Yard 520 Sampling and Analysis Plan

Pines Area of Investigation
AOC II
Docket No. V-W-'04-C-784

Appendix C
Quality Assurance Project Plan

ENSR Corporation
June 3, 2005

Document Number 01776-020-150A

QUALITY ASSURANCE PROJECT PLAN
YARD 520 SAP
PINES AREA OF INVESTIGATION
Revision 0
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ACRONYMS

AOC I	Administrative Order on Consent, 2003 and as amended, 2004; Docket No. V-W-03-730
AOC II	Administrative Order on Consent, 2004; Docket No. V-W-'04-C-784
bgs	Below Ground Surface
CAS	Columbia Analytical Services
CCB	Coal Combustion By-product
CCBK	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
COC	Chain of Custody
COPC	Constituents of Potential Concern
COPEC	Constituents of Potential Ecological Concern
CVAAS	Cold Vapor Atomic Absorption Spectrometry
DOE	Department of Energy
DOT	Department of Transportation
DQL	Data Quality Level
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
ENSR	ENSR Corporation
ERA	Ecological Risk Assessment
ESL	Ecological Screening Level
FS	Feasibility Study
FSP	Field Sampling Plan
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GEL	General Engineering Laboratory
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GPS	Global Positioning System
HASP	Health and Safety Plan
HHRA	Human Health Risk Assessment
HRGC/HRMS	High Resolution Gas Chromatography/High Resolution Mass Spectrometry
IATA	International Air Transport Association
ICAO	International Civil Aviation Organization
ICBK	Initial Calibration Blank
ICP	Inductively Coupled Plasma

ICV	Initial Calibration Verification
ID	Identification
IDL	Instrument Detection Limit
IDEM	Indiana Department of Environmental Management
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
MDA	Minimum Detectable Activity
MDL	Method Detection Limit
mg/kg	Milligram per Kilogram
mg/L	Milligram per Liter
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MSR	Management System Review
NIPSCO	Northern Indiana Public Service Company
ORNL	Oak Ridge National Laboratory
OSWER	Office of Solid Waste and Emergency Response
PAH	Polynuclear Aromatic Hydrocarbon
PCDD	Polychlorinated Dibenzodioxin
PCDF	Polychlorinated Dibenzofuran
pCi/g	Picocuries per Gram
PE	Performance Evaluation
PRG	Preliminary Remediation Goal
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
QC	Quality Control
%R	Percent Recovery
RAL	Removal Action Level
RI	Remedial Investigation
RI/FS	Remedial Investigation and Feasibility Study
RL	Reporting Limit
RPD	Relative Percent Difference
RPM	Remedial Project Manager
RSD	Relative Standard Deviation
SAP	Sampling and Analysis Plan
SMS	Site Management Strategy
SOP	Standard Operating Procedure
SOW	Statement of Work

TAL	Target Analyte List
TBD	To Be Determined
TSA	Technical System Audit
ug/kg	Micrograms per Kilogram
US	United States
USEPA	United States Environmental Protection Agency

STANDARD CHEMICAL ABBREVIATIONS

Ac	Actinium
Al	Aluminum
Ag	Silver
As	Arsenic
B	Boron
Ba	Barium
Be	Beryllium
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
Fe	Iron
K	Potassium
Hg	Mercury
Li	Lithium
Mg	Magnesium
Mo	Molybdenum
Mn	Manganese
Na	Sodium
Ni	Nickel
Pa	Protactinium
Pb	Lead
Po	Polonium
Ra	Radium
S	Sulphur
Sb	Antimony
Se	Selenium
Si	Silicon
Th	Thorium
Tl	Thallium
U	Uranium
V	Vanadium
Zn	Zinc

DISCLAIMER

This document is a document prepared under a federal administrative order on consent and revised based on comments received from the U.S. Environmental Protection Agency (USEPA) on March 24, 2005. This revised document has not undergone formal review by USEPA. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of USEPA.

SECTION A – PROJECT MANAGEMENT

A1 Introduction

In April 2004, the United States Environmental Protection Agency (USEPA) and the Respondents (Brown Inc., Ddalt Corp., Bulk Transport Corp., and Northern Indiana Public Service Company [NIPSCO]), signed an Administrative Order on Consent (AOC II) (Docket No. V-W-'04-C-784) to conduct a Remedial Investigation and Feasibility Study (RI/FS) at the Pines Area of Investigation, or Area of Investigation, as set forth in Exhibit I to AOC II, located in the environs of the Town of Pines, Indiana.

In June 2004, the Respondents submitted the first major document for the RI/FS, a Site Management Strategy (SMS) document (ENSR, 2005a), which outlined a preliminary conceptual model, data gaps, and the strategy for certain elements of the RI/FS. A revised SMS, based on comments received from the USEPA, was submitted in September 2004, and conditionally approved by USEPA in November 2004. The final SMS was submitted in January 2005. The SMS serves as the basis for development of the RI/FS Work Plan (ENSR, 2005b), including the Field Sampling Plan (FSP), Quality Assurance Project Plan (QAPP), and other supporting documents.

