitrogen (TKN) or chemical oxygen demand (COD).

5. APPARATUS AND MATERIALS

5.1 Mercury analyzer, automated, CETAC M-6000A, or equivalent

5.2 Mercury vapor lamp, electro-optically regulated, low pressure, high frequency, thermally stabilized

5.3 Nafion drying cartridge and mercury trap ($KMnO_4$), CETAC SP5894 or equivalent

5.4 Hot plate or water bath -- capable of maintaining a temperature of 95±5°C

5.5 Thermometer -- for monitoring hot plate or water bath temperature. **Use only a mercury-free type of thermometer.**

5.6 Beakers, polypropylene, disposable, 250mL - - used for soils

5.7 Centrifuge tubes with caps, disposable, 50mL - - used for liquids

5.8 pH test strips, low range, acidic – capable of testing solutions < pH2

5.9 Pipette(s), adjustable, 0.01-5.0mL

5.10 Laboratory balance -- capable of weighing to 0.01g

5.11 Test tubes, 16X100mm

5.12 Spatulas, wooden, disposable

5.13 Boiling chips, Teflon™, ChemWare PTFE Chips, VWR Cat. No. 26397-103 or equivalent

6. REAGENTS

NOTE: Only trace metals grade acids may be used. The lot # must be verified by the Metals Department prior to the preparation/analysis of samples with any new acids. Each lot of acid must be certified (no metals detected at or above the MDL).

6.1 Reagent water/deionized (DI) water, interference free

6.2 Liquid argon, 99.99% pure

6.3 Sulfuric acid (H_2SO_4), concentrated, EMD SX1247-2 or equivalent

6.4 Nitric acid (HNO_3), concentrated, JT Baker 9598-34 or equivalent

6.5 Hydrochloric acid (HCl), concentrated, JT Baker 9530-33 or equivalent

6.6 Stannous chloride solution (10% w/v): CCI 5515AL or equivalent. Dissolve a ratio of 25g stannous chloride with 25mL HCl up to a 250mL final volume with reagent water for a final concentration of 10%.

6.7 Sodium chloride - hydroxylamine sulfate solution (12% w/v): EMD SX0420-5 and GFS Chemicals 144 or equivalents. Dissolve a ratio of 12g sodium chloride

and 12g hydroxylamine sulfate in reagent water and dilute to 100mL for a final concentration of 12%.

6.8 Potassium permanganate, mercury-free (5% solution w/v): JT Baker 3227-01 or equivalent. Dissolve a ratio of 5g potassium permanganate in 100mL of reagent water for a final concentration of 5%.

6.9 Potassium persulfate (5% solution w/v): JT Baker 3238-01 or equivalent. Dissolve a ratio of 5g potassium persulfate in 100mL of reagent water for a final concentration of 5%.

6.10 Aqua regia: 3 parts concentrated HCl to 1 part concentrated HNO_3. *Made immediately before using.*

6.11 Mercury stock solution; 1000ug/mL: Purchased from two separate sources.

6.12 Intermediate mercury standards, 10ug/mL: **Two** standards are made, one using the primary source mercury stock solution, and the second using the secondary source mercury stock solution. Use 10% HNO_3 to dilute 1mL mercury stock solution to a final volume of 100mL.

6.13 Spiking solutions (working standards):

6.13.1 Spiking Solution A (100ug/L Hg): This solution is *made fresh daily* by diluting the first source 10ug/mL intermediate mercury standard 1:100 with DI water.

6.13.2 Spiking Solution B (100ug/L Hg): This solution is *made fresh daily* by diluting the second source 10ug/mL intermediate mercury standard 1:100 with DI water.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples should be collected according to an approved sampling plan.

7.2 Use sample containers obtained from the vendor pre-washed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

7.3 Aqueous samples must be acidified to a pH<2 with HNO_3. Typically, a 1L sample is collected. Analysis of the sample cannot begin until it has been acidified for at least 24hrs. The maximum holding time for an aqueous sample is 28 days from collection.

7.4 Non-aqueous samples are not chemically preserved, but are required to be refrigerated at $4\pm2^{o}C$ until analyzed. Typically, 200g of solid or waste is collected.

8. PROCEDURE

8.1 DIGESTION LOGBOOK

8.1.1 Two types of digestion logbooks are used, one for liquid samples and another for soil or solid samples. The most recent iteration of the

mercury benchsheet (Form 808) is to be used. At the time of digestion, the analyst should complete the header and footer information prompted in the digestion logbook (e.g., digestion date, method, digestion analyst, etc.)

8.1.2 Standard/Verification information -- The information needed to prepare the standard curve is pre-printed in the digestion logbook. The concentrations of these calibration standards are: 0, 0.2, 0.5, 1.0, 2.0 and 5.0ppb.

Also pre-printed in the digestion/analysis logbook are the ICV (initial calibration verification), ICB (initial calibration blank), CCV (continuing calibration verification), CCB (continuing calibration blank), and the CRA (low level check standard). Note that a calibration verification and blank must bracket every ten analytical samples (i.e., any sample except a CCV or CCB), and that a CCV and CCB must also be run to closeout the analytical sequence.

IPC -- For method 245.1, an initial performance check (IPC) solution is analyzed immediately following calibration. The IPC solution should be prepared from the same source used for the calibration standards. The IPC concentration should be near the midpoint of the calibration range. The percent recovery of the IPC must be 95-105% before sample analysis can begin.

8.1.3 Sample/Digestate information -- A 'Preparation Batch' is created in LIMS that lists the specific client samples to be digested, and well as the associated QC samples (Blanks, Blank Spikes, Laboratory Control Samples, Duplicates, Matrix Spikes and Matrix Spike Duplicates) that are digested for analysis. A Serial Dilution QC sample is also analyzed per batch, but this sample is not digested.

8.1.4 Additional documentation -- Reagent lots, support equipment ID, etc. are also recorded in the digestion/analysis logbook.

8.2 SAMPLE PREPARATION AND DIGESTION (Soils, Solids, and Wastes)

8.2.1 Label 250mL disposable polypropylene beakers with solution IDs as prepared in the digestion logbook.

8.2.2 Mix the sample by stirring with a disposable wooden spatula in order to obtain a representative aliquot. The aliquot should have a similar particle size distribution as the bulk sample. For very heterogeneous or unusual matrices, consult the Department Manager and Project Manager. If special processing prior to taking an aliquot was required, document in the comments section of the benchsheet. Record the texture (coarse, medium, fine) and color of the sample on the digestion benchsheet as well.

8.2.3 For SW7471A digestions, weigh approximately a 0.60g aliquot of sample into the appropriately labeled beaker. For CLP digestions, weigh approximately a 0.20g aliquot of sample into the appropriately labeled beaker. Record the aliquot size on the digestion benchsheet to the nearest 0.01g.

8.2.4 For soil/solid digestions, the method blank is prepared by digesting approximately 0.60g of Teflon™ chips for method SW7471A, or 0.20g of Teflon™ chips for CLP methods. Record the weight to the nearest 0.01g on the laboratory benchsheet.

8.2.5 For SW7471A digestions, the Laboratory Control Sample (LCS) is approximately 0.60g of Teflon™ boiling chips (record on benchsheet to nearest 0.01g) with a known amount of spike added. For CLP digestions, the LCS is a beaker containing approximately 0.20g of a vendor-supplied soil standard (the certified values and acceptance criteria for these soil standards are based on lot numbers and supplied by the vendor). Both types of LCSs are treated identically to the samples throughout the digestion procedure.

8.2.6 Spike the standards, check standards and matrix spike samples as described in the digestion logbook (Spike Solution and Volume).

8.2.7 Serial Dilution Sample: A 1:5 serial dilution of an additional sample digestate is prepared per 20 field samples of like matrix that are processed as a unit. If analyte concentrations are sufficiently high (at least 50X the instrument detection limit), the results of the dilution test should agree within ±10 % of the undiluted results. Sample analyte results failing this test should be flagged indicating the existence of matrix interferences.

8.2.8 For SW7471A digestions, add 5.0mL of Aqua regia to each beaker. For CLP digestions, add 2.5mL concentrated nitric acid and 5mL concentrated sulfuric acid to each beaker. Place beakers in the pre-heated water bath for 2 minutes. Remove the beakers and cool to room temperature.

8.2.9 Add 50.0mL of DI water.

8.2.10 For SW7471A digestions, add 15mL of 5% potassium permanganate solution. For CLP digestions, add 8mL of 5% potassium persulfate solution and 15mL 5% potassium permanganate solution.

8.2.11 Loosely cover the beakers with polypropylene lids and mix well. Return the beakers to the water bath for 30 minutes. Remove the beakers and allow to cool.

8.2.12 Add 6mL of 12% sodium chloride hydroxylamine sulfate solution. Mix well until the color from the potassium permanganate has disappeared. Bring all standards and samples to 100mL with DI water. The samples are now ready for analysis.

8.3 SAMPLE PREPARATION AND DIGESTION (Aqueous Samples)

8.3.1 Label 50mL disposable centrifuge tubes with solution ID's as noted in the prepared digestion logbook.

8.3.2 For each sample in the batch, use a test strip to verify that the solution pH is <2. Record the result of the pH test on the benchsheet (Form 824). **If the pH of a sample is found to be >2, concentrated nitric acid (trace metals grade) must be added and the sample held *in its original container* for a minimum of *24 hours* until verified to be pH<2.**

8.3.3 Transfer a well mixed 20g aliquot (or smaller aliquot diluted to 20mL with DI water) into the appropriately labeled tube. TCLP leachates are usually digested at a ten-fold dilution (2.0mL of leachate and 18.0mL of deionized water). Transfer the required amount of DI water, as described in the digestion logbook, into the appropriately labeled tubes for standards and quality control (QC) samples.

8.3.4 For aqueous digestions, the method blank (MB) is prepared by digesting an aliquot of reagent water.

8.3.5 A 1:5 serial dilution of an additional sample digestate is prepared per 20 field samples of like matrix that are processed as a unit. If analyte concentrations are sufficiently high (at least 50X the instrument detection limit), the results of the dilution test should agree within ±10 % of the undiluted results. Sample analyte results failing this test should be flagged indicating the existence of matrix interferences.

8.3.6 Spike the standards, check standards and matrix spike samples as described in the digestion logbook (Spike Solution and Volume).

8.3.7 Add 1.0mL of concentrated sulfuric acid to each tube.

8.3.8 Add 0.5mL of concentrated nitric acid to each tube.

8.3.9 Add 3.0mL of 5% potassium permanganate solution to each tube.

8.3.10 Add 1.6mL of 5% potassium persulfate solution to each tube.

8.3.11 Cap the tubes tightly and mix well making sure the purple color persists for at least 15 minutes. If necessary, add equal amounts of permanganate solution to all tubes in the batch until the color persists for at least 15 minutes, or re-aliquot the sample at a dilution, or re-aliquot the sample and put in a separate batch.

8.3.12 Heat the tubes in a pre-heated (95±2°C) water bath for 2 hours. Remove the tubes from the water bath and allow to cool.

8.3.13 Add 1.2mL of 12% sodium chloride hydroxylamine sulfate solution to each tube. Mix well until the color from the potassium permanganate has disappeared. The samples are now ready for analysis and should be analyzed within 24 hours of the addition of the hydroxylamine sulfate.

8.4 MERCURY ANALYSIS (using CETAC M-6000A automated mercury analyzer)

8.4.1 Complete the digestion logbook by filling in the analytical filename, date analyzed and analyst information.

8.4.2 <u>Preparing the System</u>

- Turn on the mercury lamp and auto sampler (behind the instrument) and allow to warm up for at least 10 minutes (if in stand by mode). The mercury lamp is equipped with an oven to keep it at a constant temperature of 70^{o}C. If the system has been completely shut down, the instrument requires a warm up time of 90 minutes.
- Open the mercury software by clicking on the icon and open the appropriate worksheet.
- Stannous chloride is added using a peristaltic pump that delivers a constant flow of a 10% stannous chloride solution to the sample delivery tubing through a “T” connector. Clamp the pump tubing and turn the pump on. The pump line should be in 10% stannous chloride solution and the rinse tank should be filled with 1% hydrochloric acid and 1% nitric acid solution. Allow flow through all lines for about fifteen minutes before running the analytical sequence.
- Next, lower the autosampler tip. This is done by going to the “Instrument” option, and then going to “M6000 Controls”. Then pick the “Autosampler” tab, and click the “Park” button.
- Turn the gas on at the main tank.

- Change the peristaltic pump tubing and Nafion drying cartridge as needed.

8.4.3 Software Set-up

Double click the shortcut icon on the computer desktop, then choose the worksheets. This will bring you to the instrument operating area. Choose the labels tab and type in samples (as they appear in the logbook).

8.4.4 Calibrating the System

- Make sure that the six standards (five concentrations and a blank) have been loaded into the standards rack.
- A calibration is pre-programmed into the system. Click on the read button, choose "Read Standard" and then choose "Std. 5". Click "Start" (the autosampler will go to std. 5 and give a signal and peak reading. This is to make sure the system is operating correctly). After you have checked the instrument, run the calibration curve.
- Calibration results are automatically stored, and displayed at the bottom right of the screen.
- Determination of acceptable calibration curve -- An r^2 value greater than 0.995 is acceptable. If the curve is acceptable, begin running samples.
- If the curve is not acceptable, click on the stop button. Try running the calibration sequence again and check to be certain the solutions have been mixed well. At times the instrument requires a second calibration sequence to allow for warm up time. The analytical batch must be re-digested if an acceptable calibration curve cannot be obtained.

8.4.5 Running Samples

- After the field and QC samples are loaded into their designated tubes and the racks are placed on the autosampler, the instrument can begin running samples. Note that the instrument usually starts to read samples immediately after calibration, unless the analyst stops it due to a failed calibration curve.
- ICV -- Analyze an initial calibration verification (ICV) after an acceptable calibration. This is a second source check standard. Analyze an ICB immediately following. The ICV concentration must be different from the CCV. Either the ICV or CCV must be at a concentration below the midpoint of the

calibration curve. For SW-846 methods and EPA 245.1, the ICV recovery must be within 90-110%. For CLP methods, the ICV must be within 80-120%. Cause of failure must be determined and corrected and the instrument recalibrated.

- CRA -- Analyze this reporting limit standard after the ICB. The results of this standard analysis are not formally assessed, unless otherwise directed in the applicable LIMS program specification. The purpose of this standard analysis is simply to verify the analyte reporting limit.
- CCV -- Analyze a continuing calibration verification (CCV) after every ten analytical samples. An analytical sample is every solution analyzed on the instrument except ICV/CCV or ICB/CCB. A CCV is also analyzed after the last analytical sample. Percent recovery of the CCV must be 80-120% of the true value (SW-846 methods and CLP methods). If samples are being analyzed by method 245.1, percent recovery of the CCV must by 90-110%. Cause of failure must be determined and corrected. Samples following the last acceptable CCV must be reanalyzed. All samples must be bracketed by satisfactory CCVs.
- The autosampler will follow the run log you entered under the "Labels" tab, this will be the order in which the samples are analyzed. The instrument will store the data in the folder (the data are stored by date and output sequence).

8.4.6 Shutdown Procedures

- After the sample run is complete, pull up the autosampler tip and change the pump tubing from stannous chloride over to 10% nitric acid, and then deionized water. Let both run for approximately 5 minutes.
- Shut the mercury lamp off.
- When the pump has run DI water for 5 minutes, remove all lines so that air is pumped through the system for 5 minutes. Turn pump switch off and unclamp tubing.
- Turn the gas off at the main tank.

9. QUALITY CONTROL

9.1 DEFINITION OF BATCH

An analysis batch is defined as a group of twenty (20) or less field samples of like matrix that is associated with one unique set of batch QC samples and processed as a unit. Batch QC samples are defined as the method blank (MB), laboratory control sample (LCS), matrix spike and duplicate (MS/MSD), and serial dilution sample.

All QC samples must be carried through all stages of the sample preparation and measurement steps.

9.2 BLANKS

Method blanks (MBs) are run to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Each time a batch of samples is analyzed or there is a change in reagents, a method blank must be processed. The blank concentration found must be less than the analyte reporting limit, or as otherwise specified in the applicable LIMS program specification.
TCLP leachates have associated blanks that are carried through the tumbling process with designated samples. These blanks are analyzed as though they are samples. Calculated results for these blanks must be less than the reporting limit, or as otherwise specified in the applicable LIMS program specification.

ICB -- Analyze an initial calibration blank (ICB) after the ICV. The calculated result of the ICB must be less than the reporting limit, or as otherwise specified in the applicable LIMS program specification. CCB -- Analyze a continuing calibration blank after every CCV. The calculated result of the CCB must be less than the reporting limit, or as otherwise specified in the applicable LIMS program specification.

9.3 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) is analyzed to measure the accuracy of the method. One laboratory control sample (LCS) is analyzed with each batch of 20 or fewer field samples. Percent recovery of the LCS must be 80-120% unless solid LCS is used in which case a range will be given by the vendor. If samples are being analyzed by EPA 245.1, percent recovery of the LCS must be 85-115%. Samples associated with a failed LCS must be re-digested and reanalyzed. Other limits may apply, consult applicable LIMS program specification.

Blank spikes (LCSs) are prepared for TCLP leachate samples using the blanks that were carried through the tumbling process. Two different fluids (determined by pH of the sample) may be used for TCLP extraction. These fluids are termed Fluid #1 and Fluid #2. One TCLP blank spike is analyzed for each fluid type present per batch of 20 samples or less.

9.4 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE

Matrix spikes (MS/MSDs) consist of field samples into which known concentrations of target analytes are injected and analyzed as a means of determining the effect of matrix on target analyte detection. One MS/MSD are analyzed with each batch of 20 or fewer field samples (SW846 and CLP). One MS/MSD is analyzed with each batch of 10 or fewer field samples for EPA method 245.1. For TCLP leachates, an MS/MSD set are run for each fluid type present per batch of 20 samples or less.

Analyte recovery for matrix spikes is calculated as shown below:

$$\text{MS \% Recovery} = \frac{(C_{found} - C_{native})}{C_{added}} \text{ X } 100$$

where:

C_{found}	=	analyte concentration found in the spiked sample
C_{native}	=	native analyte concentration found in the unspiked sample
C_{added}	=	spike added analyte concentration

The MSD is analyzed as a measure of the precision of the analytical results generated as is expressed as Relative Percent Difference (RPD):

$$\text{RPD} = \frac{| \text{Result}_x - \text{Result}_{Dup} |}{(\text{Result}_x + \text{Result}_{Dup}) / 2} \text{ X } 100$$

For SW-846 methods, the recovery for the matrix spiked analytes should be within $\pm$20% of the expected value. For CLP methods, the recovery of the matrix spiked analytes should be within $\pm$25% of the expected value. For EPA 245.1, the recovery of the matrix spiked analytes should be within $\pm$30% of the expected value. Other limits may apply, consult applicable LIMS program specification.

The RPD between the matrix spike and the matrix spike duplicate (all methods) should be <20, unless otherwise specified in the applicable LIMS program specification.

9.5 SAMPLE DUPLICATE

One sample duplicate (Duplicate) is analyzed with each batch of 20 or fewer field samples (SW846). One sample duplicate is analyzed with each batch of 10 or fewer field samples (EPA 245.1). The RPD between the sample and duplicate (all methods) should be <20.

9.6 SERIAL DILUTION

To assist in the assessment of possible matrix interferences, a 1:5 serial dilution of an additional sample digestate is prepared per 20 field samples of like matrix that are processed as a unit. If analyte concentrations are sufficiently high (at least 50X the instrument detection limit), the results of the dilution test should agree within ±10 % of the undiluted results, or as otherwise specified in the applicable LIMS program specification. Sample analyte results failing this test should be flagged indicating the existence of matrix interferences.

9.7 A method detection limit (MDL) study shall consist of the analysis of a blank and a minimum of seven replicate analyses at a concentration level near to the capabilities of the method and below the analyte reporting limit (RL). The MDL study shall be performed as needed (i.e., whenever there is a significant change in operator, background, or instrument response) and at a minimum, every 6 months.

10. DEVIATIONS FROM METHODS

This SOP meets the requirements of methods SW846 7470A/7471A, EPA 245.1 and CLP ILMO3.0/ILMO4.0. The laboratory performs one known deviation from method SW7471A as follows: instead of weighing out three 0.20g aliquots of soil for triplicate analysis, the laboratory weighs out approximately 0.60g for a single analysis to ensure a representative sample.

11. SAFETY, HAZARDS, AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) must be labeled at a minimum with compound name, NFPA Health, Flammability, Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The sample digestates shall be disposed of in the Aqueous Laboratory Waste (otherwise known as the CLE Waste stream)..

11.2.2 Radioactive sample disposal – solid sample residues shall be disposed of in the Radioactive Soils & Solids container. Rad sample digestates

shall be disposed of in the Radioactive Aqueous Lab Waste.

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 US EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Edition, Volume 1A, "Method 7470A" and "Method 7471A", Revision 1, September 1994.

12.2 USEPA/600/4-91/010, Methods for the Determination of Metals in Environmental Samples, June 1991, "Method 245.1", Revision 2.3, April 1991.

12.3 USEPA Contract Laboratory Program, "Statement of Work for Inorganics Analysis, Multi-media, Multi-concentration", ILMO 3.0 and 4.0.

DOCUMENT REVISION HISTORY

7/26/05: Added reference Program Specification directive in "Responsibilities".

4/10/06: Added DOCUMENT REVISION HISTORY.

8/11/07: Changed sample must be acidified to pH<2 *for a minimum of 24hrs* before analysis may begin (Federal Register, 3/26/07, Volume 72, Number 57) to Sections 7.3 and 8.3.2 (also updated Form 824 and replaced logbook pages, trained analyst). Clarified (Sections 8.1.2, 8.4.4, QC Table) that a blank is included as a calibration point. Updated Paragon practice (Sections 8.1.3, 8.2.7, 8.3.5, 9 and QC Table) to include analysis of a five-fold serial dilution with every batch of samples analyzed (re-trained analyst). Revamped QC Section 9 (9.1 calibration curve statement removed, belongs in PROCEDURE text; IPC discussion moved to 8.1.2; ICV and CCV discussion moved to 8.4.5). Further updated QC Section 9 to make it more consistent with PAR format (Definition of Batch 9.1; Blanks 9.2, etc.). Added LIMS program specification references throughout QC Section 9 and QC Table.

Analytical Method: SW 7470A/7471A; EPA 245.1; CLP ILMO3.0/ILMO4.0	**Parameter:** Mercury		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration; minimum 5-point (plus blank)	Daily at on-set of analyses or when corrective action for CCV failure does not resolve calibration verification non-compliance	Correlation coefficient (r^2) for linear regression must be $\geq$ 0.995	Check that the calibration standards were prepared properly. Evaluate/ correct instrument malfunction and reanalyze calibration standards. If quality control acceptance criterion still not met, analyses cannot proceed; a new suite of calibration standards must be prepared and analyzed. Analyses cannot proceed until an acceptable initial calibration curve is generated.
Initial Performance Check (IPC) Standard; first source (run for Method 245.1 only)	Immediately following initial calibration	Results must agree within $\pm$5% of expected value	If QC criterion not met, analyze again. If IPC still fails, IPC and initial calibration standards must be re-digested and reanalyzed.
Independent Calibration Verification (ICV); second source; run at a concentration at or below the midpoint of the calibration curve	Once after each initial calibration	Response must agree within $\pm$10% of initial calibration for SW7470A/7471A and EPA 245.1; response must agree within $\pm$20% for CLP 3.0/4.0	If QC criterion not met, analyze again. If ICV still fails, ICV and initial calibration standards must be redigested and reanalyzed.
Blanks: Preparation (Method), Initial and Continuing Calibration Blank (ICB and CCB)	ICB run following the ICV One method blank per matrix type processed and analyzed per batch of twenty or less environmental samples processed. CCB run following the CCV to bracket a set of 10 analyses and to close a run sequence	Blank value must be less than reporting limit (RL), or as otherwise specified in LIMS program specification	If QC criterion not met for ICB, locate and correct problem; repeat initial calibration. If QC criterion not met for method blank, the method blank and all associated samples must be redigested and reanalyzed. If QC criterion not met for CCB, locate and correct the problem; all samples analyzed since last acceptable CCB must be reanalyzed.