The SMS indicates that a baseline human health risk assessment (HHRA) and ecological risk assessment (ERA) will be conducted to evaluate the potential human health and ecological risks of potential exposures to coal combustion by-product (CCB)-derived constituents present in samples of environmental media within the Area of Investigation. As part of the HHRA and ERA, the presence of CCB-derived constituents within the Area of Investigation will be evaluated, and a subset of the constituents identified as constituents of potential concern (COPCs) or constituents of potential ecological concern (COPECs) will be quantitatively evaluated in the risk assessment. The purpose of the Yard 520 Sampling and Analysis Plan (SAP) is to determine whether additional parameter groups, specifically, polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs), radionuclides, and polynuclear aromatic hydrocarbons (PAHs), may be present at concentrations of potential concern in CCBs in the Area of Investigation, and whether the analytical program for the RI should include any of these constituents.

This document provides the QAPP for the Yard 520 sampling program, and incorporates the SAP by reference. The QAPP presents the organization, objectives, planned activities, and specific quality assurance/quality control (QA/QC) procedures associated with the Yard 520 sampling program. Specific protocols for sampling, sample handling and storage, chain-of-custody, and laboratory and

field analyses are described. All QA/QC procedures are structured in accordance with applicable technical standards, USEPA's requirements, regulations, and guidance. This QAPP has been prepared in accordance with the USEPA QAPP policy as presented in the Region 5 Instructions on the *Preparation of a Superfund Division Quality Assurance Project Plan* (USEPA, 2000a).

A2 Project Schedule

The proposed schedule for implementation of the Yard 520 SAP is outlined below.

Activity	Time frame (after USEPA approval)
Sample Collection Activities	1 month
Laboratory Analysis[1]	1 to 2 months
Data Validation	2 to 3 months
Database Activities[2]	3 to 4 months
Data Submittal[3]	3 to 5 months

[1] Analytical turnaround time is 3 weeks.
[2] Includes data upload of validated data to project database.
[3] Submission of electronic data as required by AOC II, no interpretation or analysis.

A3 Distribution List

The QAPP, and any subsequent revisions, will be distributed to the personnel shown on the Distribution List that immediately follows the approval page.

A4 Project/Task Organization

The lines of authority and communication specific to the Quality Assurance (QA) program for the Yard 520 sampling program are presented in Figure A-1. The responsibilities of key personnel are described below.

A4.1 Management Responsibilities

USEPA Region 5 Remedial Project Manager (RPM)

The USEPA Region 5 RPM, Timothy Drexler, has the overall responsibility for all phases of the investigation.

Respondents' Project Managers

The Project Managers for the individual Respondents are Dan Sullivan of NiSource and Val Blumenfeld of Brown Inc. They will be responsible for project direction and decisions concerning technical issues and strategies, budget, and schedule.

ENSR Project Manager

The ENSR Project Manager, Lisa JN Bradley, will be responsible for technical, financial, scheduling matters. The ENSR Project Manager also will be responsible for project coordination between the Respondents and USEPA as required.

ENSR Task Manager

The ENSR Task Manager, Paytha Elliot, will have the overall responsibility for implementing the sampling activities described in the Yard 520 SAP. Specific responsibilities of the ENSR Task Manager will include, but not be limited to, the following:

- Providing personnel and equipment for sampling activities;
- Ensuring that ENSR's associates perform their designated duties in accordance with the SAP and the Health and Safety Plan (HASP);
- Ensuring required QA/QC procedures are properly implemented and documented;
- Ensuring that sampling activities are properly carried out and completed within the approved schedule;
- Communicating any request for modifications, if necessary, to the approved SAP to the ENSR Project Manager; and
- Promptly notifying the ENSR Project Manager if unforeseen field conditions and/or analytical issues are encountered that affect achievement of the project data quality objectives (DQOs).

ENSR Health and Safety Manager

The ENSR Regional Health and Safety Manager, Joseph Sanders, will be responsible for ensuring the objectives of ENSR's corporate health and safety program are carried out. The ENSR Regional Health

and Safety Manager will also be responsible for the coordination and communication of health and safety issues for field personnel.

A4.2 Quality Assurance Responsibilities

ENSR Project QA Officer

The ENSR Project QA Officer, Debra McGrath, has the overall responsibility for quality assurance. The ENSR Project QA Officer communicates directly to the ENSR Project Manager on matters pertaining to QA, data validation, and laboratory analyses. Specific responsibilities include:

- Reviewing and approving the QAPP;
- Reviewing and approving QA procedures, including any modifications to existing approved procedures;
- Ensuring that QA audits of the various phases of the project are conducted as required by this QAPP;
- Providing technical assistance to project staff;
- Ensuring that data validation/data assessment is conducted in accordance with the QAPP; and
- Reporting on the adequacy and efficiency of the QA Program to the ENSR Project Manager and recommending corrective actions, if necessary.

ENSR Data Validator

The ENSR Data Validator reports to the ENSR Project QA Officer. The Data Validator is responsible for validating the analytical data in accordance with the QAPP.

USEPA Region 5 Quality Assurance Plan Reviewer

The USEPA Region 5 Quality Assurance Plan Reviewer, Warren Layne, has the responsibility to review and approve all QAPPs. Additional USEPA responsibilities include:

- Conducting external performance and system audits of the selected laboratory;
- Evaluating results of performance evaluation sample data; and

- Reviewing and evaluating analytical field and laboratory procedures.