Analytical Method: SW 7470A/7471A; EPA 245.1; CLP ILMO3.0/ILMO4.0	**Parameter:** Mercury		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
CRA Standard -- Low-Level Reporting Limit Standard run for CLP 3.0/4.0 only	Run immediately following the ICB	No acceptance criteria applicable	No corrective actions required.
Continuing Calibration Verification (CCV); may be first or second source; run at a concentration at or below the midpoint of the calibration curve	Run to bracket a set of 10 analyses, and to end any run sequence (must be followed by a CCB analysis)	Response must agree within ±20% of expected value (SW7470A/7471A and CLP3.0/4.0); response must agree within ±10% (EPA 245.1).	Check for calculation errors. If no calculation errors are found, analyze again. If CCV still fails, evaluate/correct instrument malfunctions; reanalyze. If CCV still fails, recalibrate system. All samples analyzed after last acceptable CCV must be reanalyzed.
Laboratory Control Sample (LCS)	One prepared and analyzed per matrix type per batch of 20 or less field samples	Recovery must be within ±15% of expected value (EPA 245.1). For SW7470A and CLP 3.0/4.0, recovery for aqueous LCS must agree within ±20% of expected value. For SW7471A, the recovery for the solid matrix LCS must agree within ±20% of expected value. For CLP 3.0/4.0 solid matrix, vendor-supplied QC limits apply. Other client-specified criteria may apply, consult applicable LIMS program specification.	Check for documentable errors (e.g., calculations and spike preparation) If no computation errors are found, all associated field and quality control samples must be redigested and analyzed.
Matrix Spike (MS)	One prepared and analyzed per matrix type per batch of 20 or less field samples for SW7470A/ 7471A and CLP 3.0/4.0 One prepared and analyzed per matrix type per batch of 10 or less field samples for Method 245.1	For SW7470A/7471A, recovery should agree within ±20% of expected value. For CLP 3.0/4.0 recovery should agree within ±25% of expected value. For EPA 245.1, recovery must agree within ±30% of expected value. Other client-specified criteria may apply, consult applicable	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample matrix effects are the most likely cause. Note in narrative and flag results appropriately.

Analytical Method: SW 7470A/7471A; EPA 245.1; CLP ILMO3.0/ILMO4.0	**Parameter:** Mercury		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	Frequency	Acceptance Criteria	Corrective Action
		LIMS program specification.	
Matrix Spike Duplicate (MSD)	One prepared and analyzed per matrix type per batch of 20 or less field samples for SW7470A/ 7471A and CLP 3.0/4.0 One prepared and analyzed per matrix type per batch of 10 or less field samples for EPA 245.1	(See MS recovery criteria above). RPD should be < = 20. Other client-specified criteria may apply, consult applicable LIMS program specification.	Check for documentable errors (e.g., calculations and spike preparation) If no errors are found, then sample matrix effects are the most likely cause. Note in narrative and flag results appropriately.
Laboratory Duplicate	One prepared and analyzed per matrix type per batch of 20 or less field samples for SW7470A/ 7471A and CLP 3.0/4.0 One prepared and analyzed per matrix type per batch of 10 or less field samples for EPA 245.1	RPD should be less than or equal to 20. Other client-specified criteria may apply, consult applicable LIMS program specification.	Check for documentable errors (e.g., calculations and spike preparation). If no errors are found, then sample heterogeneity is the most likely cause. Note in narrative and flag results appropriately.
Serial Dilution Test (1:5 dilution), analyzed to assist in the assessment of possible matrix interferences	One prepared and analyzed per matrix type per batch of 20 or less field samples	If analyte concentrations are sufficiently high (at least 50X the instrument detection limit), the results of the dilution test should agree within ±10 % of the undiluted results, or as otherwise specified in the applicable LIMS program specification	Sample analyte results failing this test should be flagged indicating the existence of matrix interferences.
Method Detection Limit (MDL) Study; run at an analyte concentration lower than the reporting limit (RL)	As needed; at minimum annually	Must yield a positive result < than the analyte reporting limit (RL).	Determine the reason for failure and fix problem with the system. Repeat the MDL study. If criteria still not met, discuss with QA Manager (RL may be adjusted if required).

Paragon Analytics

MERCURY DIGESTION - WATER/TCLP

Method: _____ SOP 812 / Rev: ____ Page ____ of ____

Digestion Date _____ Digestion Analyst _____ Spike Witness _____

Water Bath Temp. _____°C Time on _____ Time off _____

Date Analyzed _____ Analyst _____ Analytical Filename _____

Tube #	Solution ID	Spike Solution	Spike Volume (mL)	H_2O Added (mL)	Sample Aliquot (mL or g)	Final Volume (mL)	Comments
STD 1	0 ppb	-	-	20.0	-	20.0	
2	0.2 ppb	A	0.04	20.0	-	20.0	
3	0.5 ppb	A	0.1	19.9	-	20.0	
4	1.0 ppb	A	0.2	19.8	-	20.0	
5	2.0 ppb	A	0.4	19.6	-	20.0	
6	5.0 ppb	A	1.0	19.0	-	20.0	
SAMPLE 1	ICV	B	0.2	19.8	-	20.0	
2	ICB	-	-	20.0	-	20.0	
3	CRA-0.2 ppb	A	0.04	20.0	-	20.0	
4						20.0	
5						20.0	
6						20.0	
7						20.0	
8	**Use most current iteration of benchsheet.**					20.0	
9						20.0	
10						20.0	
11						20.0	
12						20.0	
13						20.0	
14						20.0	
15						20.0	
16						20.0	
17						20.0	
18						20.0	
19						20.0	
20						20.0	
21						20.0	
22						20.0	

Reagent Lots: H_2SO_4 _____ HNO_3 _____ HCl _____ $KMnO_4$- _____

$K_2S_2O_8$- _____ SnCl- _____ Hydroxylamine _____

Spike solutions:

A: 100 ppb Hg made from 100x dilution (1 mL/100 mL) of _____ Balance(s) Used: _____

B: 100 ppb Hg made from 100x dilution (1 mL/100 mL) of _____ (2nd source) Pipet(s) Used: _____

Reviewed by _____ **Date** _____ Form 808r14(a).doc (11/4/2003)

Paragon Analytics

MERCURY DIGESTION - SOIL

Method: _____ SOP 812 / Rev: ____ Page ____ of ____

Digestion Date _____ Digestion Analyst _____ Spike Witness _____

Water Bath Temp. _____°C Time on _____ Time off _____

Date Analyzed _____ Analyst _____ Analytical Filename _____

Tube #	Solution ID	Spike Solution	Spike Volume (mL)	Sample Aliquot (g)	Final Volume (mL)	Comments
STD 1	0 ppb	-	-	-	100.0	
2	0.2 ppb	A	0.2	-	100.0	
3	0.5 ppb	A	0.5	-	100.0	
4	1.0 ppb	A	1.0	-	100.0	
5	2.0 ppb	A	2.0	-	100.0	
6	5.0 ppb	A	5.0	-	100.0	
SAMPLE 1	ICV	B	1.0	-	100.0	
2	ICB	-	-	-	100.0	
3	CRA-0.2 ppb	A	0.2	-	100.0	
4					100.0	
5					100.0	
6					100.0	
7					100.0	
8	**Use most current iteration of benchsheet.**				100.0	
9					100.0	
10					100.0	
11					100.0	
12					100.0	
13					100.0	
14					100.0	
15					100.0	
16					100.0	
17					100.0	
18					100.0	
19					100.0	
20					100.0	
21					100.0	
22					100.0	

Reagent Lots: HNO_3 _____ HCl _____ SnCl- _____ Hydroxylamine _____ $KMNO_4$ _____

Spike solutions:

A: 100 ppb Hg made from 100x dilution (1 mL/100 mL) of _____ Balance(s) Used: _____

B: 100 ppb Hg made from 100x dilution (1 mL/100 mL) of _____ (2nd source) Pipet(s) Used: _____

Reviewed by _____ **Date** _____ Form 808r14(b).doc (11/4/2003)

Paragon Analytics

Documentation of Acidification and/or Filtration of Water Samples in Metals Department

Sample ID	Initial Sample pH	Initial Sample Volume (mL)	Filtered through 0.45 µm ? (Y / N)	Volume HNO_3 Added (mL)	Lot # for Conc. HNO_3	Date HNO_3 Added	Time HNO_3 Added	Initials	Sample pH after 24 hrs	Initials	Comments
				Use current iteration of benchsheet.							

Reviewed by / date _____

Form 824r1.doc (8/1/07)

Must Discard 30 Days from _____ (date printed)

See amendment last page (i.e., UCL for IS for DOE samples set at 155%).
3/9/09 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 827 REVISION 6

TITLE: DETERMINATION OF ELEMENTS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY -- METHODS EPA 200.8 AND SW6020A

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER Steve Workman DATE 8/13/07
QUALITY ASSURANCE MANAGER Deb Sacheti DATE 8/11/07
LABORATORY MANAGER [signature] DATE 8/13/07

HISTORY: Rev0, 8/26/2002; Rev1, 3/6/04; Rev2, 5/20/04; Rev3, 8/23/04; Rev4, 7/26/05 and 3/13/06; Rev5, 4/10/06; Rev6, 8/11/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references -- EPA 200.8 and SW6020A-- are used to determine the concentration of total or dissolved elements in prepared liquid and solid samples. This SOP is applicable to a large number of elements in waters and wastes after appropriate sample preparation steps are taken. Instrument detection limits (IDLs), sensitivities, and linear ranges for these elements will vary with the matrices and operating conditions. Reporting limits in relatively simple matrices will generally be below 0.1µg/L. Less sensitive elements (such as As and Se) and desensitised major elements may have reporting limits of 1.0µg/L or higher.

2. SUMMARY

This SOP describes the multi-element determination of trace elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface into a hexapole-based radiofrequency lens (collision cell). Reaction gases such as helium and hydrogen are introduced into the collision cell to facilitate ion beam focusing and minimization of molecular ion interferences. The ions are then introduced into a mass spectrometer where they are sorted according to their mass-to-charge ratios (m/z) and quantified with a detector. Interferences relating to the technique must be recognized and corrected. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by sample matrix must be corrected for by the use of internal standards.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Paragon uses custom Program Specifications which are directives and controls programmed into LIMS that govern the acquisition and reporting of project data. It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification prior to initiating handling of samples or data.

3.3 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing these methods. This demonstration may come in the form of supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Isobaric elemental interferences occur when isotopes of different elements form singly or doubly charged ions of the same nominal mass-to-charge ratio, and which cannot be resolved by the mass spectrometer (e.g., Mo98 and Ru98). A data system must be used to evaluate and correct for these interferences when they are present. Corrections for isobaric interferences may be made by measuring the intensity (response) due to the interfering element at another isotope and using its natural abundance ratios to correct for its presence at the analytical mass of interest. Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample.

4.2 Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interference may occur when a small ion peak is being measured adjacent to a large one. The

potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.3 Isobaric molecular interferences are caused by ions consisting of more than one atom or charge which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer (e.g., ArCl, ClO, Nitrogen dimer, oxygen dimer, oxide species, double charged species, etc.). These ions are commonly formed in the plasma or interface system from support gases or sample components. Predictions about the type of molecular interferences may be made using knowledge about the sample matrix. Molecular interferences can often be corrected for in the same manner as isobaric interferences, i.e., measuring the intensity present at another isotope and using isotope ratios to calculate the amount of the interfering species. For example, corrections for interferences of Ar_40Cl_{35} on As at mass 75 may be made by measuring the intensity of ArCl present at mass 77 (Ar_40Cl_{37}) and converting to the apparent intensity of ArCl at mass 75 by using the isotope ratio of Cl_{37} to Cl_{35}. Corrections for these interferences may be made based on the natural isotope ratios of the molecular ion (as described above) or by measuring the interference that occurs when the interferent is present.

4.4 Physical interferences are associated with the physical processes that govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during the excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute to deposits of material on the extraction and/or skimmer cones. Deposits can reduce the effective diameter of the orifices and therefore ion transmission. Dissolved solid levels not exceeding 0.2% (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.

4.5 Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects, or carryover, can result from sample deposition on the sampler and skimmer cones, as well as from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them.

5. APPARATUS AND MATERIALS

5.1 Micromass Platform inductively coupled plasma mass spectrometer (ICP-MS) or equivalent. System must be capable of providing resolution, less than or equal to 0.75amu at 5% peak height from 6-253amu and must be equipped with a data system that allows corrections for isobaric interferences and the application of the internal standard technique.

5.2 Autosampler, Cetac ASX-510 or equivalent

5.3 Radiofrequency generator compliant with FCC regulations

5.4 A variable speed peristaltic pump is required for solution delivery to the nebulizer

5.5 A mass flow controller on the nebulizer gas supply is required

5.6 Volumetric flasks of suitable precision and accuracy

5.7 Volumetric pipets of suitable precision and accuracy

6. REAGENTS

6.1 Hydrochloric Acid (HCl), concentrated, trace metals grade

6.2 Nitric Acid (HNO_3), concentrated, trace metals grade

6.3 Reagent water

6.4 Liquid Argon, 99.999% pure or better

6.5 Helium, high purity, 99.999% or better

6.6 Hydrogen, high purity, 99.999% or better

6.7 STANDARDS

NOTE: All standard solutions are prepared, documented, and stored in accordance with SOP 300. All standard solutions are to be contained in fresh (previously unused) polypropylene bottles.

6.7.1 Individual Elemental Standards, 10,000µg/mL or 1,000µg/mL: First source, purchased as certified solutions of 99.99% purity or greater. Element stocks should be checked for the presence of impurities that might influence the accuracy of the standard. Records of vendor supplied certificates of analysis must be maintained. Shelf life = Manufacturer's date of expiration; replaced sooner if degradation occurs.

6.7.2 Intermediate Standard Solutions (single- or multi-element): Made by the dilution of vendor purchased individual elemental standards. Care must be taken in the preparation of multi-element standards that the elements are compatible and stable. Freshly prepared solutions should be transferred to acid cleaned bottles for storage and monitored periodically for stability.

6.7.3 Calibration Standards: Prepared by diluting the individual elemental standards or the intermediate standard solutions to levels appropriate to the operating range of the instrument, using reagent water, for example, containing 1% HNO_3 and 1% HCl. Dilutions should be made with a diluent that best matches the acid strength in the samples, digestates, or their dilutions. Calibration standards should be prepared at a minimum of three concentrations, one of which should be at the reporting limit.

Example of calibration standards for U:

- 10PPB: Made daily by diluting 0.1mL of a multi-element intermediate containing 1ppm each of U to a 10mL final volume.
- 2PPB: Made daily by diluting 2mL of the 10PPB calibration standard to a 10mL final volume.
- 1PPB: Made daily by diluting 1mL of the 10PPB calibration standard to a 10mL final volume.
- 0.01PPB: Made daily by diluting 0.1mL of the 1PPB calibration standard to a 10mL final volume.

6.7.4 ICSA (Interference Check Standard-A): Made daily by diluting 0.1mL of ICSA stock solution (vendor purchased) up to a 10mL final volume. The ICSA working solution contains the following elements and concentrations:

Element	*Concentration (ppm)*
Ca	30
Fe, Na	25
C	20
Al, K, Mg, P, S	10
Mo, Ti	0.2

6.7.5 ICSAB (Interference Check Standard-AB): Made daily by diluting 0.1mL of ICSA Stock solution (vendor purchased) and 2.0mL of the high calibration standard up to a 10mL final volume. The ICSAB working solution contains the following elements and concentrations:

Element	*Concentration (ppm)*
Cl	212.15
Ca	30
Fe, Na	25

C	20
Al, K, Mg, P, S	10
Mo, Ti	0.2
Cd, Pb	0.01
As, Se	0.004
Ag, Sb, U	0.002
Tl	0.0001

6.7.6 ICV (**second source** Initial Calibration Verification Standard): Made daily by diluting 0.05mL of a second source intermediate (dilution from a second source stock) up to a 10mL final volume. The ICV working solution contains elements of interest with concentrations near the midpoint of the linear range and at a concentration other than that used for instrument calibration.

6.7.7 CCV (**first source** Continuing Calibration Verification Standard): Made daily by dilution of intermediate or calibration standard solutions. The concentrations for each element found in the CCV should be at or near the mid-point of the calibration curve.

6.7.8 CRI (**first source**, low level, reporting limit check standard): This solution will be the same concentration as the lowest calibration standard. Analysis of this solution will be a "read-back" of the low calibration standard.

6.8 Internal Standard Solutions: An internal standard intermediate containing 2ppm Be and 0.5ppm each of Rh, In, Bi, Ga, and Pt is made by diluting 0.2mL of Be (1,000ppm individual element standard) and 0.05mL each of Rh, In, Bi, Ga, Pt (1,000ppm individual element standards) up to a 100mL final volume. This intermediate is added to all standards and samples in the same proportion of 1:100. Most often this dilution is performed by adding 0.05mL of the internal standard intermediate to 5mL of sample or standard. The final concentrations of internal standards in working solutions or samples is approximately 20ppb Be and 5ppb each Rh, In, Bi, Ga, Pt.

6.9 Mass Spectrometer Tuning Solution: Consists of a solution containing elements representing all of the mass regions of interest. A vendor purchased stock (containing for example, 10mg/L of Be, Bi, Ce, Co, In, Mg, Ni, Pb and U) is diluted 1000X. The concentration of these elements in the working solution is 10ppb. Concentration of the tuning solution is not critical as the tuning solution is used to verify that the resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability.

6.10 BLANKS

6.10.1 Calibration blank: Consists of, for example, 1% (v/v) nitric acid and 1% (v/v) hydrochloric acid in reagent water. This blank is the diluent used in preparing the calibration standards, and should match (as close as possible) the strength in the samples, digestates, or their dilutions.

6.10.2 Method blank: Contains all the reagents in the same volumes as used in processing the samples. The method blank must be carried through the same entire preparation scheme as the samples, including digestion.

6.10.3 Rinse blank: Consists of 1% (v/v) nitric acid and 1% (v/v) hydrochloric acid in reagent grade water.

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 Liquid samples are collected in plastic or glass containers and must be chemically preserved with nitric acid to a pH<2. The acidified sample must remain in its original container for a minimum of 24hrs before analyses can begin. Samples for dissolved metals analyses should be filtered in the field prior to chemical preservation. Unfiltered samples must be maintained at 4±2°C. Aqueous metals samples must be prepared and analyzed within 180 days of collection.

7.3 Solid samples are collected in plastic or glass containers. Solid samples are not chemically preserved and must be maintained at 4±2°C. Solid metals samples must be prepared and anlayzed within 180 days of collection.

8. PROCEDURE

8.1 INSTRUMENT START-UP

Verify that the cooling water for the instrument is flowing. Make sure that all gas supplies are connected and switched on. Make sure that the ventilation system is running. The MassLynx™ software will check the instrument communications, including any peripheral devices before commands can be issued. Open the tune page and establish a plasma following the manufacturer's instructions. An automatic start-up procedure has also been programmed into the software. Allow a period of not less than 30 minutes for the instrument to warm up.

8.2 Tune the instrument following the manufacturer's instructions. Instrument parameters are controlled from the tune page in the software. Optimize the instrument’s sensitivity, stability, oxide levels, etc., by aspirating the tuning solution and adjusting, if necessary, any parameters. Some of these parameters include: torch position in the X, Y, and Z axis, various gas flow rates, cone voltages, etc.

8.3 PRECALIBRATION ROUTINE

Follow the pre-calibration routine below before completing the calibration of the instrument:

8.3.1 Instrument stability is demonstrated by running the tuning solution ten times with resulting standard deviations of absolute signals for all analytes of less than 10% (Reference 12.3). Data from this stability test is included with the daily raw data.

NOTE: To meet the requirements of Section 10.2.2 of EPA Method 200.8, the tuning solution shall be run a minimum of five times with resulting standard deviations of absolute signals for all analytes of less than 5%, when analyzing wastewater samples for State of California compliance monitoring,

8.3.2 Conduct mass calibration and resolution checks using the scan produced from the final replicate in the stability test described above. Resolution at low mass is indicated by magnesium isotopes 24, 25, 26. Resolution at high mass is indicated by lead isotopes 206, 207, 208. Adjust mass calibration if it has shifted by more than 0.1amu from unit mass. Adjust the spectrometer resolution, if needed, to produce a peak width <0.9amu full width at 10% peak height (SW6020A). Data showing these criteria were met are included with the data package upon client request.

NOTE: To meet the requirements of Section 10.2.1 of EPA Method 200.8, the spectrometer resolution, shall be adjusted, if needed, to produce a peak width less than 0.75amu at 5% peak height, when analyzing wastewater samples for State of California compliance monitoring.

8.4 INTERNAL STANDARDIZATION

Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For full range mass scans, a minimum of three internal standards shall be used. Generally, an internal standard should be no more than 50amu removed from the analyte. Internal standards shall be present in all samples, standards, and blanks at identical levels. This is achieved by directly adding an aliquot of the internal standard intermediate to each sample, standard, and blank. The concentration of the internal standard should be sufficiently high for good precision and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Internal standards should be added to samples, standards, and blanks in a similar manner, in order for dilution effects to be disregarded. Internal Standard performance information is available

in Level 4 data packages (see Compound Summary Report; value of '1' in PPB column signifies 100% internal standard recovery).

8.5 CALIBRATION

Before initial calibration, set up proper instrument software routines for quantitative analysis. Calibrate the instrument for the analytes of interest for the selected isotopes using the calibration blank and at least three calibration standards according to the manufacturer's recommended procedures. Flush the system with the rinse blank for at least 30 seconds between each standard solution and sample. Use the average of multiple integrations for both standardization and sample analysis. All masses that could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. These masses should be monitored either simultaneously in a separate scan or at the same time quantification occurs.

8.6 ANALYTICAL SEQUENCE

The typical autosampler analytical sequence after the initial calibration is listed below along with brief descriptions of each solution. See also Section 9 and the QC Summary Table for further details.

8.6.1 High Standard Read Back: Reanalysis of the highest calibration standard and processed as a sample. Results must be within 95-105% of the known concentration. This concentration also establishes the upper linear range of the instrument.

8.6.2 ICV: Initial calibration verification check standard (second source). Results must be within 90-110% of the expected concentration. Cause of failure must be determined and corrected and the instrument recalibrated.

8.6.3 ICB: Initial calibration blank. Analyzed immediately after the ICV. The absolute value of the blank results must be less than the analyte reporting limit, or as specified in the applicable LIMS program specification. Demonstrates that the analytical system is free from interferences and is in control.

8.6.4 CRI: Low level (reporting limit) check standard. Unless otherwise specified by LIMS program specification, run for informational purposes only. Paragon does not typically control on CRI recovery.

8.6.5 ICSA: Interference check standard A. Contains high concentrations of possible interfering elements. Analyzed at the beginning of an analytical sequence or once every 12 hours, whichever is more frequent. Analyzed to verify the magnitude of elemental and molecular-ion isobaric interferences and the accuracy of any

corrections made. Results for this check standard analysis should not contain analyte concentrations (i.e., analytes susceptible to interference) above twice the analyte reporting limit (2X MDL per DOD), consult applicable LIMS program specification.

8.6.6 ICSAB: Interference check standard B. Contains all elements in the ICSA. In addition, contains low concentrations of the elements of interest. Analyzed at the beginning of an analytical sequence or once every 12 hours, whichever is more frequent. Analyzed to verify the magnitude of elemental and molecular-ion isobaric interferences and the accuracy of any corrections made. Results for this check standard analysis should be within 80-120% of the expected concentrations for the elements of interest.

8.6.7 SAMPLES: Additional analytical samples include all samples analyzed on the instrument except ICV, ICB, CCV and CCB. The CRI, ICSA and ICSAB along with all samples in the sequence and any dilutions, post-spikes, laboratory and matrix spikes, duplicates, serial dilutions and method/preparation blanks are all considered to be analytical samples.

8.6.8 CCV: Continuing calibration check standard (first source). A CCV is analyzed at a frequency of 10% or every two hours whichever is more frequent. The CCV is also analyzed after the last analytical sample. Results must be within 90-110% of the expected concentration. Cause of the failure must be determined and corrected and the instrument recalibrated. Samples following the last acceptable CCV must be reanalyzed.

8.6.9 CCB: Continuing calibration blank. Must follow CCV analyses. The absolute value of the blank results cannot exceed the analyte reporting limit, or as specified in the applicable LIMS program specification. Demonstrates that the analytical system is free from interferences and is in control.

The sequence continues with CCV and CCB analyzed after every 10 analytical samples and at the conclusion of the sequence.

8.7 After the analytical sequence is complete, a "header and summary" section is produced which includes:

- standard information including standard identifications, expiration dates, elements and concentrations, and preparation procedures
- acid lot numbers
- pipet identification numbers

- dilution information and preparation procedures
- analytical spike information and preparation procedures
- daily and monthly maintenance items performed
- summary page with analytical sequence and elements of interest

8.8 In addition to the electronic run information provided by the instrument's output, a hardcopy Run Log is maintained as an internal Departmental record of instrument throughput.

8.9 REGULAR MAINTENANCE ITEMS
Check the following items prior to each run to ensure the instrument is in good working order:

- argon, hydrogen and helium levels; order more as needed
- printer and paper supply
- water in recirculating coolers -- fill as necessary
- pump tubing -- replace when necessary
- empty the drain containers
- tune instrument per manufacturer's procedures
- perform ten minute stability test (include results with data package)
- check / clean torch and cones for deposits
- check / clean nebulizer and spray chamber
- check / fill vacuum pump oil

There is a section in the raw data header information where the Regular Maintenance items may be initialled as completed.

8.10 MAINTENANCE LOG
A maintenance logbook is used to record all information concerning instrument maintenance that is not covered by the daily and monthly maintenance items described above. This logbook is used to document all repairs and the symptoms of the problems.

9. QUALITY CONTROL

The quality control requirements for analyses by ICP-MS consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and calibration solutions as a continuing check on performance. In addition to this Section, various quality control samples and acceptance criteria are discussed in Section 8.6 and in the QC Table at the end of this SOP.

9.1 A method detection limit (MDL) study consisting of the analysis of a minimum of seven replicate aliquots of target analytes at concentration levels 3-5 times the anticipated detection limit, shall be performed as needed and at a minimum, annually.

9.2 Instrument detection limits (IDLs) reflect instrument capability and are determined per CLP protocol. These studies are performed quarterly.

9.3 Tune Standard: The tune standard shall be prepared in the same acid matrix as the calibration standards and analyzed at least five times consecutively. If the peak width at 10% peak height is not <0.9amu, the mass calibration is not within 0.1amu, or the percent relative standard deviation (%RSD) of the absolute signals of the analytes exceeds 5% (discussed in Section 8.3.1), the analysis shall be terminated, the problem corrected, and the instrument re-tuned. All sample results reported must be associated with an instrument tune that meets these requirements

9.4 Method Blank (MB): One method blank is prepared per batch of 20 or less field samples. The method blank consists of an aliquot of reagent water that has been digested and prepared in the same manner as the associated samples.

For drinking water matrix samples analyzed for regulatory compliance purposes, values in the method blank cannot exceed 2.2 times the analyte MDL. If this criterion is not met, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable method blank values have been obtained.

For non-drinking water matrix sample analyses, the method blank cannot contain any analyte above the analyte reporting limit, or as specified in the applicable LIMS program specification. Method blank results are also acceptable if sample concentrations are greater than 10 times the concentration found in the method blank.

9.5 Laboratory Control Sample (LCS): One laboratory control sample is prepared per batch of 20 or less field samples. The LCS is a water sample with known analyte concentrations that is digested and prepared in the same manner as the associated samples. The control limits for LCS recovery are 80-120%, or as otherwise specified in the applicable LIMS program specification. All samples associated with a failed LCS must be redigested and reanalyzed.

9.6 Sample Duplicate: One sample duplicate must be prepared per batch of 20 or less field samples. The control limit for duplicate precision is that the relative percent difference (RPD) must be ≤20%, or as otherwise specified in the applicable LIMS program specification. RPD is calculated as shown below:

$$RPD\ (\%) = \frac{(Result_x - Result_{dup})}{(Result_x + Result_{dup}) / 2} \quad X \quad 100$$

The results are flagged if the RPD exceeds 20%.

9.8 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): One MS and MSD are prepared per batch of 20 or less field samples. MS and MSD samples consist of additional aliquots of a particular field sample that are spiked, digested and prepared in the same manner as the associated samples. Matrix spike samples are evaluated in terms of recovery, calculated as follows:

$$\%R = \frac{(Conc_{Found} - Conc_{Sample})}{Conc_{Target}} \quad X \quad 100$$

where:

$Conc_{Found}$ = analyte concentration found in the MS or MSD sample

$Conc_{Sample}$ = analyte concentration found in the field sample

$Conc_{Target}$ = target (anticipated) analyte concentration based on amount spiked

Matrix spike recovery is not evaluated if the analyte concentration in the unspiked sample is greater than 4 times the spike level. The quality control limit for matrix spike recovery is 75-125%, and the control limit for MS/MSD precision is that the RPD must be $\leq$20%, unless otherwise specified in the applicable LIMS program specification. RPD for the MS/MSD is calculated the same as for the Sample Duplicate (see Section 9.6 above). Results are flagged if MS/MSD recovery or precision results are outside of control limits. A post digestion spike analytical spike (i.e., sample aliquot spiked after digestion) should be performed when matrix spike recovery is outside the control limits. If recovery of the post digestion analytical spike is not within 75-125% (or other specified limits), the result is flagged indicating that matrix interference is suspected.

9.9 Serial Dilution Sample: A 1:5 serial dilution of an additional sample digestate is prepared per 20 field samples of like matrix that are processed as a unit. If analyte concentrations are sufficiently high (at least 50X the instrument detection limit), the results of the dilution test should agree within ±10 % of the undiluted results. Other client-specified control limits may apply, consult applicable LIMS program specification. Sample analyte results failing this test should be flagged indicating the existence of matrix interferences.

9.10 Linear Range: After the initial calibration, the highest calibration standard is reanalyzed and processed as a sample. Results must be within 95-105% of the known concentration. The element concentration in the highest calibration

standard defines the upper end of the analytical range. Samples whose concentrations exceed the calibration range must be diluted to bring their concentrations within the known calibration range of the instrument.

9.11 Internal Standard Responses: The responses from the internal standards should be monitored throughout the analytical sequence. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample.

For drinking water samples analyzed for regulatory compliance purposes, the absolute response of any one internal standard must not deviate more than 60-125% of the original response in the calibration blank. For non-drinking water matrix sample analyses, the absolute response of any one internal standard must not fall below 30% of the intensity of that internal standard in the initial calibration blank (Paragon evaluates against the zero standard), *or as specified in the applicable Program Specification.* If deviations greater than these are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank (CCB). If the responses of the internal standards in the calibration blank (CCB) are within limits, dilution and reanalysis of the sample is required. If the response of the internal standards in the calibration blank (CCB) is outside the control limits, terminate the analysis and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

10. DEVIATIONS FROM METHOD

10.1 There is variability between the two methods referenced by this SOP regarding the preparation and analysis of interference check standards (ICSA and ICSAB); interference check standards are not discussed in Method EPA 200.8 at all. Hence, in this SOP, the ICSA and ICSAB standards are prepared according to the specifications of Method 6020A, with the exception that the solution concentration of all the constituents is ten fold less, in accordance with the sensitivity characteristics of the ICP-MS instrument used at Paragon.

10.2 Method 200.8 states that the blanks need to be <2.2X the analyte MDL. SW6020A states that blanks must be less than 3X the current IDL for each element. For non-drinking water matrix sample analyses, Paragon's criteria requires the blank results (ICB, CCB, MB) to be less than the reporting limit, unless superceded by criterion specified in the applicable Program Specification.

10.3 Section 9.4.5 of Method 200.8 stipulates control limits of 60-125% for internal standard response, Sections 4.4 and 9.3 of SW6020A discuss internal standards response in terms of suppression (below 30%) due to physical interferences.

Unless otherwise directed by LIMS Program Specification, Paragon observes SW6020A guidance for evaluating internal standards performance as it has been Paragon's experience that the data and performance of quality control samples are not impacted when internal standard response is enhanced (i.e., above 100%).

10.4 Section 9.3.4 of Method 200.8 provides for ±15% CCV criteria. In concurrence with SW6020A, Paragon follows the more stringent CCV criteria of ±10%.

10.5 Section 9.4.2 of Method 200.8 provides for ±30% matrix spiked recovery. In concurrence with SW6020A, Paragon follows the more stringent matrix spiked recovery criteria of ±25%.

10.6 Both Methods 6020A and 200.8 calculate IDLs based on the analysis of reagent blank solution. Paragon uses a solution containing low levels of analytes for calculating IDLs.

10.7 SW6020A requires dilution of samples when post spike criteria is not met. Paragon's policy is to flag results and narrate if post spike criteria is not met.

10.8 SW6020A requires reanalysis of samples that fail duplicate precision criteria. Paragon's policy is to flag results and narrate if duplicate precision criteria is not met.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All laboratory personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids). All flammable compounds must be kept away from ignition sources.

11.1.5 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) shall be labeled at a minimum with

compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.6 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The sample digestates shall be disposed of in the Aqueous Laboratory Waste.

11.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

12. REFERENCES

12.1 Methods for the Determination of Metals in Environmental Samples - Supplement I, EPA-600/R-94-111, May 1994. "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry", USEPA Method 200.8, Revision 5.4, EMMC Version.

12.2 USEPA SW-846, Test Methods For Evaluating Solid Waste - Physical/Chemical Methods, Method 6020A, Revision 0, November 1992, Method 6020A, Revision 1, January 1998.

12.3 USEPA CLP SOW ILM05.2, "Method 6020 CLP-M", version 9.0.

12.4 Operator's Manual: Micromass, Platform ICP, User's Guide.

DOCUMENT REVISION HISTORY

7/26/05: Added reference Program Specification directive in "Responsibilities".

4/10/06: Clarified mass calibration and resolution criteria per the referenced methods, Paragon's standard practices, and other client specifications that may be applicable. Likewise clarified blank and internal standard criteria, as well as evaluation of CRI Standard response. Added DOCUMENT REVISION HISTORY.

8/11/07: Updated Section 7.3 to indicate minimum 24hr hold following acidification (instead of 16hrs) per Federal Register, 3/26/07, Volume 72, Number 57. Included LIMS program specification reference to ICSA discussion (Section 8.6.5, QC Table).

Analytical Methods: EPA 200.8, SW6020A	**Parameter**: ICP-MS Elements		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Tune Standard; analyzed at least 5 times consecutively	Daily before the initial calibration	Peak width <0.9amu at 10% peak height, mass calibration within 0.1amu and %RSD of replicates <5% (unless otherwise noted in Program Specification)	Correct problem and repeat tune standard routine.
Initial Calibration; uses at least 3 standards and a blank	Daily	Correlation coefficient (r^2) for all analytes >0.995	Correct problem and repeat initial calibration.
Reanalysis of high calibration standard as a sample	Immediately after calibration	All analytes within ±5% of expected value	Correct problem then repeat initial calibration.
Initial Calibration. Verification (ICV); second source	Daily after initiation calibration	All analytes within ±10% of expected value	Correct problem then repeat initial calibration.
Initial Calibration Blank (ICB)	Immediately following ICV	Absolute value of result for each analyte <reporting limit (RL), or as specified in applicable LIMS program specification	Correct problem then repeat initial calibration.
Continuing Calibration Verification (CCV); conc. of analytes must be different from the ICV	After every 10 samples and at the end of the analytical sequence	All analytes within ±10% of expected value	Repeat calibration and reanalyze all samples since last successful CCV.
Continuing Calibration Blank (CCB)	Immediately after every CCV	Absolute value of result for each analyte <RL, or as specified in applicable LIMS program specification	Correct problem then analyze CCB and previous 10 samples
CRI (reporting limit check) Standard	Run immediately following the ICV/ICB	Paragon does not typically control on CRI Standard response. However, if so specified by LIMS program specification, Paragon will observe the following performance criteria: recovery within 50-150% for Sb, Pb and Tl; recovery within 70-130% for all other analytes.	Reanalyze failed analytes. If still outside of control limits, halt analyses, correct problem and recalibrate. Analyses may not proceed until an acceptable CRI Standard has been analyzed.

Analytical Methods: EPA 200.8, SW6020A	**Parameter**: ICP-MS Elements		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	**Frequency**	**Acceptance Criteria**	**Corrective Action**
ICSA (Interference Check Solution A) and ICSAB (Interference Check Solution B)	At the beginning of an analytical run or every 12 hours whichever is more frequent	All analytes of interest should be within ±20% of expected value. Should not contain non-spiked analytes at concentrations above twice the analyte RL, or as otherwise specified in the applicable LIMS program specification	No directives are given in the referenced methods for this QC check. The limits indicated in this Table are used as Paragon guidelines; no corrective actions are taken on an analytical batch basis.
Method blank (MB)	One MB per batch of 20 or fewer field samples	For drinking water compliance samples, blank values must be <2.2 times the analyte MDL For non-drinking water matrix sample analyses, absolute values in MB <analyte RL, or as specified in applicable LIMS program specification	Correct problem then reprep and analyze MB and all samples processed with the contaminated blank.
Laboratory Control Sample (LCS)	One LCS per batch of 20 or fewer field samples	For drinking water compliance samples, analyte recoveries must be within ±15% of expected values. For non-drinking water matrix sample analyses, analyte recoveries must be within 80-120% of expected values for each analyte Other client-specified criteria may apply, consult applicable LIMS program specification	Correct problem then reanalyze. If still out reprep and reanalyze the LCS and all samples in the affected batch.
Sample Duplicate (DUP)	One sample duplicate per batch of 20 or fewer field samples	For each analyte RPD ≤20%, or as otherwise specified in applicable LIMS program specification	Flag results if RPD > 20%.
Matrix Spike/Matrix Spike Duplicate MS/MSD	One MS/MSD pair per batch of 20 or	Recovery limit 75-125% for each analyte, not	Flag results if MS/MSD recovery or precision results are outside

Analytical Methods: EPA 200.8, SW6020A	**Parameter**: ICP-MS Elements		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
QC Check	**Frequency**	**Acceptance Criteria**	**Corrective Action**
(MS/MSD)	fewer field samples	calculated if analyte conc > 4X the spike level. For each analyte RPD ≤20% Other client-specified criteria may apply, consult applicable LIMS program specification	control limits, perform post digestion analytical spike.
Post digestion analytical spike	Performed when MS/MSD recovery is outside ± 25% (unless analyte conc > 4X the spike level)	Recovery limit 75-125% for each analyte, or as specified in applicable LIMS program specification	Flag results if post spike recovery or precision results are outside control limits.
Internal standard responses	Monitored throughout the analytical run	For drinking water compliance samples, response of internal standard in sample must be within 60-125% of response in initial calibration blank For non-drinking water matrix sample analyses, response of internal standard for samples must be >30% of the original response in the calibration blank, or as specified in the applicable LIMS program specification *	Dilute samples until internal standard response is within criteria.
Serial Dilution	Performed on one sample per batch of 20 or fewer field samples	Results should agree within ±10% of undiluted results if analyte concentrations are sufficiently high (at least 50X the IDL)	Flag results if outside criteria.
Method Detection Limit (MDL) Study; run per method requirements and at an analyte concentration near the minimum detection capabilities of the method	As needed and, at minimum, annually	Positive result < analyte RL	Determine the reason for failure and correct problem with system; then repeat study for analytes that did not meet criteria. If MDL study still not acceptable, discuss with Department and QA Managers, RL may be adjusted, if necessary.

* Note that per DOE client specification,
IS response not to exceed 155%.
3/9/09 DAS

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 834 REVISION 7

TITLE: **DETERMINATION OF METALS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY – METHOD SW6010B (TRACE ICAP)**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 8/13/07

QUALITY ASSURANCE MANAGER _____ DATE 8/11/07

LABORATORY MANAGER _____ DATE 8-13-07

HISTORY: Rev0; 1/24/02; Rev1, 4/3/02; Rev2, 4/7/03; Rev3, 5/12/04; Rev4, 2/1/5; Rev5, 7/26/05; Rev6, 11/20/06; Rev7, 8/11/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references -- Method SW6010B (trace ICAP) -- is used to determine the concentration of total or dissolved metals in prepared liquid and solid samples. Analytes are viewed axially, providing detection limits for many analytes similar to that which can be achieved using Graphite Furnace Atomic Absorption (GFAA) analysis.

The following elements are routinely determined using this method:

Aluminum (Al)	Antimony (Sb)	Arsenic (As)	Barium (Ba)	Beryllium (Be)
Cadmium (Cd)	Calcium (Ca)	Chromium (Cr)	Cobalt (Co)	Copper (Cu)
Iron (Fe)	Lead (Pb)	Lithium (Li)	Magnesium (Mg)	Manganese (Mn)
Molybdenum (Mo)	Nickel (Ni)	Phosphorous (P)	Potassium (K)	Selenium (Se)
Silicon (Si)	Silver (Ag)	Sodium (Na)	Strontium (Sr)	Thallium (Tl)
Tin (Sn)	Titanium (Ti)	Uranium (U)	Vanadium (V)	Zinc (Zn)

2. SUMMARY OF METHOD

Sample digestates are prepared prior to analysis (SOP 806) per EPA Methods SW3005A or SW3010A (liquid samples) or SW3050B (solid samples). Filtered liquid samples, liquid samples containing low solids, or leachates may also be analyzed by direct aspiration into the ICAP instrument (i.e., without prior digestion). A computer-controlled Inductively Coupled Argon Plasma (ICAP) trace analyzer is used to

accomplish the analyses.

Samples or sample digestates are aspirated into the ICAP instrument, into a high temperature argon plasma stream. Radio frequencies are generated to induce excitation of the plasma stream that causes constituent elements contained in the sample to emit light at characteristic wavelengths. A grating spectrometer is used to disperse the resulting spectra. The light emissions are received by a photomultiplier tube, which in turn transmits a signal to the data acquisition system. The software of the data acquisition system interprets the signal by comparing it to a previously calibrated standard curve. The data are then further manipulated in the reporting process to incorporate such factors as dilution and percent solids (i.e., dry weight adjustment).

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 Paragon's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede Paragon's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 SPECTRAL INTERFERENCES

Potential spectral interferences include the following:

4.1.1 Overlap of a spectral line from another element at the analytical or background measurement wavelengths. Spectral overlap may be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element (see Section 8.8 for a description of this correction).

4.1.2 Unresolved overlap of molecular band spectra.

4.1.3 Background contribution from continuum or recombination phenomena.

4.1.4 Stray light from the line emission of high concentration elements. Background contribution and stray light may usually be compensated for by a background correction adjacent to the analyte line.

4.2 PHYSICAL INTERFERENCES

Effects associated with the sample nebulization and transport processes are considered physical interferences. Changes in viscosity and surface tension may cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, then they must be reduced by diluting the samples.

4.3 CHEMICAL INTERFERENCES

Molecular compound formation, ionization effects, and solute vaporization effects are chemical interferences. The most significant potential interference in the Trace ICAP instrument is ionization effects caused by varying levels of easily ionized elements in samples and standards. ~~The ionization effects can be reduced by adding a constant amount of an easily ionized element (such as lithium) as an "ionization buffer" to all solutions. The lithium is added using a peristaltic pump that delivers a constant flow of lithium solution to the sample delivery tubing through a "T" connector.~~ **Stricken from SOP 8/16/07 because it is not Paragon's practice to add this buffer. DAS**

5. APPARATUS AND MATERIALS

5.1 Autosampler: Thermo Jarrell Ash Model AS300 or equivalent.

5.2 ICAP: An argon plasma trace analyzer (e.g., Thermo Jarrell Ash ICAP 61E Trace Analyzer), set to simultaneous operating conditions and containing the following:

- an axially mounted torch
- an R.F. (radio frequency) generator; set at 27.12MHz, 2kW (i.e., an inductively coupled argon plasma excitation source)
- holographic grating, 2400grooves/nm, blazed at 500nm
- a 0.75m Rowland Circle spectrometer (polychromator) or equivalent, with

a Paschen-Runge mount and capable of accepting up to 63 channels

- an automated instrument control and data acquisition system (i.e., personal computer or equivalent), capable of providing various (e.g., background, interelemental) corrections
- Thermospec™ version 6.20 or higher or ICAP Manager™ version 6.10 or higher software, or equivalent

5.3 Volumetric flasks, various sizes, of suitable precision and accuracy

5.4 Volumetric pipets, fixed or adjustable, verified per SOP 321

5.5 Chemware™ PFTE Chips, VWR #26397-103 or equivalent

6. REAGENTS – Only trace metals grade solvents shall be used!!

6.1 Hydrochloric Acid (HCl), concentrated, JT Baker #9530-33 or equivalent

6.2 Nitric Acid (HNO_3), concentrated, JT Baker #9598-34 or equivalent

6.3 Reagent water, deionized (DI) water obtained from the laboratory's DI water system (SOP 319)

6.4 Liquid Argon, 99.99% pure

6.5 STANDARDS

6.5.1 All standard solutions are prepared, documented, and stored in accordance with Paragon SOP 300. All standard solutions are to be contained in fresh (previously unused) polypropylene bottles.

6.5.2 Detailed documentation of all standards associated with each ICAP acquisition (analytical sequence) is recorded in the Header Information of the ICAP software and included with the associated raw data. This documentation includes the stock and intermediate standard identification numbers, dilutions performed to create the working standards and the resulting concentrations of the working standards. (Further details pertaining to header information is provided in Section 8.4).

7. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

7.1 Samples should be collected according to an approved sampling plan.

7.2 All samples (liquid, solid) are collected in plastic or glass containers, must be maintained at 4±2°C, and must be prepared and analyzed within 180 days of collection.

7.3 Liquid samples must be chemically preserved with nitric acid to pH<2. Samples for dissolved metals analyses should be filtered in the field prior to chemical preservation. If samples are not preserved in the field, they may be acidified by the laboratory upon receipt, but must be held in their original container for a

minimum of 24 hours before transfer or analysis of the sample.

8. PROCEDURE

8.1 TYPICAL OPERATING CONDITIONS

~~Torch Gas: High Flow~~
~~Auxiliary Gas: Low~~
~~Nebulizer Gas: 25 PSI~~
~~RF Power: 1150 W~~
~~Pump Rate: 125 rpm~~
~~Sample Tubing: Orange/Orange~~
~~Rinse Tubing: Red/Red~~

Details stricken from SOP 8/16/07 because PAR now has more than one Trace ICP instrument and the settings are not exactly the same. It should be noted that the instrument software maintains an electronic file of the established instrument settings. DAS

8.2 The instrument is calibrated each day, by analyzing and processing multi-point calibration curves for each element quantitated. Second order (quadratic) calibration equations with at least 5 points are used to fit the calibration data and to determine concentration results.

8.3 The typical autosampler analytical sequence is listed below along with brief descriptions of each solution. Refer to attached quality control (QC) Table at end of SOP for performance criteria:

Autosampler Run Number	***Solution Name***	***Description***
1	Mix A	Reanalysis of the highest calibration standard for Mix A elements. Processed as a sample.
2	Mix B	Reanalysis of the highest calibration standard for Mix B elements. Processed as a sample.
3	Mix C	Reanalysis of the highest calibration standard for Mix C elements. Processed as a sample.
4	ICV	Initial Calibration Verification check standard for all elements (second source).
5	ICB	Initial Calibration Blank. Must be run following the multi-point calibration and before any samples are analyzed.
6	ICSA	Interference Check Solution A (contains high concentrations of Ca, Mg, Al, Fe).
7	ICSAB	Interference Check Solution B (contains high concentrations of Ca, Mg, Al, Fe and low concentrations of other elements).
8	CRI	Low concentration test solution containing analyte concentrations near the reporting limit; analysis of this solution is not described in Method 6010B. Run for informational purposes only, Paragon does not control on CRI recovery,

Analysis of this standard typically precedes analysis of the ICSA. DAS 8/16/07

Autosampler Run Number	*Solution Name*	*Description*
		unless required by client LIMS program specification.
9	CCV	Continuing Calibration Verification check standard for all elements (second source).
10	CCB	Continuing Calibration Blank. Must follow CCV analyses.
11 thru 20	Samples	Additional analytical samples. Analytical samples include all samples analyzed on the instrument except ICV, ICB, CCV and CCB. The CRI, ICSA and ICSAB, along with all samples in the sequence and any dilutions, post-spikes (see Section 8.6.4), laboratory and matrix spikes, duplicates, serial dilutions and method/ preparation blanks, are all considered to be analytical samples. The sequence is closed out with the following solutions: CRI, ICSA, ICSAB (analyzed at the end of each analytical sequence, and every eight hours if the analytical sequence is longer than eight hours), followed by CCV, CCB.
21	CCV	Continuing Calibration Verification check standard for all elements (second source).
22	CCB	Continuing Calibration Blank, must follow CCV analyses.
Repeat (11 through 22); the sequence continues with CCV and CCB analyzed after every 10 analytical samples.		