A4.3 Laboratory Responsibilities

Columbia Analytical Services (CAS), located in Rochester, NY will perform the chemical analyses of all native soil and suspected CCB materials. CAS Rochester will oversee the analyses of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by the CAS laboratory in Houston, TX. The radionuclide analyses will be performed by General Engineering Laboratories LLC (GEL), located in Charleston, SC.

Laboratory Director

The Laboratory Directors are ultimately responsible for the data produced by their laboratories. Specific responsibilities include:

- Ensuring that resources are adequately allocated to specific projects and that sufficient staffing, equipment, and support are provided.
- Overseeing the technical operations' Section Managers and the Laboratory QA Manager.

The CAS Laboratory Director is Mike Perry. Carey Bocklet serves in this role for GEL.

Section Manager

The individual Laboratory Section Managers report to the Laboratory Director. Specific responsibilities include:

- Supervision of employees within their specific analytical area;
- Overseeing and supporting the development, implementation, and operation of analytical technical programs;
- Coordinating sample flow and for implementing QA and QC activities in their area of authority; and
- Working in conjunction with the Laboratory QA Manager to ensure that QA/QC recommendations are reviewed and that corrective actions are implemented and effective.

Laboratory QA Manager

The Laboratory QA Manager reports to the Laboratory Director. Specific responsibilities include:

- Monitoring the QA and QC activities of the laboratory to ensure conformance with authorized policies, procedures, and good laboratory practices, and recommending improvements as appropriate;
- Informing specific Section Managers of noncompliance with the approved QA/QC criteria;
- Ensuring that all records, logs, Standard Operating Procedures (SOPs), project plans, and analytical results are maintained in a retrievable fashion; and
- Ensuring that SOPs and other controlled documents are distributed to all appropriate laboratory personnel for use in the project.

The CAS QA Manager is Lisa Reyes. Robert Pullano is the GEL QA Manager.

Laboratory Project Manager

The Laboratory Project Manager is ultimately responsible for all laboratory analyses and is the primary point of contact for issues surrounding this QAPP, including resolving technical problems, modifications to SOPs, etc. The Laboratory Project Manager is responsible for the coordination of routine day-to-day project activities including project initiation, status tracking, data review and requests, inquiries and general communication related to the project. Final approval of data packages is the responsibility of the Laboratory Project Manager.

The Laboratory Project Manager is the primary point of contact between the laboratory and ENSR. Specific responsibilities of the Laboratory Project Manager include:

- Monitoring analytical and QA project requirements for a specified project;
- Acting as a liaison between ENSR and the laboratory staff;
- Reviewing project data packages for completeness and compliance to ENSR needs;
- Monitoring, reviewing, and evaluating the progress and performance of projects; and
- Providing all analytical deliverables to ENSR in a timely manner.

The Laboratory Project Managers are Janice Jaeger (CAS) and Edith Kent (GEL).

Laboratory Staff

Laboratory staff includes the Laboratory Director, the Laboratory Supervisor, Section Managers, Group Leaders, Chemists, and Technicians. These individuals are responsible for the actual preparation, analysis, reporting, and reviewing of the analytical information. The analysts are responsible for understanding and implementing SOPs and for conformance with the Quality Assurance Program. Analysts are also responsible for the initial review of data that they generate during the analytical process and the identification of nonconforming events within their scope of concern. These individuals, in conjunction with laboratory management and the laboratory QA Manager, may also be responsible for implementing corrective actions.

Sample Receipt Personnel

Sample receipt personnel, or sample custodians, are responsible for the initial assessment of samples, including documentation of sample conditions upon receipt, and accuracy and clarity of requests on the Chain-of-Custody (COC) forms that accompany the samples. Sample receipt personnel, along with laboratory management, are responsible for the resolution and documentation of any issues associated with the initial assessment of the sample integrity on arrival. Resolution may include discussions with laboratory personnel, client contacts, and/or laboratory management.

Following the initial assessment, sample receipt personnel are responsible for the accurate input of sample information into the data management system and the assignation of laboratory batch identification and individual sample identifiers. Sample receipt personnel also initiate the internal COC process and begin laboratory tracking.

Sample custodians are Greg Esmerian (CAS) and Pete Wilber (GEL).

A4.4 Field Responsibilities

ENSR Field Operations Leader

The ENSR Field Operations Leader (Paytha Elliott) has overall responsibility for completion of all field activities in accordance with the SAP and QAPP and is the communication link between the ENSR Project Manager and the field team. Specific responsibilities of the ENSR Field Operations Leader include:

- Coordinating activities in the field;
- Assigning specific duties to field team members;
- Mobilizing and demobilizing of the field team and subcontractors to and from the Yard 520 sampling area;
- Directing the activities of subcontractors during the Yard 520 sampling program;
- Resolving any logistical problems that could potentially hinder field activities, such as equipment malfunctions or availability, personnel conflicts, or weather dependent working conditions; and
- Implementing field QC including issuance and tracking of measurement and test equipment; the proper labeling, handling, storage, shipping, and COC procedures used at the time of sampling; and control and collection of all field documentation.

ENSR Field Staff

The field staff reports directly to the ENSR Field Operations Leader. The responsibilities of the field staff include:

- Collecting samples, conducting field measurements, and decontaminating equipment according to documented procedures stated in the SAP;
- Ensuring that field instruments are properly operated, calibrated, and maintained, and that adequate documentation is kept for all instruments;
- Collecting the required QC samples and thoroughly documenting QC sample collection;
- Ensuring that field documentation and data are complete and accurate; and
- Communicating and documenting any nonconformance or potential data quality issues to the ENSR Field Operations Leader as well as documenting subsequent corrective action and effectiveness of corrective action.

Subcontractors

ENSR subcontractors will provide drilling services. The subcontractors are responsible for conducting the work in accordance with the project plans and contractual agreements and for communicating any

issues concerning the budget, schedule, or achievement of the technical specifications to the ENSR Field Operations Leader.

A5 Problem Definition and Background

A5.1 Site Background and Description

Between 2000 and 2004, the Indiana Department of Environmental Management (IDEM) and USEPA responded to homeowners by conducting sampling of private water supply wells in a portion of the Town of Pines. In some of these samples, boron (B) and molybdenum (Mo) were detected at concentrations above USEPA's Removal Action Levels (RALs) (USEPA, 1998). These concentrations in groundwater are suspected by the USEPA to be derived from coal combustion by-products (CCBs). CCBs have been disposed at a permitted Restricted Waste Facility known as Yard 520, and CCBs are suspected to have been used as fill in areas within the Area of Investigation outside of Yard 520. Yard 520 is operated by Brown Inc., and most of the CCBs at Yard 520 were generated during combustion of coal at NIPSCO's Michigan City Generating Station.

To address the boron and molybdenum detections above the USEPA RALs, the Respondents agreed to extend the municipal water service from Michigan City to selected portions of the Town of Pines. This agreement was documented in an Administrative Order on Consent, referred to as AOC I. Additional sampling of other private wells indicated some concentrations near or exceeding USEPA RALs. To address this, the Respondents voluntarily approached the USEPA to discuss extending the municipal water service to a larger area under an amendment to AOC I.

The Respondents also signed AOC II to conduct an RI/FS for the Area of Investigation, as identified in the Order. Under the Statement of Work (SOW), Task 1 is the preparation of a Site Management Strategy (SMS). A draft SMS document, which outlined a preliminary conceptual model, data gaps, and the strategy for certain elements of the RI/FS, was submitted in June 2004. The SMS was conditionally approved by USEPA in November 2004. Task 1 of the SOW was completed with the submission of the Final SMS in January 2005 (ENSR, 2005a). The SMS serves as the basis for development of the RI/FS work plans prepared under Task 2 of the SOW.

A5.2 Problem Definition

The SMS indicates that a baseline human health risk assessment (HHRA) and ecological risk assessment (ERA) will be conducted to evaluate the potential human health and ecological risks of potential exposures to CCB-derived constituents present in samples of environmental media within the

Area of Investigation. As part of the HHRA and ERA, the presence of CCB-derived constituents within the Area of Investigation will be evaluated, and a subset of the constituents identified as cconstituents of potential concern (COPCs) or constituents of potential ecological concern (COPECs) will be quantitatively evaluated in the risk assessment. The purpose of this Yard 520 SAP is to determine whether additional parameter groups, specifically, PCDDs/PCDFs, radionuclides, and PAHs, may be present at concentrations of potential concern in CCBs in the Area of Investigation, and whether the analytical program for the RI should include any of these constituents.

A6 Project/Task Description

The objective for this SAP is to determine whether or not PCDDs/PCDFs, radionuclides, and PAHs are present in the CCBs within the Pines Area of Investigation at concentrations warranting further evaluation. Background samples will also be collected from areas where there are no CCBs to determine site-specific background concentrations. To accomplish this objective, the following tasks will be implemented:

- Borings will be advanced at Yard 520 to collect samples of CCBs. Sample locations will be selected to ensure that the material encountered consists of CCBs. During sampling, any other materials encountered (e.g., interim cover) will be omitted from the sample submitted for laboratory analysis. Yard 520 was selected as the location for the sample collection because it is known to have received CCBs, and the CCBs within Yard 520 are less likely to have been affected by other sources, including atmospheric deposition and roadway runoff. The Type III (South) Area of Yard 520 was selected as the location for the sample collection because this area was known to have received CCBs only. The Type II (North) Area received a small amount of other wastes, some of which may not be easily distinguishable from CCBs (such as steel slag). The sample locations in the Type III (South) Area were laid out in two triangular grids.
- Surface soil samples will be collected from within or nearby the Area of Investigation to determine site-specific background conditions. Samples will consist of native soils. Surface soil samples will be collected to document the typical background exposure point concentrations within the Area of Investigation.
- All samples will be submitted for laboratory analysis of PCDDs/PCDFs, radionuclides, and PAHs. Background samples will also be analyzed for target analyte list (TAL) metals plus boron, molybdenum, sulfur, and silicon. Additional volume will be also be collected (approximately 1 to 2 liters in volume) and retained and may be used for later visual inspection and chemical/physical analysis, if needed.

- The concentrations of constituents in the CCB samples will be compared to concentrations in background samples and to risk-based screening levels. The screening levels to be used are presented in the HHRA Work Plan and the ERA Work Plan, which are components of the overall RI/FS Work Plan (ENSR, 2005b).

A6.1 Project/Task Summary

The number of field and QC samples that will be collected for each analytical parameter is presented in Table A-1. A summary of analytical parameters by medium is presented in Table A-2. Target compounds for each analyses are presented with their respective laboratory reporting limits, method detection limits (MDLs), and data quality levels (DQLs) in Tables A-3 (PAHs), Table A-4 (PCDDs/PCDFs), A-5 (radionuclides), and A-6 (metals and sulfur).