8.4 After the analytical sequence is complete, a "header and summary" section is produced which includes:

- Standard information including standard identifications, expiration dates, elements and concentrations, and preparation procedures
- Acid lot numbers
- Pipet identification numbers
- Dilution information and preparation procedures
- Analytical spike information and preparation procedures
- Daily and monthly maintenance items performed. (Maintenance is further discussed in Section 8.10).
- Summary page with analytical sequence and elements of interest

8.5 At the completion of the sequence, the instrument is shut down as follows:

8.5.1 Disconnect pump tubing.

~~8.5.2 Lower "purge optics" gas flow to approximately 1L/min.~~ **Stricken from SOP 8/16/07 DAS.**

8.5.3 Exit the software.

8.6 PREPARATION AND EVALUATION OF QUALITY CONTROL (QC) SAMPLES

8.6.1 Calibration Blank (STD-Blank). An aliquot of reagent water is acidified in the same manner as the sample digestates. This calibration blank is used as a component in establishing the calibration curve and is also analyzed repeatedly throughout the analytical sequence as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB). To be acceptable, the calibration blank cannot contain any analyte above the analyte-reporting limit, or greater than that prescribed in the applicable LIMS program specification. Refer to Section 10.1 for further discussion.

8.6.2 Method Blank (MB). Required by Method 6010B. One MB is prepared per 20 field samples of like matrix that are processed as a unit. The method blank consists of an aliquot of reagent water, TCLP fluid or PFTE chips that has been digested and prepared in the same manner as the associated samples. To be acceptable, the method blank cannot contain any analyte above the analyte reporting limit, or greater than that prescribed in the applicable LIMS program specification. Method blank results are also acceptable if sample concentrations are greater than 10 times the concentration found in the method blank. Refer to Section 10.1 for further discussion.

8.6.3 Sample Duplicate: One sample duplicate is prepared per batch of 20 or less field samples. The control limit for duplicate precision is that the relative percent difference (RPD) must be ≤20% or as otherwise specified in the applicable LIMS program specification. RPD is calculated as shown below:

$$RPD = \left(\frac{\text{concentration sample} - \text{concentration duplicate}}{1/2\,(\text{concentration sample} + \text{concentration duplicate})} \right)(100)$$

The results are flagged if duplicate precision is greater than 20% RPD.

8.6.4 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): One MS and one MSD are prepared per batch of 20 or less field samples. MS and MSD samples consist of additional aliquots of a particular field sample that are spiked, digested and prepared in the same manner as the associated samples.

Matrix spike samples are evaluated in terms of recovery, calculated

thusly:

$$\%R = \left(\frac{\text{concentration detected} - \text{conc. sample}}{\text{concentration spiked}} \right) (100)$$

Matrix spike recovery is not evaluated if the analyte concentration in the unspiked sample is greater than 4 times the spike level. The quality control limits for matrix spike recovery are 80 to 120%. The control limit for MS/MSD precision is that the RPD must be ≤20%. RPD for the MS/MSD is calculated the same as for the Sample Duplicate is shown in Section 8.6.3 above. Results are flagged if MS/MSD recovery or precision results are outside control limits.

A post digestion spike analytical spike (i.e., sample aliquot is spiked after digestion) should be performed when matrix spike recovery is outside the control limit. If recovery of the post digestion analytical spike is not within 75-125%, the result is flagged indicating that matrix interference is suspected.

8.6.5 Laboratory Control Sample (LCS): One laboratory control sample is prepared per 20 field samples of like matrix that are processed as a unit. LCSs for water batches are prepared by spiking known concentrations of analytes into reagent water. LCSs for TCLP leachate batches are prepared by spiking the appropriate TCLP leaching fluid (fluid #1, fluid #2). Client-specific requirements determine the LCS to be used for solid digestion batches. Solid LCSs are either prepared by spiking onto 1.0g of PFTE chips, or by use of a commercially prepared soil matrix reference material.

LCSs are evaluated in terms of recovery:

$$\%R = \left(\frac{\text{concentration detected}}{\text{concentration spiked}} \right) (100)$$

Per Method 6010B, the control limits for LCS recovery are 80-120%. If a commercial certified reference material was used, the manufacturer's control limits as stipulated apply. Consult applicable LIMS specification for other client-specified criteria. All samples associated with a failed LCS must be redigested and reanalyzed.

8.6.6 Serial Dilution Sample: A 1:5 serial dilution of an additional sample digestate is prepared per 20 field samples of like matrix that are processed as a unit. If analyte concentrations are sufficiently high (at least 50X the instrument detection limit), the results of the dilution test

should agree within ±10 % of the undiluted results, or as otherwise specified in the applicable LIMS program specification. Sample analyte results failing this test should be flagged indicating the existence of matrix interferences.

8.7 LINEAR RANGE

The element concentrations in the Mix A and Mix B High Standards define the upper end of the analytical range. Samples whose concentrations exceed the calibration range must be diluted to bring their concentrations within the known calibration range of the instrument.

8.8 INTERELEMENT SPECTRAL INTERFERENCE CORRECTIONS

Interelement spectral interferences are determined by analyzing a solution (Interference Check Standard A, ICSA) that contains a high concentration of a potentially interfering element and observing the "apparent" concentration arising from the solution in other element channels. Interelement interference correction factors are calculated from these observations. *For example*: a 500ppm Al solution produces an apparent Pb concentration of 0.15ppm. The interelement correction factor K is calculated as follows:

$$K = \frac{Apparent\ Conc.\ in\ ppm}{Conc.\ of\ Interfering\ element\ in\ ppm}$$

In this example, K = 0.15 / 500 = 0.00030.

The interelement correction factor K is the amount of interference produced by 1ppm of the interfering element on the element being interfered with. Interference correction factors are used by the software to calculate corrected concentrations using the following equations:

Corrected Conc. (ppm) = Uncorrected Conc. (ppm) – [K * Conc. Of Interfering Element (ppm)]

High concentrations of elements (such as Fe and Al in solid digestates) are the most likely sources of significant spectral interferences. Interference Check Standard B contains all elements in the ICSA, and in addition, low concentrations of the elements of interest. Results for these check standards should be within 80-120% of the expected concentrations for the elements of interest. Concentrations of non-spiked analytes should not exceed twice the RL, or as otherwise specified in the applicable LIMS program specification. The ICSA and ICSAB are analyzed at the beginning and end of each analytical sequence, or once every 12 hours, whichever is more frequent, to verify that the spectral interferences arising from Al, Fe, Ca, and Mg are being corrected properly.

An interelement interference study is conducted every six months or after a

significant instrument change by analyzing single element solutions of each analyte at high concentrations. The study is used to verify or update interelement interference correction factors. Because the instrument is a direct reading polychromator with fixed detectors, interelement interference correction factors usually remain quite constant.

Due to software improvements, hardcopy record no longer maintained. 8/16/07 DAS

8.9 ~~In addition to the electronic run information provided by the instrument's output (analyst, date, time, sample ID, etc.), a hardcopy Run Log is maintained as an internal Departmental record of instrument throughput. Standard intensities for selected elements are noted as comments, these recordings are used to verify that operating conditions remain the same. If a variation or trend is noticed in intensity readings, the cause should be determined and corrected if necessary.~~

8.10 REGULAR MAINTENANCE ITEMS

The following items should be checked prior to each run to ensure the instrument is in good working order.

- check argon level; reorder as needed
- check printer, paper supply and ribbon; replace as needed
- check filters on rear of instrument and vacuum monthly
- check water level in drain bottle and empty if necessary
- check pump tubing -- replace necessary
- check that the previous day's work is properly recorded and processed

There is a section in the raw data header information where the Regular Maintenance items may be initialed as completed.

8.11 MAINTENANCE LOG

A maintenance logbook is used to record all information concerning instrument maintenance that is not covered by the daily and monthly maintenance items described above. This logbook is used to document all repairs and the symptoms of the problems

8. QUALITY CONTROL

9.1 Various quality control indicators are discussed in Sections 8.3 and 8.6.

9.2 A method detection limit (MDL) study consisting of the analysis of a minimum of seven replicate aliquots of target analytes at concentration levels 3-5 times the anticipated detection limit, shall be performed as needed, and at a minimum, annually.

9.3 Instrument detection limits (IDLs) reflect instrument capability and are determined per CLP protocol. These studies are performed quarterly.

10. METHOD MODIFICATIONS

10.1 The calibration blank acceptance limit used by Paragon is different from the acceptance limit given in Method SW6010B (Section 8.6.1.3). Paragon requires that calibration blank results must be less than the reporting limit. Method SW6010B (Sec. 8.6.1.3) states: "The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples." The calibration blank acceptance limits given in Method SW6010B are not clearly defined. Two types of acceptance limits are described in Method SW6010B -- one based on an IDL, the other on a background mean. Method SW6010B does not give guidance on how the IDL is measured or how 3 times the standard deviation of the background mean is determined. Paragon also notes that Draft Update Method SW6010C uses entirely different criteria for evaluating Calibration Blanks than Method SW6010B. Method SW6010C requires that Continuing Calibration Blanks must "not contain target analytes above 2-3 times the MDL for the curve to be valid." Additionally, Method SW6010C requires that the "absolute value of the results of the calibration blank should be less than the value of the MDL check sample for each analyte or less than the level of acceptable contamination specified in the approved quality assurance project plan." Given the somewhat ambiguous and cumbersome guidance stated in Method SW6010, Paragon's criteria for evaluating Calibration Blanks will continue to be the Report Limit unless specific client or regulatory needs demand otherwise. These specific client or regulatory needs are communicated to the laboratory via LIMS program specifications, which relate criteria that supercede Paragon's default performance criteria. The calibration blank acceptance limit based on the reporting limit is clearly defined thereby allowing straightforward data validation and also providing adequate assurance that instrument calibration is in control. Please note that although Paragon's default for addressing Calibration Blanks is the reporting limit, Paragon can employ use of a client-specific LIMS program specification to govern the processing of client data as requested by the client.

10.2 Method SW6010B (Section 5.7) states, "The CCV should be prepared in the same acid using the same standards used for calibration...". This SOP describes preparing the CCV from a source different from the source used for the calibration standards. CCVs prepared from a second source are equivalent to CCVs prepared from the first source for providing assurance that instrument calibration is in control.

10.3 Method SW6010B (Section 7) discusses instrument calibration by the use of a first order (linear) calibration curve. As provided for in Section 7.2.5 of Method SW6010B, Paragon employs a second order (quadratic) calibration curve with typically five points for *all* trace metals analytes, based on historical experience

that this type of calibration curve (quadratic) provides a better fit of the calibration data.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 The building is equipped with a safety shower, eye wash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

11.1.2 Read the MSDSs before preparing standards or using any solvents or reagents for the first time.

11.1.3 Wear gloves, safety glasses, and lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples), handling materials or equipment potentially contaminated with chemicals or within a laboratory area.

11.1.4 Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

11.1.5 All flammable compounds must be kept away from ignition sources.

11.1.6 Any non-original containers used to hold reagents (e.g., wash bottles or automatic dispenser bottles) must be labeled at a minimum with compound name, NFPA Health, Flammability and Reactivity ratings, and date.

11.1.7 Food and drink are prohibited in all lab areas.

11.2 WASTE DISPOSAL

11.2.1 The sample digestates shall be disposed of in the Aqueous Laboratory Waste.

11.2.2 Radioactive sample disposal - solid sample residues shall be disposed of in the Radioactive Soils & Solids container. Radioactive sample digestates shall be disposed of in the Radioactive Aqueous Lab Waste.

11.2.3 All empty solvent bottles are disposed of according to the appropriate SOPs. ***Please note that all labels and markings must be defaced prior to disposal.***

12. REFERENCES

12.1 USEPA SW-846, Test Methods For Evaluating Solid Waste - Physical/Chemical Methods, 3rd edition, Final Update III, Method 6010B, Revision 2, December 1996.

12.2 Operator's Manual, ICAP Trace Analyzer.

DOCUMENT REVISION HISTORY

7/26/05: LIMS program specification references added.

11/20/06: SOP was updated to apply to newly acquired second trace ICAP instrument as well. Abbreviation 'ICP' was updated to 'ICAP' throughout. Element list verified, updated and presented in tabular form, Section 1. LIMS program specification reference augmented, Section 3.3. Simplified standards discussion, Section 6.5, and included reference to information contained in software header. Reorganized Section 7 and added comment that if acidified by laboratory, sample must be held in original container for at least 16hrs prior to processing. Typical Operating Conditions added, Section 8.1. QC information taken out of analytical sequence Table (Section 8.3); QC Table at end of SOP referenced instead. References to LIMS program specification requirements added to QC Table where appropriate, MDL Study information added to Table. DOCUMENT REVISION HISTORY Section added.

8/11/07: Updated Section 7.3 to indicate minimum 24hr hold following acidification (instead of 16hrs) per Federal Register, 3/26/07, Volume 72, Number 57. Augmented ICSA/B and interelement correction discussion Section 8.8 and included LIMS program specification references (QC Table also).

Analytical Method: SW 6010B	**Parameter:** ICAP Metals		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Actions
Initial Calibration using 4 standards and a blank	Daily	Correlation coefficient (r^2) for all analytes $\geq$0.995	Correct problem and repeat initial calibration.
Reanalysis of Mix-A, Mix-B and Mix C cal standards as samples	Immediately after calibration	All analytes within ±5% of expected value	Correct problem then repeat initial calibration
ICV (Initial Calibration Verification) check std (second source); at or below midpoint	Daily after initial calibration	All analytes within ±10% of expected value	Correct problem then repeat initial calibration
ICB (Initial Calibration Blank)	Immediately following ICV	Absolute value of result for each analyte < reporting limit, or as specified in applicable LIMS program specification	Correct problem then re-analyze ICB
CCV (Continuing Calibration Verification) check std; concentration of analytes must be different from ICV	After every 10 samples and at the end of the analytical sequence	All analytes within ±10% of expected value	Repeat calibration and reanalyze all samples since last successful CCV
CCB (Continuing Calibration Blank)	Immediately after every CCV	Absolute value of result for each analyte < reporting limit, or as specified in applicable LIMS program specification	Correct problem then analyze CCB and previous 10 samples
ICSA (Interference Check Solution A) and ICSAB (Interference Check Solution B)	At the beginning and the end of an analytical run or once every 12 hours, whichever is more frequent	All analytes within ±20% of expected value. Concentrations of non-spiked analytes should not exceed twice the RL, or as otherwise specified in the applicable LIMS program specification.	Terminate analysis, correct problem, reanalyze ICSA, reanalyze all affected samples
MB (Method blank)	One MB per batch of 20 or fewer field samples	Absolute value of result for each analyte < reporting limit, or as specified in applicable LIMS program specification	Correct problem then reprep and analyze MB and all samples processed with the contaminated blank

Analytical Method: SW 6010B	**Parameter:** ICAP Metals		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Actions
LCS (Laboratory Control Sample)	One LCS per batch of 20 or fewer field samples	For spiked LCS all analytes within ±20% of expected value For commercially prepared solids use vendor's QC limits See applicable LIMS program specification for client-specified limits	Correct problem then reanalyze. If still out reprep and reanalyze the LCS and all samples in the affected batch
Sample Duplicate	One sample duplicate per batch of 20 or fewer field samples	For each analyte RPD ≤20%, or as otherwise specified in the applicable LIMS program specification	Flag results if RPD > 20%
MS/MSD (Matrix Spike/Matrix Spike Duplicate)	One MS/MSD pair per batch of 20 or fewer field samples	Recovery limit 80-120% for each analyte, not calculated if analyte concentration > 4X the spike level. For each analyte RPD ≤20% Other limits may apply, consult applicable LIMS program specification	Flag results if MS/MSD recovery or precision results are outside control limits, perform post digestion analytical spike
Post digestion analytical spike	Performed when MS/MSD recovery is outside ±20% (unless analyte concentration > 4X the spike level)	Recovery limit 75-125% for each analyte, or as otherwise specified in the applicable LIMS program specification	Flag results if post spike recovery or precision results are outside control limits
Serial Dilution	Performed on one sample per batch of 20 or fewer field samples	Results should agree within ±10% of undiluted results if analyte concentrations are sufficiently high (at least 50X the IDL), or as otherwise specified in the applicable LIMS program specification	Flag results if outside criteria
Method Detection Limit (MDL) Study	As needed, at minimum, annually	Concentrations for the MDL study shall be at a level ≤ to that of the reporting limit	Determine the reason for failure and fix problem with system; repeat study for those analytes that did not meet criteria. If criteria still not met, discuss with Department and

Analytical Method: SW 6010B	**Parameter:** ICAP Metals		**Summary of Internal Quality Control (QC) Procedures and Corrective Actions**
Quality Control Check	Frequency	Acceptance Criteria	Corrective Actions
			QA Managers (RL may be adjusted, if needed).

Must Discard 30 Days from _____ (date printed)

Amendments made by Scheib 3/12/09

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 901 REVISION 7

TITLE: VERIFYING WEIGHTS

FORMS: 315 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 2/27/07

QUALITY ASSURANCE MANAGER _____ DATE 2/27/07

LABORATORY MANAGER _____ DATE 2/27/07

HISTORY: Rev0, SOP 324, 10/15/93; Rev1, SOP 324, 4/9/96; Rev2, SOP 324, 1/10/00; Rev3, SOP 324, 4/19/02; Rev4, SOP 901, 1/02/03; Rev5, 4/3/04; Rev6, 7/20/05; Rev7, 2/27/07.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the in-house procedures used to verify weights that are used for laboratory balance calibration verifications. ~~Laboratory weights less than or equal to 100g are categorized as ASTM Class 5 (OIML Class M_1). Weights greater than 100g are categorized as ASTM Class 6 (OIML Class M_2).~~ Quality Assurance (QA) Department staff or a delegate performs in-house weight verifications annually by verifying ~~them~~ the laboratory weights against Class S (ASTM Class ~~2~~ 1 or) ~~Master~~ weights that are NIST-traceable and certified annually by a qualified vendor. Note that it is Paragon's policy that weights lower than 20mg cannot be appropriately verified in-house, needed weights less than 20mg (e.g., 2mg) are sent outside for vendor certification.

Laboratory weights are classified as OIML Class F2, which is most comparable to NBS Class P / ASTM Class 4.

2. SUMMARY

All laboratory weights are identified with a unique number. The QA Department maintains a database Table of all weights and their locations. Weights/weight sets used for daily operations are located strategically throughout the laboratory. Additional weights are stored in reserve by the QA Department. Only weights that have been currently verified may be used for laboratory operations. All weights are stored in protective containers when not in use. Upon successful verification, a sticker, indicating the following information is placed on the container:

- weight(s)' identity
- date the verification is valid through
- initials of the individual who verified the weight
- date the verification was performed

Acceptance criteria derived from American Standard Test Methods (ASTM) and International Organization of Legal Metrology (OIML) tolerances, along with balance capabilities, are used to accept or reject the tested weight. Rejected weights are removed from service immediately. Unverified weights stored in reserve by the QA Department

are labeled **"**DO NOT USE - NOT VERIFIED***."*** Records of both vendor certifications and in-house verifications are maintained by the QA Department.

3. RESPONSIBILITIES

3.1 The QA Department is responsible for maintaining an inventory of suitable Master and laboratory weights. Currently Paragon's weight inventory is managed via a database Table maintained by the QA Department. The QA Department shall coordinate the annual vendor-certification of weight Masters and other needed weights that cannot be appropriately verified in-house. The QA Department is responsible for the content of this SOP and for maintaining all weight certification and verification records.

3.2 It is the responsibility of the Technician verifying the laboratory weights to perform these procedures according to this SOP and to thoroughly complete all required documentation.

3.3 It is the responsibility of all laboratory personnel to handle and store laboratory weights properly and to report any concerns or anomalies promptly to the QA Department.

4. INTERFERENCES

4.1 Make sure the balances used for testing are stable and level and that the balance pan is clean. Use a Kimwipe™ or brush to clean the pan as needed. As applicable, the pan's surrounding chamber should also be free of debris. In the event of a spill, consult the operating manual if more thorough cleaning is required.

4.2 Drafts can cause the balance to drift and produce unstable readouts. Draft shields either integral to or external to the balance must be used where needed.

4.3 Use gloves, a Kimwipe™, or some other barrier (e.g., tweezers) when handling the weights. Do not handle the weights with bare hands. The weights must be clean and free from all deposits. If the weights must be cleaned, use acetone or another suitable solvent and a Kimwipe™. Make sure the weights have air-dried completely before using them.

4.4 A balance's total capacity is usually incorporated in the model designation. For example, an AE104 balance has a total operational capacity of 104 grams. ***Know the limits of the balance being used. Never attempt to weigh anything whose mass exceeds the balance's capacity.***

5. APPARATUS AND MATERIALS

5.1 The most sensitive balance capable of handling the mass to be loaded must be used to verify the test weights. The balance's certification by an outside vendor must be current (refer to balance's calibration sticker, good through one year from

date of certification).

5.2 NBS Class S (ASTM Class 1 or 2) Master weights with current certification (valid within ~~one-year~~ 5 years of vendor calibration).

5.3 ~~ASTM Class 5 (OIML Class M_1) and ASTM Class 6 (OIML Class M_2)~~ OIML Class F2 (NBS Class P; ASTM Class 4) laboratory weights to be verified, and a database printout of all weights.

5.4 Blank verification stickers (obtainable from the QA Department), scissors, clear tape.

6. PROCEDURE

6.1 Record all test data on Form 315. Form 315 must be completely filled-out with regard to all information requested (e.g., balance number, serial number of weight, etc.).

6.2 Select a suitable balance to use for testing (see 5.1 above). *Weight verifications are customarily performed in the Ra/Sr Lab, using balance #13 for lower mass weights, and balance #21 for larger mass weights.* If not already on, power the balance on. Make sure that the balance pan is clean, and that the daily verification (SOP 305) has been performed on all balances used for verification. Make sure all weights used (Master, laboratory) are clean.

6.3 ESTABLISH WEIGHT MASTER AND BALANCE PERFORMANCE
Choose a certified Master weight per each order of magnitude of mass to be weighed on the balance (e.g., 100g, 10g, 1g, 100mg, 20mg). Tare the balance. Carefully place and weigh each Master weight, allowing the balance reading to stabilize before recording the reading. Re-tare the balance between each order of magnitude change in mass loading. Confirm that the Master weights are within the acceptance limits for its nominal value as listed on Form 315.

6.4 TEST AND VERIFY LABORATORY WEIGHTS

NOTE: ~~Where necessary, previously verified weights may be used to supplement Master weights in order to achieve the total mass loading needed~~. The balance's upper and lower limit of performance verified must bracket the largest and smallest laboratory weights tested.

6.4.1 Tare the balance. Place and weigh each laboratory test weight, record the observed value. Retare the balance between each order of magnitude change in mass loading.

NOTE: Duplicate weights in the same set will usually be distinguished with a period stamped next to the nominal value.

6.4.2 Calculate and record the difference between the test weight and Master weight, where available, or the test weight yielded and its nominal value. Confirm that the difference falls within the acceptance limits listed on Form 315.

If a laboratory weight is demonstrated to perform within acceptance limits, then the weight has been successfully verified. Place a sticker on the weight's case indicating the weight's identity, the date the verification is valid through, the initials of the person who verified the weight, and the date verified.

6.4.3 Re-clean and re-test any weight that fails. If a weight fails twice, it must be removed from service immediately (this weight will be discarded or stored in the QA Department after clearly labeling "DO NOT USE"; status information for this weight will be subsequently updated in the database).

Obtain a replacement weight from the QA Department and test as described above. Place the replacement weight in service after successful testing is completed. Annotate Form 315, and the database printout as applicable. Submit all data collected to the QA Department.

6.5 The QA Manager or designee will update the weight database Table as necessary, and will ensure that any weights stored in reserve and not tested are clearly labeled "DO NOT USE - NOT VERIFIED".