All data generated through field activities or through the analytical program will be reviewed internally through a tiered review process and validated prior to reporting. All of the data will be validated, either as full or limited validation. The data will be validated using USEPA and Department of Energy (DOE) guidance in conjunction with ENSR data validation protocols (provided as an attachment). The USEPA and DOE guidance will be modified to reflect any differences in analytical methodology and to incorporate the project-specific acceptance criteria defined in Section A7 of this QAPP or the method criteria, whichever is more stringent. A complete description of the data verification and data validation procedures to be used is included in Section D1 of this QAPP.

ENSR's Project QA Officer and/or Field Operations Leader will be responsible for internal technical system audits (TSAs) to verify that field sampling procedures and field sampling measurements are properly followed. Additionally, laboratory TSAs are conducted periodically by ENSR's Project QA Officer or other qualified pesonnel. TSAs are conducted at project start up and then periodically while the project is under way. A detailed discussion of the QA assessments that will be performed during the course of the project is provided in Section C1 of this QAPP.

Validated project data will be compared to the project measurement criteria (Relative Percent Difference (RPD) values for precision, for example). Sensitivity, representativeness, and completeness assessments will also be performed. A complete description of how validated data will be reconciled with DQOs and how the overall assessment of the data will be performed is included in Section D3 of this QAPP.

QA reports will be generated by the ENSR Project QA Officer on an as-needed basis. A complete listing and description of all documents and reports that will be generated and maintained in the project files is included in Section A9 of this QAPP.

A7 Quality Objectives and Criteria for Measurement Data

A7.1 Data Quality Objectives

The Yard 520 investigation will consist of a sampling program and chemical analyses of suspected CCB materials and native soil. The field investigation is designed to provide information on the presence of PCDDs/PCDFs, PAHs, and radionuclides in CCBs in the Area of Investigation. Therefore, the sampling and analysis program incorporates the following QA elements:

- A sampling program designed to obtain sufficient data to determine levels of constituents in media of interest,
- The use of sample collection and handling procedures that will ensure the representativeness and integrity of the samples,
- An analytical program designed to generate definitive data of sufficient quality and sensitivity to meet the project objectives (see Section A5.2), and
- Data deliverables that will allow verification and validation of the data and reproducibility of the reported results.

At the completion of the work outlined in the SAP, it is possible that additional information may be needed to meet RI objectives. At this time, it is not possible to anticipate what additional work may be needed, as it is dependent on the results of the activities proposed. AOC II allows for additional phases of work. If needed, a memorandum documenting the need for additional data will be submitted to USEPA, per AOC II Section VIII. 32.

The design of the Yard 520 SAP was based on the DQO process (USEPA, 2000b), a multi-step, iterative process that ensures that the type, quantity, and quality of environmental data used in decision-making is appropriate for its intended application. This process is summarized below.

DQO Step	Description
State the Problem	As documented in the Site Management Strategy, CCBs from within the Area of Investigation may contain PCDDs/PCDFs, radionuclides, and/or PAHs.
Identify the Decision	The purpose of collecting samples from Yard 520 is to confirm whether or not PCDDs/PCDFs, radionuclides, and PAHs are present in the CCBs from within the Area of Investigation above levels of potential concern. If they are not present above levels of potential concern, no further evaluation of these constituents will be needed during the RI/FS. Background samples will be analyzed for PCDDs/PCDFs, radionuclides, PAHs, TAL metals plus boron, molybdenum, sulfur, and silicon. This information will be used in the RI/FS for purposes such as characterization and risk assessment.
Identify Inputs to the Decision	Samples of CCBs will be collected from the Type III (South) Area of Yard 520. The concentrations of PCDDs/PCDFs, radionuclides, and PAHs in samples will be determined. Background samples will be collected from the Area of Investigation where no CCBs are suspected to be present to determine site-specific background concentrations.
Define Study Boundaries	Samples will be collected from the Type III (South) Area of Yard 520. Background samples will be collected from the ground surface within or nearby the Area of Investigation where no CCBs are suspected to be present.
Develop a Decision Rule	The concentration of PCDDs/PCDFs, radionuclides, and PAHs in the CCB samples will be compared to concentrations in background samples and to risk-based screening levels. Additional evaluation of these constituents in the RI/FS will be performed only if concentrations in CCBs are above both site-specific background and risk-based screening levels.
Specify Decision Error Limits	A formal statistical design will not be developed for this sampling. However, the data will be considered acceptable if they are collected according to this Sampling and Analysis Plan and they meet the appropriate quality objectives for field and laboratory activities.
Optimize the Study Design	Since a formal statistical design is not being utilized, the iterative process for optimizing the sample design will not be used. However, CCB sample locations were established based on a triangular grid. Ten samples from each medium (CCBs and background surface soil) will be collected to enable statistical evaluation of results.

A7.2 Data Quality Objectives for Measurement Data

The principal objectives of the QAPP pertain to the collection of data that are sufficient to evaluate the possible presence of CCB-derived constituents in the media of interest. Therefore, the quality of the data gathered in this project can be defined in terms of the following elements: precision, accuracy, completeness, sensitivity, and representativeness. These elements are discussed below.

Precision

Precision is a measure of the degree to which two or more measurements are in agreement. Field precision is assessed through the collection and measurement of field duplicates at a rate of one

duplicate per ten field samples. Precision will be measured through the calculation of relative percent difference (RPD). The objectives for field precision RPDs are 25% RPD for aqueous samples and 30% RPD for solid samples.

Precision in the laboratory is assessed through the calculation of RPD for duplicate samples, either as matrix spike/matrix spike duplicates (MS/MSDs) or as laboratory duplicates, depending on the method. Precision control limits for laboratory analyses are provided in Table A-7.

Accuracy

Accuracy is the degree of agreement between the observed value and an accepted reference or true value. Accuracy in the field is assessed through the use of equipment blanks and through the adherence to all sample handling, preservation, and holding time requirements. Field rinsate blanks will be collected at a rate of one per ten samples (or less) collected per sampling event. The objectives for equipment blanks are shown in Table A-7.

Laboratory accuracy is assessed through the analysis of MS/MSDs, laboratory control samples (LCSs), and the subsequent determination of percent recoveries (%Rs). Accuracy control limits are given in Table A-7.

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. "Normal conditions" are defined as the conditions expected if the sampling plan was implemented as planned.

Field completeness is a measure of the amount of valid samples obtained during all sampling for the project. The field completeness objective is greater than 90 percent.

Laboratory completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. The laboratory completeness objective is greater than 95 percent.

Representativeness

Representativeness is the extent to which the sampling design adequately reflects the environmental conditions of the site. The data will be considered representative of the site if all sampling and analysis activities are conducted according to the Yard 520 SAP and QAPP.

Sensitivity

Sensitivity of analytical data is demonstrated by the laboratory reporting limits. The target reporting limits for the constituents to be analyzed are presented in Tables A-3 (PAHs), A-4 (PCDDs/PCDFs), A-5 (radionuclides) and A-6 (metals and sulfur). These tables also contain the DQLs, which were developed using human health and ecological risk screening levels, including USEPA Region 9 Preliminary Remediation Goals (PRGs), USEPA Region 5 Ecological Screening Levels (ESLs), and Oak Ridge National Laboratory (ORNL) Phytotoxicity Screening Values. The target reporting limits were selected in part by consideration of the DQLs to be achieved and in part by consideration of the likelihood of detectable concentrations above the DQL, as in the case of several of the metals, the actual ability of the laboratory to attain reporting limits at the DQLs, and the cost-effectiveness of implementing additional, more sensitive methods in the initial stage of the investigation. The laboratories will use their most recent detection limit study results to report analytical results.

Alternative analytical methods will be evaluated if the need arises, and the QAPP will be amended, if necessary.

A8 Special Training/Certification

A8.1 Training

Field personnel will be experienced in the suspected CCB materials and native soil sampling techniques proposed in the SAP. Data validators will be familiar with the USEPA and DOE validation guidelines. Additionally, prior to starting work, personnel will be given instruction specific to the project, covering the following areas:

- Organization and lines of communication and authority;
- Overview of the SAP;
- QAPP requirements;
- QA/QC requirements;
- Documentation requirements; and
- Health and safety requirements.

Instructions will be provided and documented by the ENSR Project Manager, ENSR Task Manager, ENSR Field Operations Leader, ENSR Health and Safety Officer, and ENSR Project QA Officer.

Personnel responsible for shipping samples will also be trained in the appropriate regulations, e.g., Department of Transportation (DOT), International Civil Aviation Organization (ICAO), and International Air Transport Association (IATA).

A8.2 Certifications

Laboratories utilized for routine testing of native soils and suspected CCB materials will have appropriate certification for the test methods.

As specified in the RI/FS Work Plan (ENSR, 2005b), the RI Task Manager, Ms. Perry, is a Professional Geologist licensed to practice in Indiana. This certification will be maintained throughout the project.

A9 Documents and Records

A9.1 Project Files

The project files will be the central repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this QAPP. ENSR is the custodian of the project files and will maintain the contents of the project files for the investigation, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews in a secured, limited access area and under custody of the ENSR Project Manager.

The project files will include at a minimum:

- Field logbooks;
- Field data and data deliverables;
- Photographs;
- Drawings;
- Sample collection logs;
- Laboratory data deliverables;

- Data validation reports;
- Data assessment reports;
- Progress reports, QA reports, interim project reports, etc.; and
- All custody documentation (COC forms, airbills, etc.).

Electronic versions of correspondence, reports, drawings, and statistical analyses will be stored in the project-specific network file. The original electronic data deliverables (EDDs) received from the laboratories, and the project database, will also be stored on the network, which is backed up daily and periodically archived off-site in accordance with ENSR Information Management policy.

Records associated with this sampling will be retained with all the project records for the duration of AOC II and for a minimum of 10 years after its termination. USEPA, NIPSCO and Brown Inc. will be notified in writing 90 days prior to destruction of the records (per AOC II Section XIII. 44.).

A9.2 Field Records

Field logbooks will provide the primary means of recording the data collection activities performed during the sampling activities. As such, entries will be described in as much detail as possible so that persons going to the field could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in the project files when not in use. Each logbook will be identified by a project-specific document number.