7. SAFETY AND HAZARDS

7.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

7.2 Safety glasses, a lab coat, and gloves must be worn at all times when working in the laboratory.

7.3 Food and drink are prohibited in all lab areas.

8. REFERENCES

8.1 Annual Book of ASTM Standards, Volume 14.02, Standard E617-97, 2002.

8.2 International Organization of Legal Metrology (OIML), Specification R111 -- Weights of Classes E_1, E_2, F_1, F_2, M_1, M_2 and M_3, 2004.

DOCUMENT REVISION HISTORY

2/27/07: Removed LIMS Program Specification text from RESPONSIBILITIES because it's not applicable. Under PROCEDURE, the balance(s) used for verification must pass the daily calibration verification check, but it is not necessary to perform this check using the Master weight set; text was updated/corrected accordingly. Additionally, some organizational changes were made to PROCEDURES for clarity. DOCUMENT REVISION HISTORY Section added.

Form 315r14.doc (7/7/08) ***Paragon Analytics***

WEIGHT VERIFICATION FORM

Master Weights NBS Class S (1000g - 20g ASTM Class 1; 10g - 20mg ASTM Class 2), most comparable to OIML Class E2, vendor certified every 5 years: **#31945** (15 piece set), good through 4/15/2012 **#08-711912-2** (200g), good through 5/14/2013 **#04-51936** (500g), good through 5/12/2013 **#08-711912** (1000g), good through 5/14/2013 **#08-711912-1** (1000g), good through 5/14/2013

Note that based on limit of capability, Paragon does not verify any weight smaller than 20mg in-house.
2mg weights, used for Oil & Grease determinations, are vendor certified annually (see QA Department records).

Laboratory Weights OIML Class F2 (most comparable to NBS Class P / ASTM Class 4) **SOP 901r __ Init / Date _____**

BALANCE # __ **Obtain logbook. Perform daily balance check per assigned scheme, using Master weights; record in logbook.**
BALANCE CERTIFICATION DATE 6/11/08 **(valid for one year from date certified).**

Weight/Set Identifier	Nominal Value of Weight (units)	Observed Weight (grams)	Reference Weight (grams) or Nominal Value	Difference Between Reference & Test Weight (g) or Nominal Value	OIML F2 Acceptance Criteria Met? (Y / N per Table below)	Comments
Master						
Master						
Master						
Master						
Master						
Master						

Weight	Accept (g)	%
2kg	± 0.03	0.0015%
1kg	± 0.02	0.0020%
500g	± 0.01	0.0020%
200g	± 0.0030	0.0015%
100g	± 0.0015	0.0015%
50g	± 0.0010	0.0020%
20g	± 0.0008	0.0040%
10g	± 0.0006	0.0060%

Weight	Accept (g)	%
5g	± 0.0005	0.01%
2g	± 0.0004	0.02%
1g	± 0.0003	0.03%
500mg	± 0.0003	0.06%
200mg	± 0.0002	0.10%
100mg	± 0.0002	0.20%
50mg	± 0.0001	0.20%
20mg	± 0.0001	0.50%

Imaged updated 3/12/09 DAS

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 923 REVISION 8

TITLE: VERIFICATION OF THERMOMETERS

FORMS: 304 (use current iteration)

APPROVED BY:

TECHNICAL MANAGER Deb Schenk DATE 2/28/07

QUALITY ASSURANCE MANAGER Deb Schenk DATE 2/28/07

LABORATORY MANAGER [signature] DATE 3-1-07

HISTORY: SOP 312, Rev0, 8/05/92; SOP 312, Rev1, PCN #81, 1/12/94; SOP 312, PCN #523, Rev2, 9/05/95; SOP 923, Rev0, 9/08/95; SOP 923, Rev1, 4/02/97; SOP 923, Rev2, 8/15/99; Rev3, 3/01/00; Rev4, 4/17/02; Rev5, 4/3/04; Rev6, 7/20/05; Rev7, 9/11/06; Rev8, 3/1/07.

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) outlines the process for the annual standardization of laboratory thermometers (liquid-in-glass, electronic, infrared) to a thermometer traceable to the National Institute of Standards (NIST).

2. SUMMARY

All laboratory thermometers are identified with a unique number. Only thermometers that have been currently verified may be used for laboratory operations (***exception***: the electronic thermocouple used by the Radiochemistry Department to independently estimate the performance temperature of muffle furnaces -- a non-critical measurement).

Laboratory (test) thermometers and a current, independently certified, Master (reference) thermometer are placed together in applicable (i.e., relevant to the thermometer's use) test environments. After the thermometers and temperature have stabilized, readings are taken and recorded (Form 304). With the exception of the infrared (IR) temperature device used by the Radiochemistry Department (non-critical measurement conducted), the difference between the test and reference thermometer must not exceed ±1°C in order for the test thermometer to be accepted. The acceptance limits for the Radiochemistry Department IR temperature device is ±10°C

If the test thermometer cannot perform within the established acceptance limits, the thermometer is removed from service. At the conclusion of the standardization effort, verification tags, indicating the thermometer's serial number, the date the standardization is valid through, the initials of the test technician, and the date the standardization was performed, are applied to each thermometer successfully verified (***exception***: in some cases, the temperature of the unit the thermometer is assigned to chars the sticker, making it friable and unreadable; in these cases, the verification sticker is placed directly on the unit). Records of both Master vendor certifications and in-house verifications are maintained by the Quality Assurance (QA) Department.

3. RESPONSIBILITIES

3.1 The laboratory staff is charged with coordinating with the QA Department to ensure that all thermometers in use have been verified, and that the thermometer in use at each location, has the same identification number as indicated in the daily temperature logbook for that location. It is the responsibility of all laboratory personnel to handle the thermometers properly and to report any concerns or anomalies promptly to the QA Department, so that appropriate corrective action may be taken.

3.2 The QA Department shall coordinate the annual certification of thermometer Masters by a NIST-approved vendor prior to the annual in-house verification effort. The QA Department will also coordinate the standardization of all laboratory thermometers in use annually. The QA Department is responsible for the content of this SOP, for maintaining a suitable inventory of laboratory thermometers and batteries, and for maintaining all thermometer certification and verification records.

3.3 It is the responsibility of the Technician verifying the thermometers to perform these procedures according to this SOP and to thoroughly complete all required documentation.

4. INTERFERENCES

When standardizing thermometers, it is important to ensure that the temperature of the test environment and any material the thermometer or probe is immersed in has stabilized before readings are obtained.

5. APPARATUS AND MATERIALS

5.1 ***Freezer Environment.*** Choose an operating laboratory freezer with space sufficient to accommodate the Master and laboratory test thermometers.

5.2 ***Ambient Environment.*** Choose an area with sufficient benchtop space to accommodate the Master and laboratory test thermometers, and that is not susceptible to drafts.

5.3 ***Oven Environment.*** Choose an operating laboratory oven (or ovens) maintained at a suitable test temperature with space sufficient to accommodate the Master and laboratory test thermometers. Coordinate use of the oven(s) for thermometer verification purposes, with the Department so as not to impact production.

5.4 ***Master (Reference) thermometers*** -- must be currently certified by an independent calibration service using NIST reference standards. *Note that these thermometers are maintained by the QA Department with restricted access, these thermometers are to be used for verification purposes only, and are not to be used by laboratory staff for general purposes.*

5.5 ***Test thermometers*** -- laboratory thermometers currently in use, and those held in reserve by the QA Department for replacement.

5.6 Blank verification stickers (obtainable from the QA Department), scissors, clear tape.

5.7 A 'Thermometers' database Table printout.

6. PROCEDURE

6.1 OVERVIEW

The thermometers shall be tested under conditions applicable to their use. Note that the particular thermometer assigned to an application, takes into consideration the method requirements (e.g., range, graduations, etc.) for that thermometer's performance. Only thermometers meeting method criteria may be used.

Where possible, the standardization of thermometers at *two* test points is desirable (not possible with short range thermometers).

- Electronic min/max thermometers used to monitor cooling units or ambient conditions shall be tested under freezer and ambient conditions.
- Sample receiving infrared temperature devices (IR guns) shall be tested under refrigerator conditions, and the Radiochemistry IR gun shall be tested using oven conditions.
- General use thermometers shall be tested under both ambient and oven conditions.

6.2 GENERAL PROCEDURES

- The standardization effort should be conducted at such a time and in such a manner that the impact to the laboratory is minimized.
- It is easiest to gather one type of thermometer (e.g., min/max, short range oven, general use) at a time for testing. Collect laboratory thermometers in use, as well as those held in reserve by the QA Department for replacement.
- Use the thermometer database printout to ensure that all thermometers are collected. **Verify the thermometer identity at its location upon collection, and annotate the database printout as necessary.**
- Wipe thermometer (or probe) clean before testing, and visually inspect unit for damage (e.g., readability of etchings, integrity of liquid column, etc.). Replace unreadable thermometers (i.e., substitute an appropriate replacement thermometer for testing; dispose of unreadable

thermometer appropriately; annotate database printout with change; *remember to replace thermometer logbook with one that indicates updated thermometer identity!*).

If necessary, reconstitution of a thermometer's liquid column can be attempted per manufacturer's instructions (see QA Department for information). Otherwise, the thermometer must be properly disposed (see Section 7 below).

- Where the test thermometer or probe is immersed in liquid, the Master thermometer should also be immersed in the same (or equivalent) material.
- It is important to ensure that the temperature of the test environment and any material the thermometer or probe is immersed in, has stabilized before readings are obtained. *Tip*: it may be easiest to set-up the test and allow the thermometers to equilibrate overnight.
- The process of obtaining readings may destabilize the test environment, necessitating the readings to be taken in small batches. Similarly, it may be necessary to reposition the Master thermometer to nearer proximity to selected test thermometers, in order to obtain accurate readings in smaller batches.

6.2.1 Conduct one or two-point environment tests, as applicable for the thermometer type, as described in OVERVIEW and below.

6.2.2 Neatly record all test data on Form 304 (forward the benchsheets to the QA Department when completed).

6.2.3 Place a current verification label (thermometer number, date verification is valid through, technician's initials, and date of verification) on each successfully verified thermometer (or assigned unit, where necessary) before placing the thermometer back into service (or reserve storage). Cover the verification sticker with a piece of clear tape to help preserve the sticker. **For thermometers placed back into service, check again that the right thermometer is returned to the designated location, and that the associated logbook indicates the correct thermometer identity.**

6.2.4 The QA Manager or designee will update the thermometer database Table as necessary, and will ensure that any thermometers stored in reserve and *not* tested are labeled "DO NOT USE - NOT VERIFIED". The QA Manager or designee will also update any laboratory logbooks as necessary due to replaced thermometers.

6.3 FREEZER ENVIRONMENT TEST

6.3.1 Clear space in a suitable freezer unit so that the Master and all test thermometers and probes can be held securely without disturbance for the duration of the test. *Tip*: It has been determined that the electronic min/max probes are interchangeable. Therefore, it is not necessary to keep the probes matched to particular electronic min/max units. For ease in reading then, the attachment ends of the probes can be left external to the cooling unit so that rapid readings may be acquired by connecting a min/max thermometer unit sequentially through the probe attachments.

6.3.2 Place the thermometers/probes in the freezer unit, allowing space around each container. Let the thermometers stabilize (i.e., 0°C change over 3 minutes). If not equilibrated overnight, check the environment temperature initially after 1 or more hours, then repeat in 20-minute intervals until stable readings of the thermometers can be obtained.

6.3.3 After the thermometers/probes have stabilized, record the temperature readings of the reference thermometer and all test thermometers to the nearest degree (Form 304).

6.3.4 Evaluate each test reading to determine the acceptability of the thermometer. The test thermometer must agree within $\pm$1°C of the reference thermometer.

If the test reading does not meet acceptance limits, reposition the thermometers and retest. If still unacceptable, the test thermometer must be removed from service and replaced with a successfully verified thermometer. See the QA Department for a suitable replacement thermometer. The QA Manager will initiate appropriate corrective action, as needed.

6.4 IR TEMPERATURE DEVICES

6.4.1 ***Sample Receiving IR Guns.*** First, successfully verify the min/max thermometer assigned to cooling unit RU#20. Document the current temperature reading of this thermometer as the reference temperature (Form 304).

Use the one-liter amber water check bottle stored in RU#20 to conduct the verification of each Sample Receiving IR gun as follows:

- Hold the bottle away from your body and down toward the floor.
- Point the IR gun at the center of the bottle and hold the gun tip about 1-2 inches from the bottle's surface.

- Depress the gun's trigger and obtain a temperature reading of the water check bottle. Record this reading as the test temperature.
- Compare the test temperature to the reference temperature. The IR gun reading must agree within ±1°C of the reference temperature to be successfully verified.

6.4.2 ***Radiochemistry IR Gun.*** *Tip*: It is easiest to conduct this verification in the LLRP lab, however, any laboratory oven may be used as the test environment.

- First, successfully verify the thermometer assigned to the laboratory oven.
- Obtain a current temperature of the laboratory oven and document as the reference temperature (Form 304).
- Because a heavy-duty PyrexTM beaker is generally used to contain the laboratory sand the oven thermometer is held in, reading the surface of this beaker will yield results that are biased low (the glass used in this type of beaker is formulated to retard heat conduction). Consequently, it is important to use the actual type of glassware (e.g., condensers, glass joints) that is dried in this oven to conduct this test.

  Quickly point the IR gun at the center of several pieces of glassware, depressing the trigger and noting the readings obtained. Work quickly to avoid the oven temperature dropping due to the open oven door. Record the average reading on Form 304.
- Compare the test temperature to the reference temperature. The IR gun reading must agree within ±10°C to be successfully verified.

  NOTE: The acceptance limits for the Radiochemistry IR gun are greater than that applied to other thermometers because this particular device is not used for critical measurements. Note also that the verification acceptance limits for the Radiochemistry IR gun are half the criteria allowable for the established daily use check.

6.4.3 If any IR temperature device does not successfully verify, consult with the QA Manager. The device may need to be removed from service and an alternative provided. The QA Manager will initiate appropriate corrective action, as needed.

6.5 AMBIENT ENVIRONMENT TEST

Conduct the Steps described for the FREEZER ENVIRONMENT TEST, using a suitable benchtop area without drafts, as the test environment.

6.6 OVEN ENVIRONMENT TEST

Conduct the Steps described for the FREEZER ENVIRONMENT TEST, using a suitable laboratory oven(s) as the test environment. *Tip*: it is helpful to place the Master and test thermometers in containers of silica sand or Drierite™ and allow them to equilibrate overnight. Also, testing of probe stem thermometers may require that a water bath high temperature test be conducted in lieu of the oven environment test, so that the entire probe stem thermometer is not incubated (oven incubation of the entire probe stem thermometer may effect the thermometer's liquid crystal display, preventing readings from being obtained).

7. CORRECTIVE MEASURES

For the most part, malfunctioning thermometers are noted during routine temperature checks and are addressed as discussed in SOPs 320, 326 and 663. However, with the annual verification effort, some thermometers may be selected for replacement based on diminished readability (accuracy not impaired, no impact to data), still others may simply not test successfully. These thermometers must be replaced as discussed above. In cases where the thermometer has not tested successfully, usually the thermometer performs just outside the ±1°C control criterion and impact to data is not likely, in rarer instances, a break in the thermometer's liquid column might not have been noticed. In all instances, however, the occurrence must be further investigated (QA and Departmental participants), and professional judgment applied as to the nature and extent of the corrective action that should be taken. Corrective actions may include retraining, and notification to clients where deemed appropriate.

8. SAFETY, HAZARDS AND WASTE DISPOSAL

8.1 SAFETY AND HAZARDS

8.1.1 The building is equipped with a safety shower, eyewash station, fire extinguisher, fire blanket, as well as a first aid kit. All lab personnel must be trained in the use and location of these items.

8.1.2 Safety glasses, a lab coat, and gloves must be worn at all times when working in the laboratory.

8.1.3 Food and drink are prohibited in all lab areas.

8.2 WASTE DISPOSAL

Thermometers that are broken or are rendered unusable due to damage are to be immediately removed from service and transferred to Waste Disposal personnel. The unusable or broken (spirit-filled) thermometers must be placed in containers that can be safely sealed to contain the broken pieces and thermometer contents.

Notify the QA Department immediately so that the unusable thermometer can be noted and a replacement thermometer provided.

NOTE: Mercury-filled thermometers can only be handled for cleanup and disposal by the laboratory Health & Safety Manager or designee. ***Under no circumstances are other laboratory personnel to handle or dispose of these mercury-containing materials.***

9. REFERENCES

Current NELAC standard

Applicable client quality assurance documents

DOCUMENT REVISION HISTORY

9/11/06: Added RAD IR gun to exception from ±1°C quality control criteria in Summary text. Expanded equipment text for Master thermometer to note that Masters are not for general use. In OVERVIEW, added statement that only thermometers that meet method requirements for that application may be used. Added CORRECTIVE MEASURES section to PROCEDURE. Added DOCUMENT REVISION HISTORY.

3/1/07: Indicated in SUMMARY and Step 6.2.3 that in certain instances, the verification sticker may be placed directly on the unit the thermometer is assigned to. Minor text clarifications/format corrections throughout. For maximum interchangeability, non-high temperature min/max thermometers shall be tested under freezer and ambient conditions (brackets potential range of use); text pertaining to refrigerator test environment removed.

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Paragon Analytics

THERMOMETER VERIFICATION WORKSHEET

Technician(s) _____ **Verification Date** _____ **SOP/Rev** _____			**Thermometer Type Being Verified:** _____ _____			**Reference Therm. ID:** **Certification or Verification Date**[1] _____			**Units = °C**	
Low Test Data						***High Test Data***				
Time Test Started:			**3rd Reading (time/temp):**			**Time Test Started:**			**3rd Reading (time/temp):**	
1st Reading (time/temp):			**4th Reading (time/temp):**			**1st Reading (time/temp):**			**4th Reading (time/temp):**	
2nd Reading (time/temp):			**Equilibrium**[2]**:** Y N			**2nd Reading (time/temp):**			**Equilibrium**[2]**:** Y N	
Test Thermometer/IR Gun ID	**Location Name**	**Location Number**	**Test Reading (Low)**	**Reference Reading (Low)**	**Difference**[3]	**Test Reading (High)**	**Reference Reading (High)**	**Difference**[3]	**Comments**	
			Use most current iteration of benchsheet							

[1] Good for 1 year. [2] 0°C change in 3 minutes. [3] Must not exceed ±1°C (thermometers); ±10°C (Radiochemistry IR Gun)

Form304r13 (6/8/05)

Must Discard 30 Days from _____ (date printed)

See various red font amendments. 3/9/09 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 926 REVISION 8

TITLE: REVIEW, REVISION, DISTRIBUTION AND ARCHIVING OF CONTROLLED DOCUMENTS

FORMS: 059, various laboratory benchsheets

APPROVED BY:

TECHNICAL MANAGER _____ DATE 6/9/06

QUALITY ASSURANCE MANAGER _____ DATE 6/9/06

LABORATORY MANAGER _____ DATE 6-9-06

HISTORY: Rev0, 7/08/93; Rev1, PCN #4, 8/26/93; Rev2, PCN #551, 10/18/95; Rev3, 7/15/99; Rev4, 10/15/01; Rev5, 3/2/02; Rev6, 4/17/02; Rev7, 4/3/04; Rev8, 6/8/06.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes Paragon's requirements for reviewing, revising, distributing and archiving controlled documents. Examples of controlled documents include -- SOPs, laboratory logbook forms, and Paragon plan guidance documents, such as the Laboratory Quality Assurance Plan (LQAP), Chemical Hygiene Plan (CHP), Emergency and Contingency Plan (ECP), Radiation Protection Plan (RPP) and Waste Management Plan (WMP). Non-conformance reports (NCRs) are also controlled documents, however, processes governing NCRs are detailed separately in SOP 928.

Documents that are controlled contain a revision number that is incremented with each iteration (i.e., change in content and issuance). Controlled documents may be electronic images that are posted to designated 'read only' network directories. A hardcopy controlled document original is identifiable by its printing on controlled (i.e. red-stamped) paper.

Laboratory logbooks, and the controlled forms that are used to create them, are managed by the Quality Assurance (QA) Department. The QA Department is responsible for assigning a unique identifier, and for creating and distributing requested logbooks. SOPs and Paragon plan documents are published by the QA Department through use of the SOP and Training Records database application.

The QA Department is responsible for ensuring that laboratory logbooks are made only from the most current benchsheet form. The QA Department is also responsible for ensuring that only the most current iteration of SOPs and Paragon plan documents are posted to the designated network directory. This is verifiable by any laboratory staff by comparing the network postings to the Table of Contents report of the SOP and Training Records database.

The intent of controlling documents and their distribution is to ensure that everyone who needs it, has a copy of the document, and that all recipients have the proper and most current information with which to work. Controlled distribution ensures that all

employees are following the same procedures, and helps to document when changes to procedures became effective. Controlled documents are issued and archived by the QA Department.

2. SUMMARY

With the exception of NCRs and laboratory logbook forms, a primary author is assigned to all controlled documents. The primary author is responsible for the content of the document, although actual revision and distribution of the document is accomplished by QA Department staff. Anyone may suggest a change or correction to a controlled document, the primary author is responsible for evaluating the suggestion and deciding whether or not it should be incorporated into the document. Controlled documents are reviewed for revision and distribution according to an established schedule that is determined by management staff. The primary author is responsible for adhering to the established schedule. Laboratory staff are responsible for reading the controlled document (if assigned) in a timely manner (i.e., within ~~10 work-days~~ of it's release), and for promptly implementing any procedural changes that are relayed in the document. This timely reading and implementation helps to establish when changes became effective. Department Managers are responsible for ensuring that all of the required controlled documents are assigned to each individual within their Departments, and for enforcing their timely reading. The QA Department maintains reading compliance records.

14 calendar days (3/9/09 DAS)

3. RESPONSIBILITIES

3.1 It is the responsibility of every employee to work *only* from approved versions of controlled documents. This means that employees may *not* refer to documents that have been hand-corrected as a means of updating the procedure, without properly processing the revision through the processes described in this SOP. Any employee may suggest a change or correction to a controlled document by submitting the request to the primary author. Each employee is responsible for reading the controlled documents assigned to them in a timely manner, and for signing the required reading compliance documentation.

3.2 Primary authors are designated by appropriate management staff. The content of the document is the primary author's responsibility, and it is the responsibility of the primary author to provide approved revisions to the QA Department for processing, according to schedule. The Department and QA Managers and the Laboratory Director are responsible for establishing the controlled document review and revision schedule.

3.3 It is the responsibility of every Department Manager to ensure that staff has adequate access to controlled documents, and to ensure that only the proper documents are referenced to accomplish the work. The Department Manager is also responsible for ensuring that all of the required controlled documents are assigned to each individual within their Department, and for enforcing their timely reading and submission of required reading compliance documentation to the QA Department.

3.4 It is the responsibility of the QA Department to process and distribute controlled documents in a timely fashion. The QA Department is responsible for maintaining an archive of controlled document versions. QA Department staff are responsible for providing oversight to the controlled document process, and for enforcing reading compliance. The QA Department maintains records of controlled document distribution and reading compliance. The QA Department maintains an archive of laboratory logbook form versions, manages a database for issuing laboratory logbooks, and is responsible for creating and distributing requested logbooks. Further details regarding laboratory logbooks are provided in SOP 303. Archiving of laboratory logbooks and other laboratory records is discussed in SOP 069.

, including review requirements, (3/9/09 DAS)

4. PROCEDURE

4.1 GENERAL REQUIREMENTS

4.1.1 Each individual's reading list (managed and accessible through Paragon's SOP and Training Records database) is determined by that individual's Supervisor, who must ensure that the reading list is current and appropriate. The SOP and Training Records database automatically updates the version of the assigned reading each time new version is released.

14 calendar days (3/9/09 DAS)

4.1.2 Each individual is responsible for reading all items on their reading list in a timely manner (i.e., annually; within ~~10 work days~~ of release for new/revised publications). Everyone has access to printing their reading list from the SOP and Training Records database (your Supervisor can show you how). The individual must inform their Supervisor that items have been read. Typically this is accomplished by providing an annotated reading list (i.e., read dates filled-in by hand by the individual) to the Supervisor, who in turn promptly enters the information into the SOP and Training Records database. Compliance with reading requirements appears as read dates shown for items on the reading list in the database. The SOP and Training Records database automatically archives off read dates that are greater than 1 year. Blank spaces on the reading list indicate items that are not compliant (i.e., have not been read within requirements).