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be entered. The names of visitors to the work location, and the purpose of their visit, will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in permanent ink, signed, and dated and no erasures or obliterations will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark and the correct entry will be made, signed and dated by the person making the correction. Whenever a sample is collected, or a measurement is made, a detailed description of the sampling location, which includes compass and distance measurements, or latitude and longitude information (e.g., obtained by using a Global Positioning

System (GPS)) unit will be recorded. All equipment used to make measurements will be identified, along with the date of calibration. The coordinate system that the GPS unit displays will be recorded.

Information specific to sample collection will include:

- Sample identification number;
- Time and date of sample collection;
- Sample description (color, texture, etc.);
- Samplers' initials;
- Requested analyses;
- Depth of sample interval below ground surface (bgs) as measured with a steel measuring tape; and
- Location (GPS coordinates and description).

To streamline data recording, information will be recorded on standardized forms when this approach is logical. Examples of these forms are presented in the field SOPs included in Appendix B of the SAP.

Descriptions of geologic materials and CCBs will be logged in accordance with Indiana guidance (IDEM, 1988).

Representative photographs of sample locations will be taken with a digital camera and the camera picture frame number, date, direction facing, and subject will also be recorded in the logbook.

COC forms will be maintained as part of the field records as described in Section B3.3.1.

A9.3 Laboratory Records and Deliverables

Laboratory data reduction procedures will be performed according to the following protocol. All information related to analysis will be documented in controlled laboratory logbooks, instrument printouts, or other approved forms. All entries that are not generated by an automated data system will be made neatly and legibly in permanent, waterproof ink. Information will not be erased or obliterated. Corrections will be made by drawing a single line through the error and entering the correct information

adjacent to the cross-out. All changes will be initialed, dated, and, if appropriate, accompanied by a brief explanation. Unused pages or portions of pages will be crossed out to prevent future data entry. Analytical laboratory records will be reviewed by the supervisory personnel on a regular basis, and by the Laboratory QA Manager periodically, to verify adherence to documentation requirements.

Data deliverables will be provided within standard turnaround time (21 calendar days). The laboratory will provide at least one copy of a hard copy report and one copy of an EDD. The format of the EDD is discussed in Section B11. The hard copy data package will be equivalent to a Contract Laboratory Program (CLP) deliverable, i.e., consisting of all the information presented in a CLP package, including CLP-like summary forms. This information is summarized below:

- Analytical report;
- Chain of custody information;
- Notes concerning special client requests and telephone records;
- Instrument raw data;
- Standards information;
- Preparation information;
- Sample results, including units;
- Detection limits and reporting limits, including units;
- Results for MS/MSDs, method or preparation/calibration blanks, LCSs, laboratory duplicates, inductively coupled plasma (ICP) serial dilutions, and ICP interference check samples; and
- Raw data for samples and laboratory QC samples, including labeled and dated chromatograms/spectra.

A10 References

This QAPP was prepared using the following documents:

DOE. 1982. EML Procedures Manual. HASL-300.

DOE. 1997. Evaluation of Radiochemical Data Usability.

ENSR. 2005a. Site Management Strategy. Pines Area of Investigation. AOC II. Docket No. V-W-'04-C-784. January 2005.

ENSR. 2005b. RI/FS Work Plan, Pines Area of Investigation, Volumes 1 through 7. May 23, 2005.

IDEM. 1988. Technical Guidance Document, Volume 1 – Requirements for Describing Unconsolidated Deposits. Indiana Department of Environmental Management. Draft, Revised November 18, 1988.

USEPA. 1992. Specifications and Guidance for Contaminant-Free Sample Containers. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. December 1992.

USEPA. 1997a. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846. Third Edition. United States Environmental Protection Agency. May 1986, revised June 1997.

USEPA. 1997b. *Region 5 Standard Operating Procedure for Validation of CLP Organic Data*. April 1991, Revised February 1997.

USEPA. 1998. Clarification to the 1994 Revised Interim Soil Lead Guidance for CERCLA Sites and RCRA Corrective Action Facilities. OSWER Directive 9200.4-27. August 1998.

U.S. EPA. 1999. *Contract Laboratory Program, National Functional Guidelines for Organic Data Review*. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. October 1999.

USEPA. 2000a. *Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan.* United States Environmental Protection Agency, Region 5. Revision 0. June 2000.

USEPA. 2000b. Guidance for the Data Quality Objectives Process, EPA QA/G-4. EPA/600/R-96/055. U.S. Environmental Protection Agency. August, 2000.

USEPA. 2001. *EPA Requirements for Quality Assurance Project Plans*, EPA QA/R-5. United States Environmental Protection Agency, Quality Staff. March 2001.

USEPA. 2002. *National Functional Guidelines for Dioxin Data Review*. United States Environmental Protection Agency.

USEPA. 2004. *Contract Laboratory Program, National Functional Guidelines for Inorganic Data Review*. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. October 2004.

SECTION B – MEASUREMENT/DATA ACQUISITION

B1 Sampling Process Design

The rationale for the sample design is provided in Sections 4.2 (CCBs) and 4.3 (background soil samples) of the SAP.

B2 Sampling Methods Requirements

B2.1 Field Measurements

The field measurements taken in conjunction with the native soil and suspected CCB sampling at Yard 520 will be limited to GPS measurements. These measurements will be taken as described in Section 4.4.1 of the SAP

B2.2 Sampling Procedures

The SOPs that will be utilized for sampling of CCBs and native soils are listed below and provided in Appendix B of the SAP.