4.1.3 Only current, approved versions of controlled documents may be used or referenced to accomplish work.

4.1.4 Anyone can suggest changes or corrections to controlled documents by submitting the request to the document's primary author. Primary authors are indicated on the Table of Contents report available from the SOP and Training Records database.

4.1.5 Review and revision of controlled documents is to occur according to a prescribed schedule, that is determined by management.

Although an overall biennial publication schedule is maintained, revision comments received are addressed as promptly as practicable. (3/9/09 DAS)

4.1.6 The version of the controlled document must be incremented with each publication that contains changes in content.

4.1.7 Controlled documents are distributed per a distribution list, that is derived from information contained in the SOP and Training Records database. Upon request, certain clients and agencies may be part of the document's distribution list. Typically, controlled documents are distributed by posting the image to the network in a designated 'read only' directory, and by issuing document release notifications that are produced from the SOP and Training Records database. The returned, signed document release notifications are maintained by the QA Department as reading compliance records. Past iterations of the document are maintained by the QA Department in archives.

4.1.8 Paragon does not typically issue addendums to documents between publications. Addendums may be issued only by the QA Department and must be distributed in the same manner as the associated primary document. The signature and date of the QA Manager and Laboratory Director must be present on the addendum.

4.2 PRIMARY AUTHORS

4.2.1 The primary author is a person knowledgeable about the processes described in the document and is designated by appropriate management staff.

The Quality Assurance Manager is the primary author for the LQAP. The Health & Safety Manager/Radiation Safety Officer is the primary author for the CHP, ECP and RPP. The Facilities Manager/Waste Coordinator is the primary author for the WMP.

annually (3/9/09 DAS)

4.2.2 The primary author is responsible for the document's content and must review the document for revision ~~according to schedule~~. The primary author must ensure that the document is compliant with referenced methods or guidance, and that the document reflects actual Paragon practices.

The primary author must review suggested changes and corrections and must incorporate the suggestions into the document as applicable. Typically some suggested changes and corrections are prompted by internal or external audit Findings. An audit Findings Table is available to everyone in LIMS. This Table can be sorted by status and SOP to find all OPEN Findings pertinent to the SOP in consideration.

Reviewed documents and their approved revisions are submitted to the QA Department for processing and distribution.

4.3 SOPS AND PLANS

4.3.1 To facilitate future revision, the QA Department makes electronic working copies of SOPs and Plans available to primary authors by posting them in restricted network directories each time a new version is released. The primary author can use this working copy to evaluate, manage and/or track suggested changes or corrections that are submitted to them.

When the revised document is ready to be published, the QA Department is notified by e-mail or through the SOP and Training Records database and the working copy is further processed for distribution.

- The QA Department is similarly notified when a document has been reviewed and it is determined that it can be re-released without revision.

- The QA Department is similarly notified when it is determined that a document can be retired (i.e., removed from active service).

More than one existing SOP can be consolidated into a single document at the discretion of the primary author, Department Manager and QA Manager.

If it is determined that a new SOP must be created, the primary author or Department Manager must obtain an SOP number from the QA Department.

'Operator Aids' are quick references, intended to be posted on a wall for easy viewing, that exist as an appendix of some SOPs. The Operator Aid is reviewed along with the main portion of the SOP per each review/revision cycle. Examples of Operator Aids include two Dishwasher's aids (one associated with SOP 334, the other with SOP 720), which are posted proximate to each laboratory sink that is used to clean glassware in the stable chemistry and radiochemistry laboratory areas, respectively. Another Operator Aid is the Preservations reference that is used in the Sample Receiving Department when bottle kits are made per SOP 205. The Operator Aids are posted in protective plastic sleeves, and are replaced with each distribution of the associated SOP.

4.3.2 Upon receiving notification from the primary author, the QA Department will further process the document in a timely manner.

- Revisions are reviewed for content changes; the QA Manager resolves any questions or issues that arise with the primary author.

- The format of the document (e.g., general, version number, history, etc.) is updated as needed.

- A hardcopy of the finalized document is provided to the primary author and Laboratory Director for review and signature; the Quality Assurance Manager also signs the document before it is published. With regard to the LQAP, Department Managers must additionally review and sign the master document before it can be published.

- The document is published through the SOP and Training Records database, notifications of release are distributed for returned signature attestation of reading compliance within ~~10 work-days~~ 14 calendar days (3/9/09 DAS) of release (the due date for return of these attestations is marked on the QA Manager's calendar so that compliance can be enforced), the network image for the document is replaced, where applicable, Operator Aids are replaced, and an appropriate working copy of the document is made available in the restricted primary author directory. The QA Department maintains distribution and reading compliance records.

4.3.3 Controlled documents that are printed out for reference or review are only valid for 30 calendar days from the date printed. An embedded document header identifies the document, and directs the person printing the document to write-in the date printed, and to discard the printout within 30 days. (3/9/09 DAS)

4.4 LABORATORY LOGBOOK FORMS

4.4.1 When distributed, custom spiral-bound laboratory logbooks contain a colored sheet (Logbook Reminder, Form 059), placed near the end of the logbook, that the user tears out and submits to the QA Department when that sheet is reached. This sheet contains information necessary to create a replacement logbook. The user may indicate changes that need to be made to the laboratory logbook form by writing comments on this sheet or by submitting a mark-up of a logbook page as an attachment.

4.4.2 A library of laboratory logbook forms is maintained in a restricted directory by the Quality Assurance Department. If changes to a form have been requested and are acceptable, the QA Manager works from the most current electronic version of the form to make the requested changes, but uses the 'Save As' command to create a new electronic file, advancing the version number of the filename by a value of '1' (e.g., edited Form 635r3.doc would be 'Saved As' Form 635r4.doc).

4.4.3 Further details about the issuance of laboratory logbooks can be found in SOP 303.

5. REFERENCES

This SOP describes an in-house procedure developed by Paragon. The requirements established herein are compliant with various quality assurance guidance documents, such as the most current versions of the National Environmental Laboratory Accreditation Conference (NELAC) Standard, the Department of Energy (DOE) Quality

Systems for Analytical Services (QSAS) document, and the Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories.

DOCUMENT REVISON HISTORY

6/8/06: Content completely restructured; text detail added; discussion of Operator Aids added; 'References' Section enhanced; 'Document Revision History' Section added; Forms incorporated as part of the SOP.

Paragon Analytics

It's time to request a new logbook from the QA Department!

Please tear-out this page and submit it to the QA Department.

Logbook Title: _____

Department: _____

Form Reference: _____

Comments: _____

If applicable, also submit a mark-up of any changes desired. If applicable, note in comments above any special requests for copying/binding.

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 928 REVISION 8

TITLE: NON-CONFORMANCES AND CORRECTIVE ACTIONS

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 3/7/08

QUALITY ASSURANCE MANAGER _____ DATE 3/6/08

LABORATORY MANAGER _____ DATE 3-7-08

HISTORY: Rev0, 12/6/93; Rev1, PCN #553, 10/18/95; Rev2, 2/27/98; Rev3, 11/20/98; Rev4, 11/20/01; Rev5, 3/2/02; Rev6, 4/6/03; Rev7, 6/8/06; Rev8, 3/6/08.

1. SCOPE AND APPLICATION

A non-conformance is any instance (i.e., deviation, equipment failure, or laboratory error) that results in an established acceptance limit, policy or client-specified criteria not being met. Corrective actions are those measures taken to correct or mitigate the non-conformance, along with the steps taken to prevent the incident from happening again.

Examples of non-conforming events include, but are not limited to:

- tracer recovery exceeded laboratory-derived acceptance limits;
- continuing calibration verification (CCV) results not within method-defined control limits;
- performance parameter (e.g., lumex, negative activity, etc.) exceeded established Paragon limits;
- client criteria (e.g., LCS, DER, etc.), differs from Paragon Standard criteria and client criteria was not met;
- glassware broke and sample was lost;
- sample was erroneously double-spiked with surrogate;
- wrong date of collection was entered upon sample login;
- current IDLs were not presented in the electronic data deliverable (EDD).

Examples of corrective/preventive actions include, but are not limited to:

- further analyses were performed on both a traced and untraced fraction of a reduced aliquot of sample
- sample was resubmitted for preparation and analysis;
- a sample cleanup was performed;
- document in narrative, matrix contribution is the most likely cause;
- LIMS program specification was updated to clarify client requirement
- matter was discussed with staff and retraining was provided

Non-conformances are reported (documented) through the laboratory's LIMS interface (LIMS\ Laboratory\NCR Menu). The series of tabs that comprise the LIMS interface mimic the sections contained in the former hardcopy report (Form 313) that was previously circulated. Use of the hardcopy NCR Forms has been discontinued, as the LIMS interface yields a sequential, uniquely-identified, Controlled report that takes its place. Additional new features are also provided for via the current LIMS NCR interface. The NCR process also serves to initiate corrective action. NCRs are also used to address client inquiries, and to investigate Performance Test (PT) sample failures. The specific corrective measures taken are contingent upon the type and extent of the incident, and are coordinated by the laboratory Department and applicable Project Manager(s), and the QA Department. It is Paragon's policy to complete corrective action within the assigned date, which is not to exceed 21 calendar days. Note that exceptions may be applied where prudent, at the QA Manager's discretion (*example*: root cause is thought to be instrument malfunction, instrument is sent off-site for refurbishment and retained by vendor for 3 weeks, instrument must be re-installed and re-calibrated before corrective action can be complete, hence, corrective action cannot be completed within established 21 calendar days policy).

This standard operating procedure (SOP) provides an overview of Paragon's NCR/corrective action processes. Further details pertaining to these topics are contained in the Paragon NCR User's Guide (posted to the network, for internal use only), and Section 11 of the Laboratory Quality Assurance Plan (LQAP).

2. SUMMARY

Like before, NCRs are available to all laboratory staff and *anyone* who notices an error or discrepancy that results in the failure to meet an established limit, policy or client-specified criteria, is responsible for initiating an NCR in a timely manner (i.e., when the problem is noted). The general NCR process flows from the initiator, through their immediate Supervisor and/or Department Manager, to the Project Manager (discussions with the client, and between the PM and DPM occur as necessary), and finally to the Quality Assurance Manager. Authorized signatures (PM, DPM, QA) are required at various steps. Signature authority can be delegated as needed to cover key staff outages.

Paragon maintains a full-disclosure environment with regard to internal communications and dialogue with our clients. Non-conformance reporting facilitates these communications and is essential in helping to identify issues as early in our processes as possible, thus enhancing operational efficiency and the ability to provide outstanding customer service. NCRs also provide a means of identifying trends, giving us the ability to correct deficiencies in training, and insights into improving our processes and product.

3. RESPONSIBILITIES

3.1 It is important, and is everyone involved's responsibility, to initiate and complete NCRs in a timely manner. Rapid determination and application of needed corrective

measures may be necessary to meet sample hold times, client deadlines, etc.

3.2 It is the responsibility of all personnel who work with samples to document any discrepancies (non-conformances) that occur with sample handling.

Chemists who prepare samples for analysis must document any problems noted during preparation. Refer to LQAP for details regarding use of Quality Assurance Summary Sheets (QASS) and initiation of NCRs.

Analyst's are responsible for monitoring the proper functioning of the analytical system prior to, during and following sample analysis, and for documenting any problems that are noted.

3.3 The Project Manager (PM), with assistance from the Department Manager (DPM) as necessary, is responsible for assessing the severity of the non-conformance and its impact on project requirements. If client contact is necessary to determine appropriate corrective action, the PM contacts the client and documents it in the NCR interface. The specific corrective measures to be taken are also recorded in the NCR interface.

The Department Manager is responsible for ensuring that the corrective measures applied were completed, and that overall, NCRs are initiated and completed when necessary.

PM and DPM signatures are required in various places via the NCR interface to track the flow of the correction and to attest that the measures taken were appropriate and complete.

3.4 The Quality Assurance (QA) Department is responsible for providing final approval of each NCR and oversight of the entire NCR process. The QA Department provides monthly NCR feedback to Management staff. Archives of hardcopy NCRs are maintained in QA Department files. Documents generated through the NCR interface are maintained (archived) through established electronic backup and archiving protocols.

3.5 Reporting Group staff are responsible for ensuring that completed NCRs are included in laboratory data package reports, as applicable.

4. PROCEDURE

4.1 Whoever notices an error or discrepancy that results in the failure to meet an established limit, policy or client-specified criteria, is responsible for initiating an NCR in a timely manner (i.e., when the problem is noted).

4.2 The steps for initiating and processing NCRs are generally the same regardless of whether the NCR is used to document a non-conformance, to research a client inquiry, or to request a corrective action investigation (see Section 4.6). NCRs used to document non-conformances are typically initiated by laboratory staff; an

NCR used to research a client inquiry is typically initiated by the Project Manager; an NCR used to request corrective action investigation (e.g., resolution of an internal audit Finding, investigation of a PT result failure, etc.) is typically initiated by the QA Department.

4.3 Refer to the Paragon NCR User's Guide for instructions on interacting with the LIMS NCR interface. The NCR interface contains various controls and lockdown features. Contact the QA Department should any information need to be edited. If, after initiating an NCR, it is subsequently determined that the NCR was not needed, contact the QA Department so that the NCR can be properly voided.

The Project Manager, at his or her discretion, may or may not contact the client to discuss options based on the nature of the non-conformance. Means for documenting client contact are provided for in the NCR interface.

The NCR is considered to be complete when all final approval signatures (PM, DPM, QA, or designees) are in place.

4.4 The Reporting Group discusses any anomalies described on the NCR in the data package narrative, and includes a copy of the NCR in the data package report (as applicable for the level of the data deliverable generated).

4.5 The QA Department tracks NCRs as they are finalized, so that systematic problems or trends can be readily identified and responded to promptly. The QA Manager, at his or her discretion, may initiate corrective action investigation for recurrent events (see 4.6 below). On a monthly basis, the QA Department summarizes the NCR occurrences and distributes this summary, along with additional comments, to key laboratory staff for their further consideration.

4.6 Formal corrective action requests (i.e., additional efforts that are mandated that are beyond the scope of NCRs), are managed through a different LIMS interface, namely the LIMS Audit Finding Table (LIMS\Quality Assurance\Audit Findings). All laboratory staff have read access to this Table, the QA Department manages the Table's contents. The LIMS AF Table is also used to manage corrective actions requests associated with external audits.

Each formal corrective action is assigned a unique identifier. The QA Department uses a sequential identifier of "CA-yymm###" to designate corrective actions that are initiated internally. Internal corrective action requests are issued at the QA Department's discretion, and may be used to investigate and resolve trends, internal audit Findings, PT sample result failures, etc.

All corrective actions must be resolved in the most timely manner practicable. Corrective actions associated with NCRs are typically completed within turnaround time requirements for the data. In general, corrective actions are to be

completed within 21 calendar days or less as assigned. Exceptions or extensions may be granted at the QA Department's discretion, contingent upon the particular incident's circumstances.

The QA Department is responsible for maintaining supporting documentation pertaining to corrective action investigations and outcomes; this information is archived on the network.

5. REFERENCES

This SOP describes an in-house procedure developed by Paragon. The requirements established herein are compliant with various quality assurance guidance documents, such as the most current versions of the National Environmental Laboratory Accreditation Conference (NELAC) Standard, the Department of Energy (DOE) Quality Systems for Analytical Services (QSAS) document, and the Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories.

DOCUMENT REVISION HISTORY

6/8/06: Completely reformatted; 'Responsibilities' Section enhanced; greater detail added; management aspects of NCR use and evaluation included; scope broadened to include corrective action and audit Finding management; 'References' Section enhanced; 'Document Revision History' added, Forms incorporated as part of SOP.

3/6/08: Complete re-write as NCRs are now electronic in LIMS. Updated Title. Removed Forms, which are no longer applicable.

Must Discard 30 Days from _____ (date printed)

See amendment, Section 3.2 (i.e., internal auditor qualifications). 3/9/09 DAS

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 937 REVISION 7

TITLE: INTERNAL AUDITS

FORMS: 168, 169 (use most current iterations)

APPROVED BY:

TECHNICAL MANAGER _____ DATE 6/9/06
QUALITY ASSURANCE MANAGER _____ DATE _____
LABORATORY MANAGER _____ DATE 6-9-06

HISTORY: Rev0, PCN #513, 8/1/95; Rev1, 9/22/97; Rev2, 8/10/99; Rev3, 10/8/01; Rev4, 4/17/02; Rev5, 9/9/03; Rev6, 4/24/04; Rev7, 6/8/06.

1. SCOPE AND APPLICATION

An audit is a formal assessment of a procedure or product that documents the evaluation of that procedure or product against relevant guidelines and requirements. Audits help to ensure that good laboratory practices are being observed and serve as a management tool for evaluating the appropriateness of quality assurance policies. This Standard Operating Procedure (SOP) describes how Paragon conducts its internal audits. Consult Chapter 12 of the Laboratory Quality Assurance Plan (LQAP) for similar information regarding external audits and Performance Test (PT) study evaluations.

2. SUMMARY

Near to the beginning of each calendar year, the Quality Assurance (QA) Manager creates an audit schedule. The annual audit schedule is designed to touch upon all laboratory Departments at least once, and to evaluate critical elements of laboratory and quality systems. Note, however, that the Facilities and Waste Department and the Health & Safety Department are responsible for determining and managing their own internal assessments per their applicable quality and regulatory requirements.

Qualified personnel prepare for, conduct and document each internal audit. Corrective actions are determined and applied as necessary. Follow-up is performed and documented as applicable. Senior Departmental staff and management are made aware of audit outcomes.

The QA Department maintains archives of internal audit records.

3. RESPONSIBILITIES

3.1 The QA Department is responsible for developing the annual internal audit schedule, managing the internal audit program, approving individuals as qualified to conduct internal audits, evaluating and enforcing corrective actions, distributing audit reports to appropriate personnel, and maintaining an archive of internal audit records.

3.2 The designated internal auditor shall be a person who possesses previous knowledge or experience in the area being audited, or who has been trained in the concepts of the area being audited. As a Laboratory Director or QAM designee, the internal auditor is empowered with the same authority/autonomy as that defined for QA Dept. staff, and shall have unlimited access to all laboratory areas. It may be appropriate, however, in some instances (such as IS Dept. evaluations), for the unfettered accesses to be given by proxy. The internal auditor shall conduct themselves, at all times, professionally, exercising courtesy and respect. 3/9/09 DAS

3.3 Department Managers and laboratory staff are responsible for supporting the internal audit program (e.g., being available, cooperating, fully disclosing, etc.), for determining the root cause of any noted non-compliances, effectively implementing corrective actions, and where applicable, submitting required corrective action documentation to the QA Department.

3.4 The Laboratory Director is responsible for providing adequate resources for conducting the internal audit program and for applying agreed-upon corrective measures where necessary.

4. PROCEDURE

4.1 GENERAL INFORMATION

4.1.1 The QA Manager establishes an annual audit schedule near to the beginning of each calendar year and assigns designations for each internal audit. Internal audits are typically identified as 'IAyymmdd'.

4.1.2 Internal audits are conducted by QA staff or qualified designees as determined by the QA Manager. Where possible it is desirable that the auditor be independent of the area being audited.

4.1.3 Technical method audits are performed for the Departmental audits. This type of audit is called a 'performance audit'. Elements evaluated during technical method audits typically include:

- compliance with method requirements;
- performance of actual practices per procedures stated in the SOP;
- performance and documentation of instrument maintenance;
- proper preparation, storage, use and documentation of standards;
- appropriate documentation via benchsheet, logbook and/or Laboratory Information Management System (LIMS) entries;
- initiation of Non-Conformance Reports (NCRs), where applicable;
- proper performance and documentation of data review;
- review of method data package deliverables, including aspects of data integrity.

Specific processes are evaluated during a 'systems audit'. Examples of laboratory system audits that are conducted annually include:

- electronic practices;
- project instructions and program specifications;
- sample receiving, handling and chain-of-custody;
- prescreening;
- compliance with Paragon's Standards Database;

- logbook records and reviews; and
- operations and manager's meetings.

Quality systems elements evaluated annually include:

- SOP review and revision;
- SOP reading compliance;
- Demonstrations of Capability (DOC) and other training records;
- internal audit program status (includes the annual Quality Systems Audit-QSA, the Annual Managerial Review-AMR and PT study performance);
- certifications;
- Non-conformance Reports (NCRs), corrective actions and audit Findings response;
- Method Detection Limits (MDLs);
- Quality Control (QC) limits;
- records and archiving;
- master and support equipment; and
- client interface.

Overall, Paragon performs approximately 13 internal audits annually, additional audits may be performed as needed (e.g., corrective action, per client request, as requested by laboratory management, etc.). The internal audit system is designed such that the compilation of all individual audits serve together as the QSA and AMR.

4.2 PRE-AUDIT ACTIVITIES

4.2.1 Before the audit, the auditor identifies the scope, intent, and expected duration of the audit to the Department Manager and any other appropriate laboratory staff, and coordinates the time the audit is to be conducted.

4.2.2 The auditor prepares an audit questionnaire (a Form 169 equivalent is used to conduct the audit, as this document also serves as the audit report; Form 168 is used to document and report the QSA). The questionnaire is developed from reading applicable documents such as the SOP, LQAP and/or client quality plans or contracts, and the Paragon Program Specification, as applicable.

4.3 AUDIT CONDUCT AND REPORTING

Internal audits are conducted in a professional manner, in the most efficient and effective way possible:

- keep on track, have a respectful and conversational demeanor.

- perform the audit through interview, observation and investigation; conduct the audit using the prepared questionnaire as a guide.
- ask focused but open questions (i.e., do not reveal the desired answer by the manner in which you ask the question); record responses on the audit questionnaire.
- if information given raises a question or possible concern, continue to explore the topic (i.e., it is not necessary or appropriate to stick strictly to the prepared questionnaire).
- a Finding is a non-compliance that requires correction, an Observation is food for thought. Discuss Findings and Observations with participants as they occur, as well as possible corrective actions or improvements.

  Corrective actions may be taken when an item is noted or an appropriate corrective action plan may be discussed. The possible effects the corrective actions may have on any in-process work or product already released to the client must be considered. The QA Manager and Laboratory Director will determine the need for and pursue client notification as deemed necessary. Where warranted, clients will be contacted in the most timely manner practicable.

  Be sure to document these topics discussed on the audit guide.
- give the auditee the chance to provide any other information they feel is pertinent.
- add summary auditor comments to the questionnaire as applicable and indicate on the audit guide whether or not follow-up is necessary.
- have participants initial the audit questionnaire.
- promptly debrief the area Supervisor; the area Supervisor is responsible for providing clarification as needed.
- attach notes or indicate references used to conduct the audit; submit the internal audit documentation to the QA Manager.

The QA Manager:

- in a timely manner, reviews the completed audit questionnaire and further discusses corrective actions with the Department Manager and Laboratory Director as necessary.

  Content and time frame (contingent upon extent of Finding, typically within 12 business days) for corrective action implementation are defined, as well as parties responsible for implementing the corrective action.
- Additional notes are made on the audit questionnaire/report and the information for the Finding is entered into the LIMS audit database for all parties to reference and follow further. The date for follow-up is marked on the QA Manager's calendar as well.

- A copy of the audit report is distributed to the Department Manager and Laboratory Director and is archived on the network.
- It is the joint responsibility of the QA Manager (or designee) and Department Manager (or designee) to ensure that agreed upon corrective measures were applied and are effective and to 'close-out' (i.e., deem the audit concerns as fully satisfied) the audit. Additional documentation is provided to the QA Department where necessary and added to the network archives. The information contained in the LIMS audit database must also be updated accordingly.

4.4 ANNUAL QUALITY SYSTEMS AUDIT (QSA)

Results of individual internal audits are compiled to comprise the annual QSA, which is a lab-wide review of conformance to Paragon's quality system. The QSA shall be conducted, managed and reported according to the procedures described in this SOP. PT study results and status of external audit responses are also highlighted in the QSA.

4.5 ANNUAL MANAGERIAL REVIEW (AMR)

A lab-wide Managerial Review shall be performed annually to asses operational effectiveness in terms of meeting Paragon's business goals. The AMR serves as a tool for evaluating and tracking potential improvements to laboratory facilities, services, processes, etc.

The AMR is performed by a designee under the direction of the Laboratory Director. The general techniques of scoping, assessment interview, reporting and follow-up outlined in this SOP shall be used to conduct the AMR. Interview of the Laboratory Director may be an integral component of the AMR.

Inputs to the AMR may include, but are not limited to:

- a snapshot summary of product generated (i.e., number of samples analyzed and the types of analyses performed);
- various business assessment reports (e.g., TAT, on- time delivery);
- output from the annual QSA (i.e., problem areas identified);
- interview of laboratory staff; and
- presentation of items discussed during strategic planning sessions and/or Manager's meetings.

The contents of the AMR are considered to be confidential. A confidential footer must appear as a component of the AMR report.

5. REFERENCES

This SOP describes in-house procedures developed by Paragon. The requirements established herein are compliant with various quality assurance guidance documents, such as the most current versions of the National Environmental Laboratory Accreditation Conference (NELAC) Standard, the Department of Energy (DOE) Quality

Systems for Analytical Services (QSAS) document, and the Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories.

DOCUMENT REVISON HISTORY

6/8/06: Content completely restructured and level of detail revamped; 'References' Section enhanced; 'Document Revision History' Section added; Forms incorporated as part of the SOP.

Form 169 equivalent

(Internal Audit Number) conducted by (Name)(Date)

_____ (Name, Position) and _____ (Name, Position) interviewed
(initials) (initials)

workorders reviewed: _____ copied to (DPM), KDC (Date)(Initials)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 670 REVISION 11

TITLE: ANALYSIS OF TOTAL ORGANIC CARBON BY METHODS EPA 415.1, SW9060, AND SM5310 C

FORMS: 647 (current iteration)

APPROVED BY:
TECHNICAL MANAGER _____ DATE _____
QUALITY ASSURANCE MANAGER _____ DATE _____
LABORATORY MANAGER _____ DATE _____

1. Name some of the types of carbon that can be analyzed by this procedure.
   - soluble, nonvolatile organic carbon (e.g., natural sugars)
   - soluble, non-purgeable volatile organic carbon (e.g., mercaptans, alkanes, low molecular weight alcohols)
   - insoluble, partially volatile carbon (e.g., low molecular weight oils)
   - insoluble, particulate carbonaceous materials (e.g., cellulose fibers)
   - soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter (e.g., oily matter adsorbed on silt particles).

   _____

   _____

2. Based on the operating theory of the method, what is the first thing that occurs during TOC analysis? (inorganic carbon -- dissolved CO_2, HCO_3^- and $CO_3^=$ -- in the presence of an H_3PO_4 acid reagent, is purged from the sample, otherwise, high bias would result) _____. Then what happens? (organic C is oxidized to CO_2 by persulfate in the presence of UV light) _____

3. Question #3, etc. _____

Auditor's Comments _____

_____

_____ **Is follow-up required?** _____

Paragon Analytics

Quality Systems Review Checklist _____ (year)

Summary Positive Period of Performance Comments (1) (2) (3) Negative Period of Performance Comments (1) (2) (3) Areas of Focus for the Coming Year (1) (2) (3) (4) (5)	
Internal Audit Elements	Internal Audit Program NCRs and CAs PT Performance (ordering and login, reporting to vendor, results tracking) Data Review QC Limits OSA AMR
External Audits	
Training Records	Annual Ethics New Hire Orientation DOCs (MBMS forms, database, annual assessment) LQAP and sign-offs SOP and reading list compliance
MDLs	

Initials/Date _____ Page 1 of 2 **Form 168r1.doc (6/6/06)**

Paragon Analytics

Quality Systems Review Checklist _____ (year)

Certifications	
Support Equipment (Balances, Weights, Thermometers, RUs, Ovens, Equipment List)	Verification Database
Forms and Logbooks	
Archives	Annual Purge Effort Shredder Management Imaging
Client Interface	
Special Projects	Method Validation documentation requirements
Miscellaneous Notes: (1) (2) (3)	
QA's IS list: (1) (2) (3)	

Initials/Date _____

Form 168r1.doc (6/6/06)

Must Discard 30 Days from _____ (date printed)

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 939 REVISION 3

TITLE: MANUAL RE-INTEGRATION POLICY AND PROCEDURES

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE 11-14-07

QUALITY ASSURANCE MANAGER _____ DATE 11/12/07

LABORATORY MANAGER _____ DATE 11-14-07

HISTORY: Rev0, 9/10/01; Rev1, 4/8/03; Rev2, 3/13/06; Rev3, 11/12/07.

1. SCOPE AND APPLICATION

The intent of this standard operating procedure (SOP) is to define Paragon's policy and procedures for manual re-integrations of peaks integrated and stored by chromatography software systems. This SOP describes acceptable re-integration practices that will ensure consistently integrated and defensible data. This SOP is intended to ensure that Paragon achieves requirements set forth by Good Automated Laboratory Practices (GALP).

The policies and procedures described in this SOP are applicable to all data collected, processed, reported, and stored by a chromatography software system (e.g., gas chromatography, liquid chromatography, mass spectrometry, ion chromatography).

2. SUMMARY

Paragon's analysts optimize peak integration parameters to ensure that standard and sample responses are integrated correctly and consistently. Field samples and high-level standards may not be detected and integrated as consistently by the software systems. Although **Paragon's policy is to perform minimal re-integration,** in cases where the software has incorrectly identified or quantified a peak, it is necessary to re-integrate that peak.

All peaks that are integrated by a software system are reviewed by Paragon's analysts, reviewers, and/or Department Managers. The intent of reviewing the data system's integration is to ensure that:

- each peak has been identified correctly by the chromatography system (i.e., each qualitative identification is accurate); and
- each peak has been integrated correctly by the chromatography system (i.e., quantitative integration/calculation is correct).

If an analyst judges (and subsequent reviewers concur) that a peak has been misidentified and/or improperly integrated, then it is appropriate to overrule the data system's determination and manually re-integrate a peak, thereby adding or subtracting area from the

peak. **All manual re-integrations must be performed consistently throughout a given analytical process, and documented properly by the analyst and reviewers.**

3. RESPONSIBILITIES

3.1 The analyst who generates the raw data has the primary responsibility for the correctness and completeness of the data. It is the responsibility of the analyst to perform any manual re-integrations according to the policies outlined in this SOP and to complete all documentation during for review.

3.2 The analyst and reviewer are responsible for the generation and compilation of the data. These employees must ensure that all manual re-integrations are acceptable and properly documented. Any improper manual re-integrations must be corrected immediately and discussed with the analyst and Department Manager.

3.3 It is the responsibility of all personnel who perform data review to document any anomalies, out-of control events, or non-compliant events associated with the analysis of the samples. The reviewer must ensure that all manual re-integrations are properly documented.

3.4 The Department Manager is required to provide adequate training on the use of the data system and documentation requirements associated with manual re-integration. The Department Manager is also required to provide adequate training on the requirements set forth in this SOP and is responsible for monitoring manual re-integration practices.

4. PROCEDURE

4.1 There are many valid reasons to manually re-integrate a peak and this SOP does not address all possible situations. The following are examples of acceptable reasons to manually re-integrate a peak:

4.1.1 The data system has mis-identified a peak within a prescribed retention time window. An example is given in Figure 4.1.1a. The smaller peak identified and integrated by the data system is further from the center of the retention time window than the larger peak. If no retention time shifts were observed within the analytical run, then the peak closer to the center of the retention time window is the correct identification. In this case, the analyst shall reassign the qualitative identification of the peak as shown in Figure 4.1.1b.

4.1.2 The data system has integrated a peak incorrectly. Non-Gaussian peaks often cause inappropriate integrations and the analyst shall correct such over-integrations or under-integrations. A “tailing peak” is an example of a non-Gaussian peak that may be integrated incorrectly. An example is given in Figure 4.1.2a and 4.1.2c, which shows examples of pyridine and

benzoic acid integrated incorrectly. In this case, the analyst shall reassign the endpoint at the end of the peaks (see Figures 4.1.2b and 4.1.2d).

Excess column loading and detector saturation/shutdown are other examples of conditions that may result in non-Gaussian peaks.

4.1.3 The data system has interpreted an electronic spike as the baseline. This situation is encountered in end-to-end integration techniques used to quantify standards and samples for petroleum hydrocarbons (e.g., GRO, DRO). An example is given in Figure 4.1.3a, which shows a misinterpretation of the baseline by the data system as a result of an electronic spike. In this case, the analyst shall reassign the baseline to eliminate area as shown in Figure 4.1.3b.

4.1.4 The data system has mis-identified isomeric pairs. Examples of adjacent peaks that may require re-integration include: 1,3-dichlorobenzene and 1,4-dichlorobenzene; benzo(b)fluoranthene and benzo(k)fluoranthene; chrysene and benzo(a)anthracene. An example is given in Figure 4.1.4a, which shows incorrect identification of an isomeric pair. In this case, the analyst shall reassign the baseline as shown in Figure 4.1.4b.

4.1.5 A manual re-integration shall be performed if the intent is to ensure consistency between calibration standards and samples at similar concentrations. That is, if one manually re-integrates a standard, then the sample(s) shall be re-integrated in a similar fashion. In most cases, a data system will properly integrate a standard (in which matrix effect is not a factor) if the peak recognition algorithms have been optimized in the method file. Integration of a field sample may be complicated by co-extractives that cause the data system to treat a peak in a field sample differently from the same peak in a calibration standard.

4.2 The following are several **unacceptable** reasons to manually re-integrate a peak:

4.2.1 Manual re-integrations shall **not** be performed if the analyst doesn't "like the looks" of the data system's integration and believes that he or she can achieve a better-looking peak via manual re-integration. A peak should not be manually re-integrated for subjective, artistic reasons. If the re-integration will not change the area of the peak by more than 2-5%, then the re-integration should not be performed. In such marginal cases, it is preferable -- and more defensible -- to allow the data system to determine the integration.

4.2.2 Manual re-integrations shall **not** be performed in order to achieve initial or continuing calibration criteria. For example, removing area from a properly integrated peak in a continuing calibration verification (CCV)

standard with the intent of achieving the percent difference criterion is prohibited ("peak shaving"). Similarly, adding area to a properly integrated peak in an initial calibration verification (ICV) standard with the intent of achieving the percent difference criterion is prohibited ("peak enhancement").

Manual re-integrations shall **not** be performed in order to achieve established control limits for surrogates, internal standards, or spiking compounds. For example, removing area from a properly integrated internal standard with the intent of meeting the 50-200% criterion is prohibited ("peak shaving"). Similarly, adding area to a properly integrated surrogate compound with the intent of meeting a lower control limit is prohibited ("peak enhancement").

4.2.3 Manual re-integrations shall **not** be performed in order to verify tuning compounds. It is prohibited to circumvent the autotune checking function in the Enviroquant® software. The software chooses the apex of the tuning compound and one scan on either side of the apex. The autotune checking software also performs a background subtraction.

4.2.4 Manual re-integrations shall **not** be performed in order to achieve a quantitation of a target compound that is below the reporting limit (RL) or method detection limit (MDL).

4.2.5 Manual re-integrations shall **not** be performed in order to compensate for column degradation or instrument maintenance problems.

4.2.6 **Note that Paragon supports and enforces a zero tolerance policy for unacceptable manual re-integrations.**

4.3 The following documentation shall be provided for every peak that is manually re-integrated:

4.3.1 A printout of the data system's original integration and the analyst's manual re-integration along with the mass spectra. These printouts are known as "before" and "after" spectra. The intent of including both in the data package is to demonstrate the result of the manual re-integration. The "after" spectra printout shall be signed and dated by the analyst.

NOTE: As part of Paragon's data review process (SOP 052), a second reviewer's initials are documented on the associated data's review checklist. This data review checklist in not normally included in the client data package report.

4.3.2 The "after" spectra shall be annotated with the custom stamp provided to the laboratory.

4.3.3 The manual re-integration shall be identified on the raw data quantitation report. Most software systems append a qualifier flag ("m") that makes manual re-integrations apparent to all reviewers of the data. If the software system does not have the ability to append a flag, then the analyst must annotate the quantitation report with a flag that indicates manual re-integration.

4.3.4 The case narrative shall state how a data validator may locate manual re-integrations if they have been performed.

5. REFERENCES

5.1 EPA 2185 -- GOOD AUTOMATED LABORATORY PRACTICES; EPA's Recommendations For Ensuring Data Integrity In Automated Laboratory Operations With Implementation Guidance, 1995.

5.2 STATEMENT OF WORK FOR ORGANIC ANALYSIS, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program, Document Number OLM04.1.

5.3 Test Methods for Evaluating Solid Waste, SW-846 3rd Edition, USEPA OSWER, November 1986.

5.4 "Chromatographic Integration Methods", Norman Dyson, The Royal Society of Chemistry, Thomas Graham House, Cambridge, 1990.

DOCUMENT REVISION HISTORY

11/12/07: Incorporated Figures electronically.

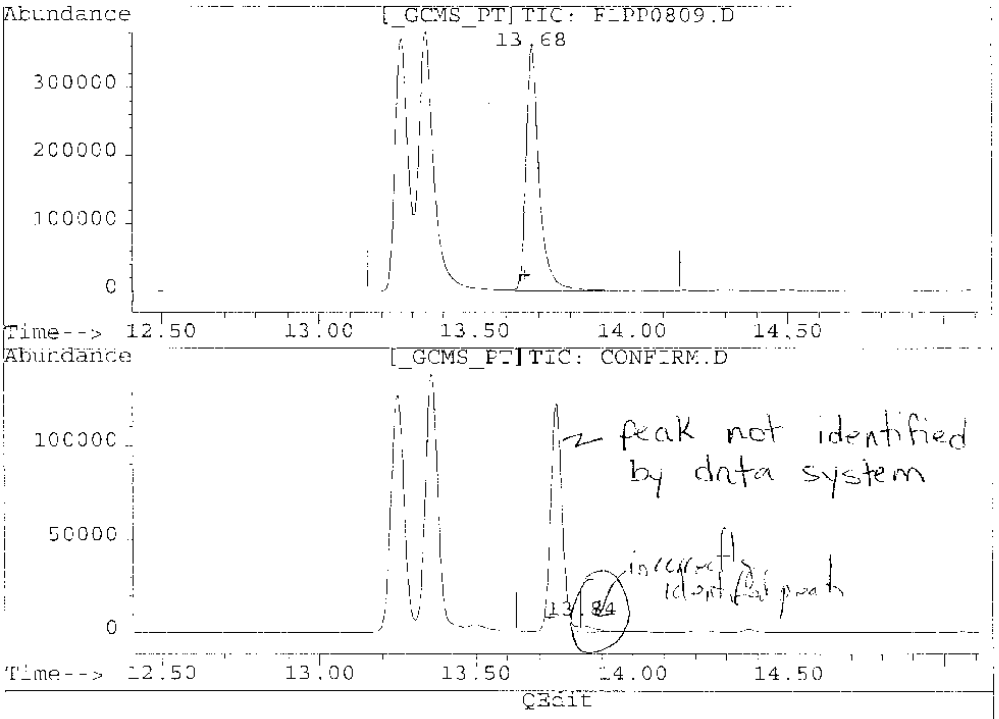
Both peaks identified + integrated FIGURE 4.1.1 (4)

Quantitation Report

Signal #1 : C:\HPCHEM\5\DATA\03C42C01\F1PP0809.D Vial: 19
Signal #2 : C:\HPCHEM\5\DATA\03C42C01\F1PP0809.D\CONFIRM.D
Acq On : 04 Mar 01 09:58 AM Operator: CH FUELS1
Sample : ccv1 8021B 4March2001 Inst : FUELS 1
Misc : 5µlHC500052-001,hc500051-001,hc300022-00 Multiplr: 1.00
Quant Time: Mar 9 13:16 19101

Method : C:\HPCHEM\5\METHODS\PP030201.M
Title : 8021B for volatile aromatic organic compounds
Last Update : Sat Mar 03 08:30:41 2001
Response via : Multiple Level Calibration

BEFORE



(13) 1,2-Dichlorobenzene (T)
13.68min 50.69ppb
response 1046966

Baker PKG 4March01

(13) 1,2-Dichlorobenzene #2 (T)
13.84min 0.37ppb } the smaller peak
response 12493

(T) = Expected Retention Time
F1PP0809.D PP030201.M Fri Mar 09 13:17:24 2001 GC_FUELS

(5)

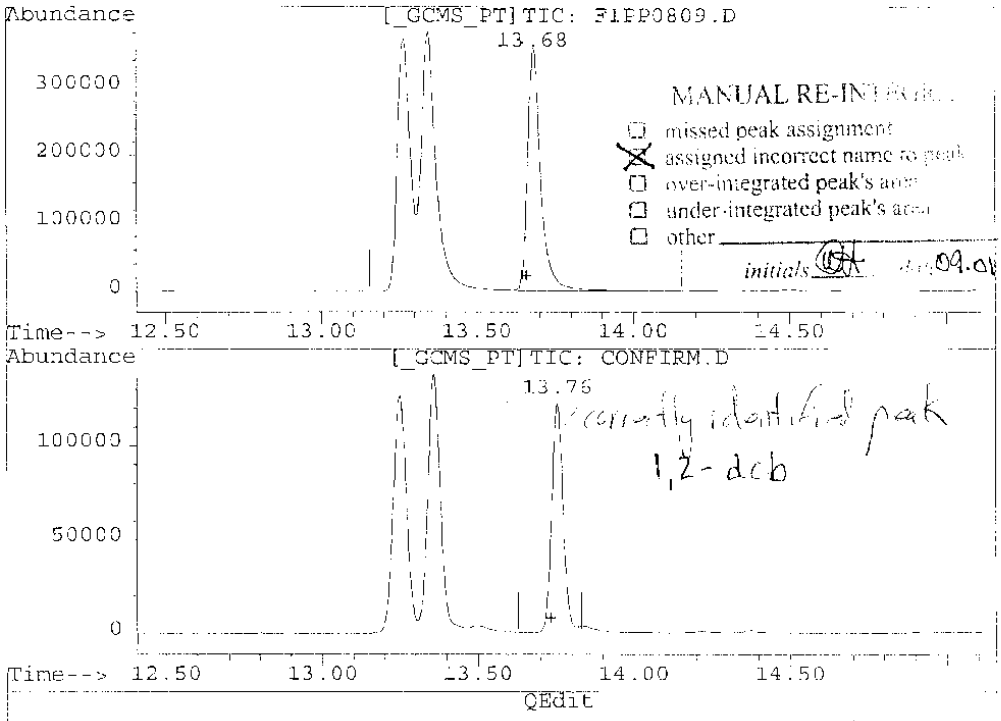
FIGURE 4.1.6

Quantitation Report

Signal #1 : C:\HPCHEM\5\DATA\03042C01\F1PPC809.D Vial: 19
Signal #2 : C:\HPCHEM\5\DATA\03042C01\F1PPC809.D\CONFIRM.D
Acq On : 04 Mar 01 09:58 AM Operator: CH FUELS1
Sample : ccv1 8021B 4March2001 Inst : FUELS 1
Misc : 5µlHC500052-001,hc500051-001,hc300022-00 Multiplr: 1.00
Quant Time: Mar 9 13:18 19101

Method : C:\HPCHEM\5\METHODS\PPC30201.M
Title : 8021B for volatile aromatic organic compounds
Last Update : Sat Mar 03 08:30:41 2001
Response via : Multiple Level Calibration

AFTER



(13) 1,2-Dichlorobenzene (T)
13.68min 50.69ppb
response 1046966

(13) 1,2 Dichlorobenzene #2 (T)
13.76min 46.67ppb m
response 320166

bigger peak chosen closer to center of RT window

(+) = Expected Retention Time
F1PP0809.D PPC30201.M Fri Mar 09 13:38:25 2001 GC_FUELS

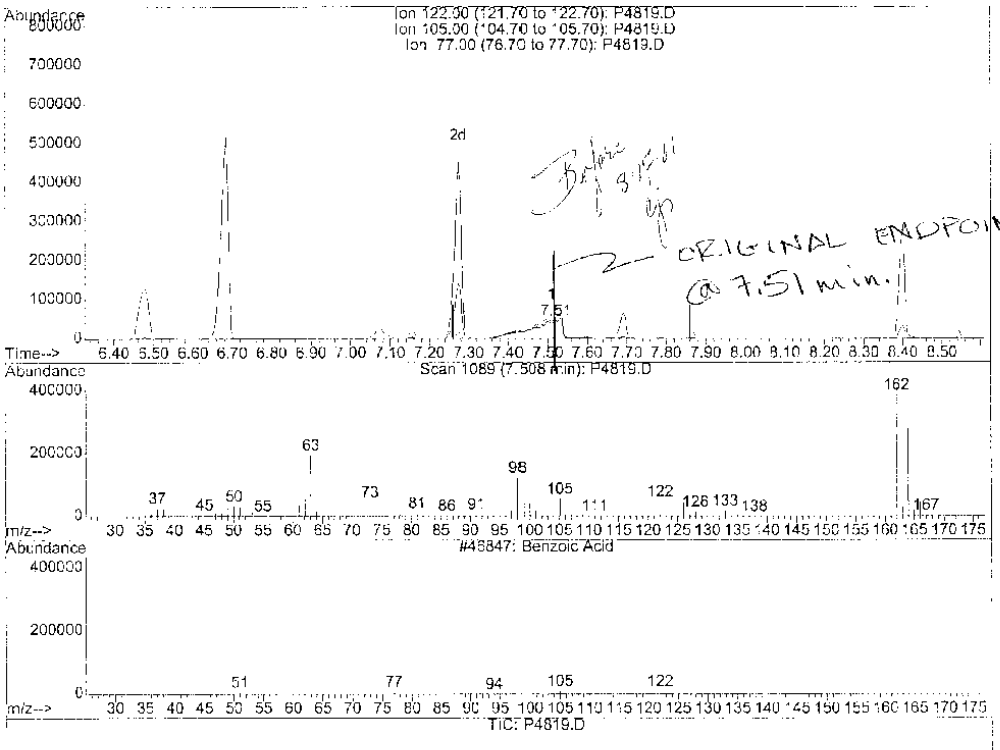
6

FIGURE 4.1.2.(a)

Quantitation Report (Qedit)

Data File : C:\HPCHEM\1\DATA\081601\P4819.D Vial: 8
Acq On : 16 Aug 2001 10:00 pm Operator: cjones S
Sample : ICAL SVSTD120 Inst : HPSV 2
Misc : 2078-78-1 Multiplr: 1.00
MS Integration Params: rteint.p
Quant Time: Aug 17 11:05 2001 Quant Results File: temp.res

Method : C:\HPCHEM\1\METHODS\081601S2.M (RTE Integrator)
Title : GC-MS Semivolatiles SOP no. 506
Last Update : Thu Aug 16 12:07:49 2001
Response via : Multiple Level Calibration



(29) Benzoic acid (T)

7.51min 94.65ng/u_

response 222145

Ion	Exp%	Act%
122.00	100	100
105.00	122.50	121.60
77.00	91.00	113.01#
0.00	0.00	0.00

"TAILING"

P4819.D 081601S2.M Fri Aug 17 11:06:15 2001

(7)

FIGURE 4.12(b)

Quantitation Report (Qedit)

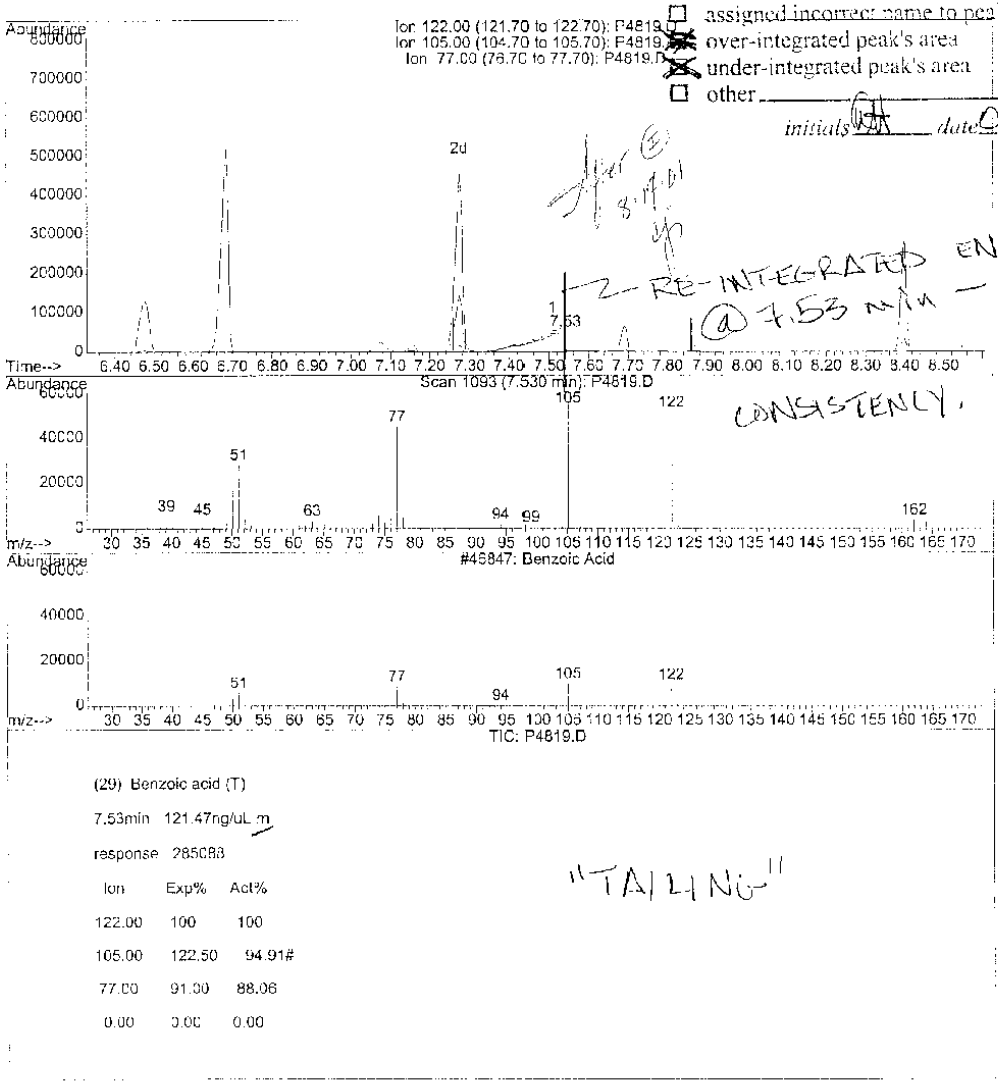
Data File : C:\HPCHEM\1\DATA\081601\P4819.D Vial: 8
Acq On : 16 Aug 2001 10:00 pm Operator: cjones S
Sample : ICAL SVSTD120 Inst : HPSV-2
Misc : 2078-78-1 Multiplr: 1.00
MS Integration Params: rteint.p
Quant Time: Aug 17 11:06 2001 Quant Results File: temp.res

Method : C:\HPCHEM\1\METHODS\081601S2.M (RTE Integrator)
Title : GC-MS Semivolatiles SOP no. 505
Last Update : Thu Aug 16 12:07:49 2001
Response via : Multiple Level Calibration

MANUAL RE-INTEGRATION

- ☐ missed peak assignment
- ☐ assigned incorrect name to peak
- ☒ over-integrated peak's area
- ☒ under-integrated peak's area
- ☐ other

initials [illegible] date 09.01.2001



2 - RE-INTEGRATED ENDPOINT @ 7.53 min — FOR CONSISTENCY.

(29) Benzoic acid (T)

7.53min 121.47ng/uL m

response 285083

Ion	Exp%	Act%
122.00	100	100
105.00	122.50	94.91#
77.00	91.00	88.06
0.00	0.00	0.00

"TAILING"

P4819.D 081601S2.M Fri Aug 17 11:06:22 2001

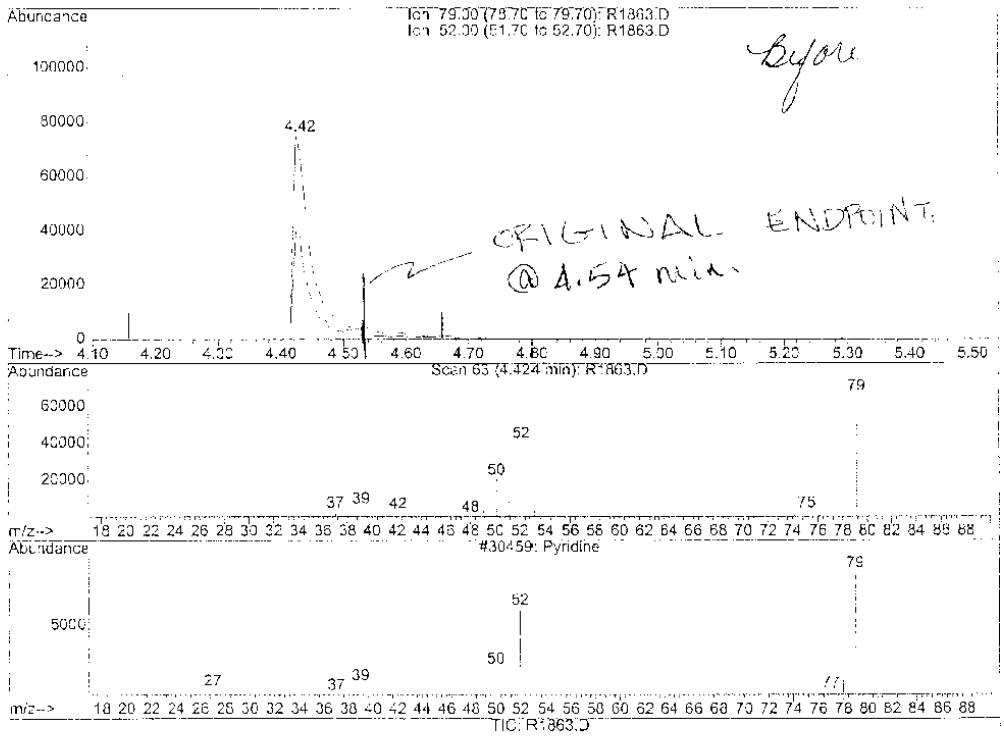
(8)

FIGURE 4.1.2 (E)

Quantitation Report (Qedit)

Data File : C:\HPCHEM\1\DATA\061401\R1863.D Vial: 4
Acq On : 14 Jun 2001 3:30 pm Operator: gcherg SOP
Sample : SVSTDC10 Inst : HPSV 3
Misc : 2078-61-8 Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Jun 14 16:57 2001 Quant Results File: temp.res

Method : C:\HPCHEM\1\METHODS\061401S3.M (RTE Integrator)
Title : GC/MS Semivolatiles SOP no. 506
Last Update : Thu Jun 14 19:11:50 2001
Response via : Multiple Level Calibration



(2) Pyridine (T)

4.42min 9.83ng/uL

response 15033

Ion	Exp%	Act%
79.00	100	100
52.00	47.40	49.11
0.00	0.00	0.00
0.00	0.00	0.00

"TAILING"

(9)

R1863.D 061401S3.M Thu Jun 14 19:23:21 2001

FIGURE 4.1.7 (d)

Quantitation Report (Qedit)

Data File : C:\HPCHEM\1\DATA\061401\R1863.D Vial: 4
Acq On : 14 Jun 2001 3:30 pm Operator: gcherg SOP
Sample : SVSTD010 Inst : HPSV-3
Misc : 2078-61-8 Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Jun 14 19:23 2001 Quant Results File: temp.res

Method : C:\HPCHEM\1\METHODS\061401S3.M (RTE Integrator)
Title : GC-MS Semivolatiles SOP no. 506
Last Update : Thu Jun 14 19:11:50 2001
Response via : Multiple level Calibration

After ICC 06.15.01

@4.78 min — RE-INTEGRATED ENDPOINT — INTENT IS CONSISTENCY W/ HIGHER CONC STDS + SPLS.

(2) Pyridine (T)

4.42min 11.22ng/uL m

response 171616

Ion	Exp%	Act%
78.00	100	100
52.00	47.40	43.02
0.00	0.00	0.00
0.00	0.00	0.00

"TAILING"

MANUAL RE-INTEGRATION

- ☐ missed peak assignment
- ☐ assigned incorrect name to peak
- ☒ over-integrated peak's area
- ☒ under-integrated peak's area
- ☐ other

initials CH date 06.01.2001

R1863.D 061401S3.M Thu Jun 14 19:23:26 2001

(10)

FIGURE 4.1.3(a)

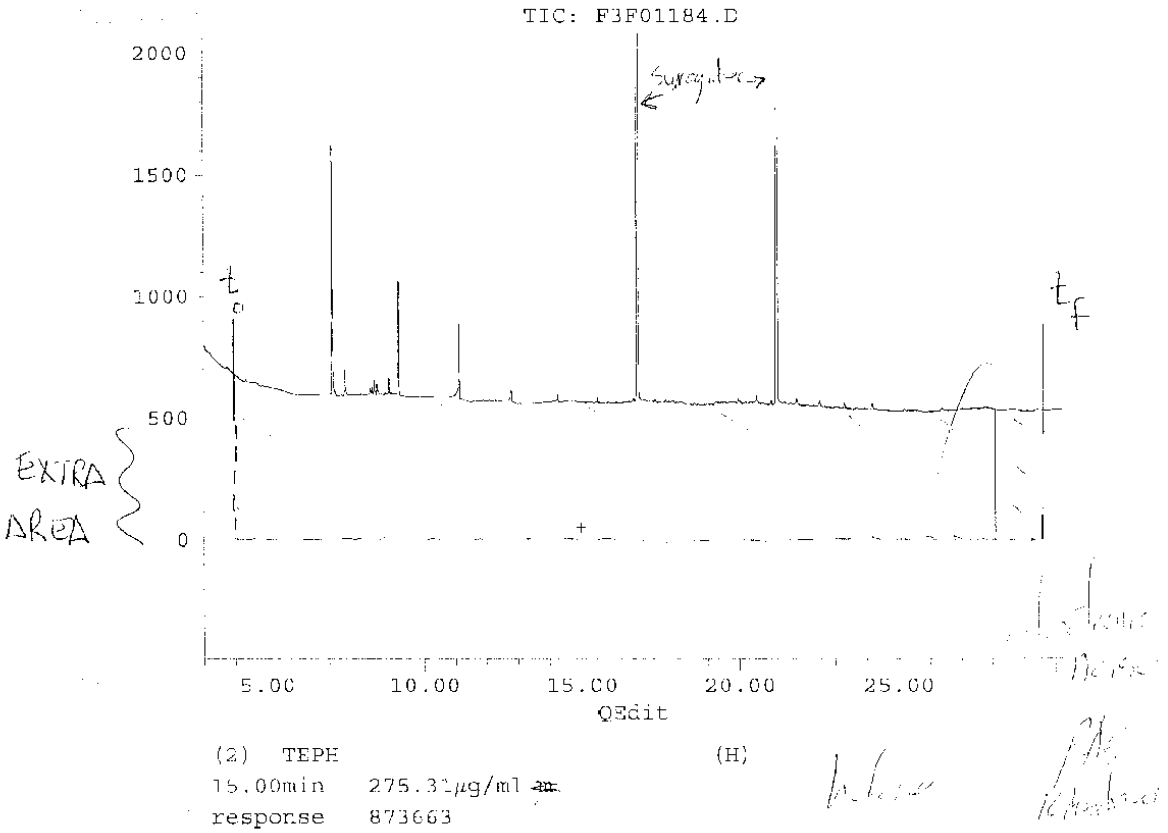
Quantitation Report

Data File : C:\HPCHEM\5\DATA\03082C01\F3F01184.D
Acq On : 09 Mar 01 02:15 PM
Sample : EX010224-4MB
Misc :
Quant Time: Mar 9 15:00 19101

Vial: 35
Operator: Mathiesen Fu
Inst : FUELS3
Multiplr: 1.00

Method : C:\HPCHEM\5\METHODS\D030801.M
Title : Total Extractable Petroleum Hydrocarbons
Last Update : Thu Mar 08 17:13:33 2001
Response via : Multiple Level Calibration

BEFORE



(2) TEPH (H)
15.00min 275.31µg/ml
response 873663

(+) - Expected Retention Time
F3F01184.D D030801.M Sat Mar 10 08:31:58 2001

(11)

FIGURE 4.1.3(b)

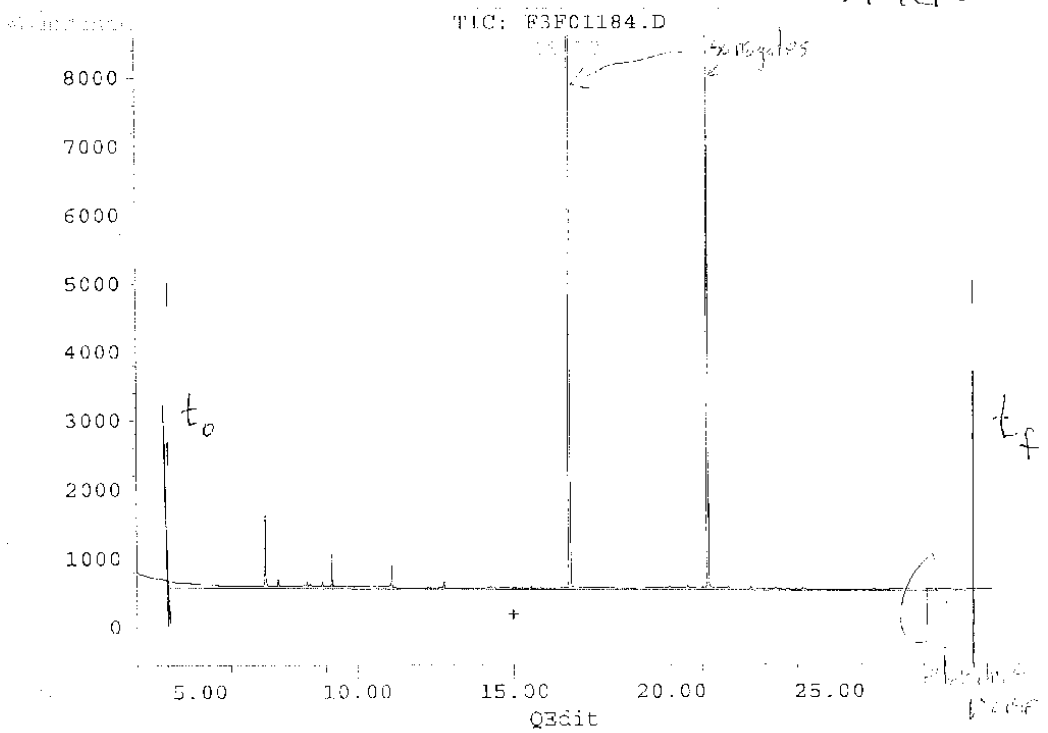
Quantitation Report

Data File : C:\HPCHEM\5\DATA\03082001\F3F01184.D
Acq On : 09 Mar 01 02:15 PM
Sample : EX010224-4MB
Misc :
Quant Time: Mar 10 8:22 1910

Vial: 35
Operator: Mathiesen Fu
Inst : FUELS3
Multiplr: 1.00

Method : C:\HPCHEM\5\METHODS\D030801.M
Title : Total Extractable Petroleum Hydrocarbons
Last Update : Thu Mar 08 17:13:33 2001
Response via : Multiple Level Calibration

AFTER



(2) TEPH (H)
15.00min -57.11µg/ml m
response 56685

MANUAL RE-INTEGRATION

- ☐ missed peak assignment
- ☐ assigned incorrect name to peak
- ☒ over-integrated peak's area
- ☐ under-integrated peak's area
- ☐ other

EXTRA AREA DELETED --

t_o and t_f UNCHANGED

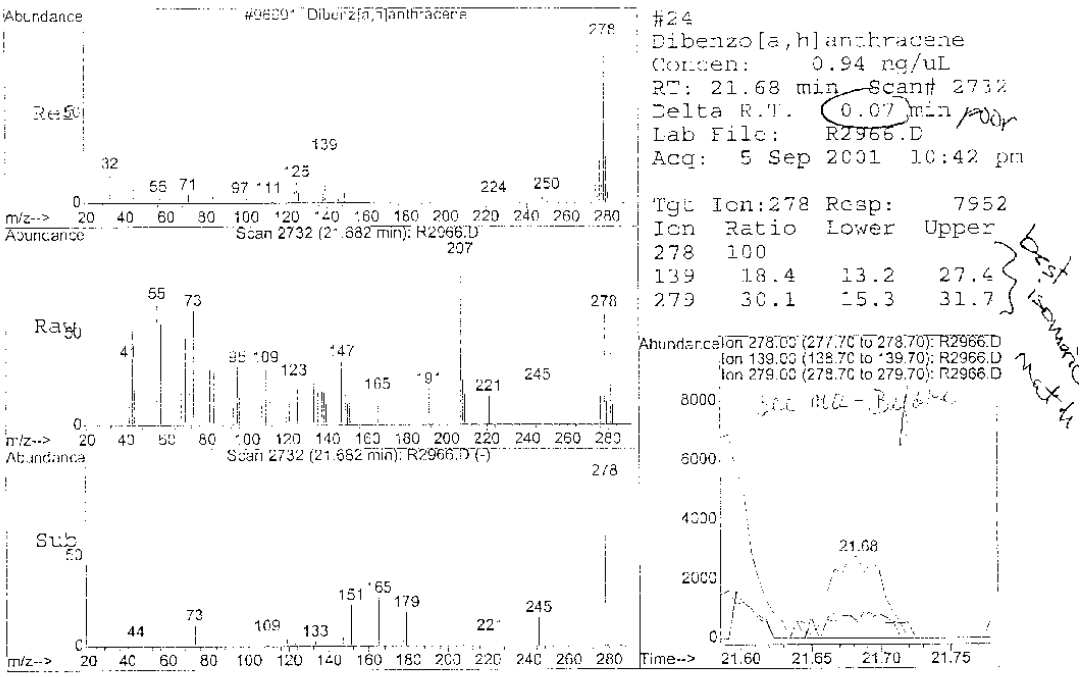
initials MA date 09.01.2001

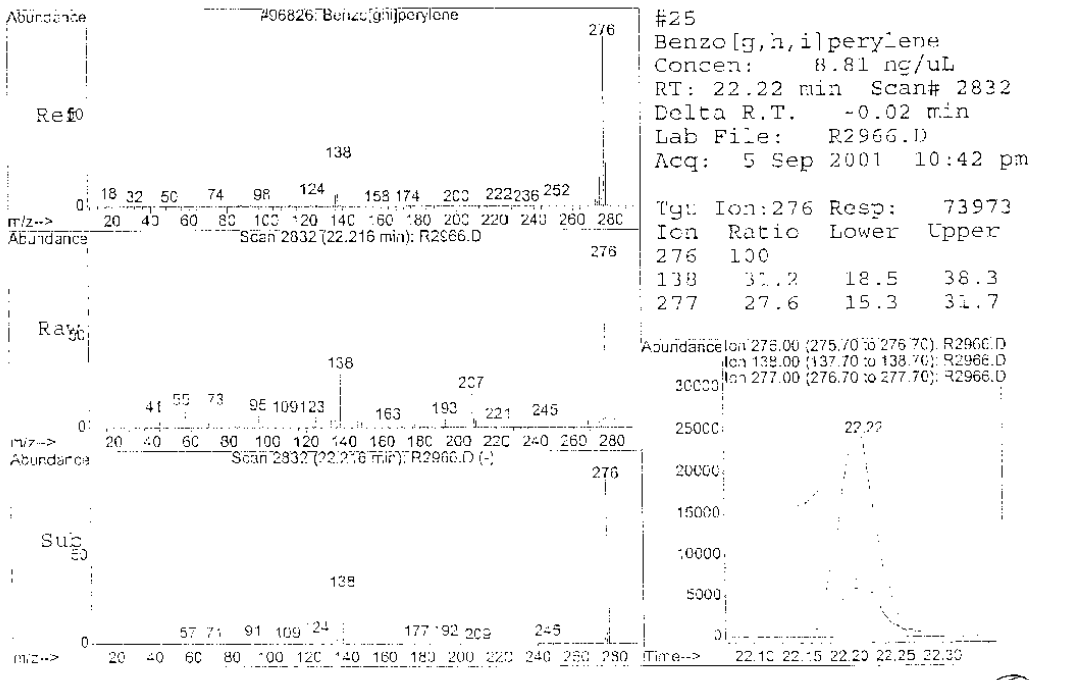
(+) = Expected Retention Time
F3F01184.D D030801.M Sat Mar 10 08:23:48 2001

(12)

BEFORE

FIGURE 4.1.4(9)





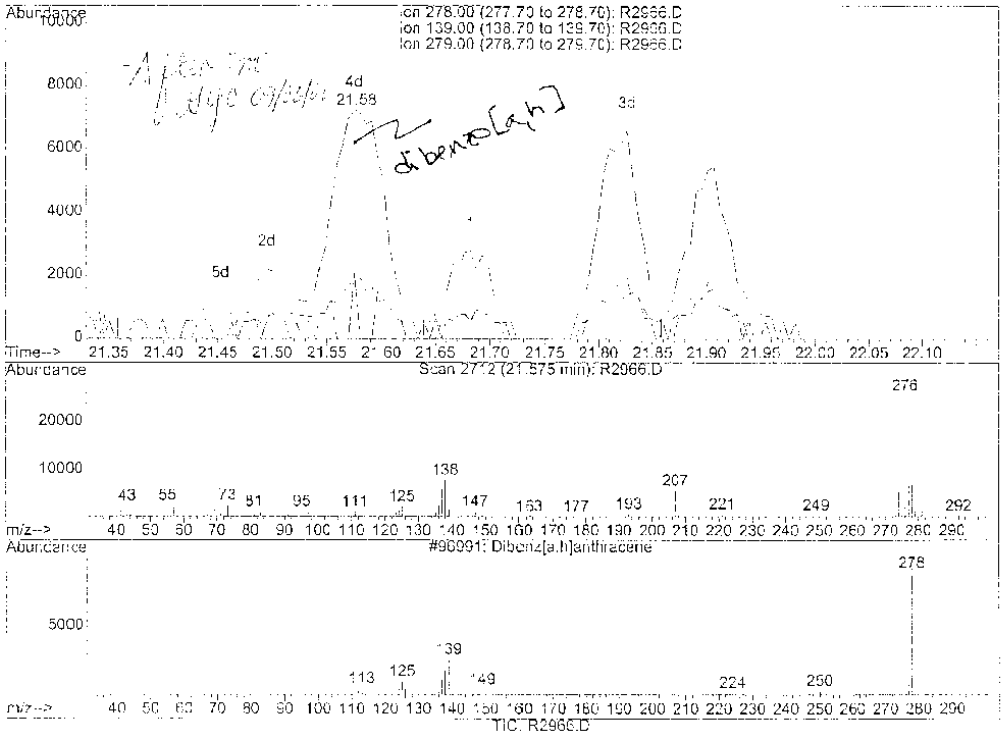
13

AFTER

Quantitation Report (Qedit) FIGURE 4.1.4(b)

Data File : C:\HPCHEM\1\DATA\090501\R2966.D Vial: 13
Acq On : 5 Sep 2001 10:42 pm Operator: gcheng SOP
Sample : 0108214-11 Inst : HPSV-3
Misc : SOIL 8270PAH Multiplr: 1.00
MS Integration Params: RTEINT.P
Quant Time: Sep 6 11:49 2001 Quant Results File: temp.res

Method : C:\HPCHEM\1\METHODS\090501P3.M (RTE Integrator)
Title : GC-MS Semivolatiles SOP no. 506
Last Update : Thu Sep 06 10:59:48 2001
Response via : Multiple Level Calibration



(24) Dibenzo[a,h]anthracene (TV)

21.58min 2.89ng/uL m

response 24489

Ion	Exp%	Act%
278.00	100	100
139.00	20.30	5.37#
279.00	23.50	9.79#
0.00	0.00	0.00

MANUAL RE-INTEGRATION

- ☐ missed peak assignment
- ☒ assigned incorrect name to peak
- ☐ over-integrated peak's area
- ☐ under-integrated peak's area
- ☐ other _____

initials WA date 09.01.2001

R2966.D 090501P3.M Thu Sep 06 11:51:48 2001

(14)