- ENSR SOP No. 7116Pines – Subsurface Soil Sampling by GeoProbe™ Methods
- ENSR SOP No. 7110Pines – Surface Soil Sampling

B2.2.1 GeoProbe™ Sampling of Yard 520 Locations

CCB materials will be collected in accordance with Section 4.4.3 of the SAP.

B2.2.2 Surface Soil Sampling at Background Locations

Surface soils will be collected in accordance with Section 4.4.4 of the SAP.

B2.3 Cleaning and Decontamination of Equipment/Sample Containers

Guidance on equipment decontamination is included in ENSR SOP No. 7600Pines (Appendix B of the SAP). In general, equipment used will be decontaminated using the following procedure:

- Tap water rinse to remove gross contamination;
- Non-phosphate and non-borate detergent water rinse;
- Tap water rinse;
- 10% nitric acid rinse (metal sample locations only);
- Tap water rinse;
- Pesticide-grade methanol rinse (twice);
- Deionized water rinse;
- Air dry or wrap in aluminum foil for later use.

If sample collection tools consist entirely of disposable implements and bowls, then no equipment decontamination is necessary for these items.

Non-disposable and non-dedicated sampling equipment will be decontaminated prior to initial use and between samples. The effectiveness of the decontamination procedures is measured by collecting and analyzing equipment blank samples.

Sample containers will be purchased new. Specifications for these containers are addressed in Section B3.1.

B2.4 Inspection and Acceptance Requirements for Supplies/Sample Containers

For this project, critical supplies for field activities will be tracked through ENSR's system in the following manner.

Critical Supplies and Consumables	Inspection Requirements and Acceptance Criteria	Responsible Individual
Sample bottles	Visually inspected upon receipt for cracks, breakage, and cleanliness. Must be accompanied by certificate of analysis.	Field Operations Leader
Chemicals and reagents	Visually inspected for proper labeling, expiration dates, appropriate grade.	Field Operations Leader
Sampling equipment	Visually inspected for obvious defects, damage, and contamination.	Field Operations Leader
Field measurement equipment	Functional checks to ensure proper calibration and operating capacity.	Field Operations Leader

Supplies and consumables not meeting acceptance criteria will initiate the appropriate corrective action. Corrective measures may include repair or replacement of measurement equipment, and/or notification of vendor and subsequent replacement of defective or inappropriate materials. All actions will be documented in the project files.

The laboratory system of inspection and acceptance of supplies and consumables is discussed in Section B9.

A description of the procedures and documentation activities employed to ensure field and sampling equipment are available in working order when needed is provided in Section B6 of this QAPP.

B3 Sample Handling and Custody

B3.1 Sample Containers, Preservation, and Holding Times

Sample bottles and chemical preservatives will be provided by the laboratory. The containers will be cleaned by the manufacturer (to be determined) to meet or exceed all analyte specifications established in the latest USEPA's *Specifications and Guidance for Contaminant-Free Sample Containers* (USEPA, 1992). Certificates of analysis will be provided with each lot of containers and maintained on file to document conformance to USEPA specifications. All sample bottles and chemical preservatives provided by the laboratory will be shipped with a custody seal affixed to the outside of the cooler. The laboratory will be responsible for maintaining the certificates of analysis for the bottleware and for tracking which lot number of containers were provided with each shipment.

A summary of sample container, preservation, and holding time requirements is presented in Table B-1.

B3.2 Sample Labeling

Immediately upon collection, each sample will be labeled with an adhesive label. Samples will be assigned unique sample identifications (IDs) based on an alphanumeric code that identifies the matrix, location, date, and type of sample, as described below.

- Name of location in five digits (e.g., SS002, etc.). These location names will correspond to logs of the geologic materials, as well as sample locations posted on maps. Names of borings at Yard 520 will start with CB001; background samples will start at SS001.

- Single letter signifying depth of sample (A, B, C, etc. for samples taken at increasing depth, X if this field is not being used). The actual depth measured in the field in feet will be recorded in the field records.

- Two letters signifying the sample matrix (CB for CCBs, SS for surface soil).

- Sampling date consisting of the number corresponding to the month (2 digits), day (2 digits) and year (2 digits), for example, 061405 for samples collected on June 14, 2005.

- Letter denoting the type of sample. Codes for this field include: S – sample; D – field duplicate; B – equipment rinsate blank.

No dashes will be used to separate fields. An example sample ID for this sampling would be: SS001ASS101105D indicating a surface soil sample collected at location SS001 on October 11, 2005. This sample is a field duplicate, and the A represents the sample depth. The sample depth of 0 to 6 inches for this surface sample will be recorded in the field logbook.

Samples designated as MS/MSDs will be noted as such in the comments field of the chain of custody (COC) form.

The sample identification code will be recorded on the label, in the field logbook, on the COC form, and will be carried through the analytical process to reporting. An example of a sample label is included as Figure B-1.

B3.3 Custody Procedures

Custody is one of several factors that are necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for

admissibility: relevance and authenticity. Sample custody is addressed in two parts: field sample collection and laboratory analysis.

A sample is considered to be under a person's custody if:

- The item is in the actual possession of a person;
- The item is in the view of the person after being in actual possession of the person;
- The item was in the actual physical possession of the person but is locked up to prevent tampering; and
- The item is in a designated and identified secure area.

B3.3.1 Field Custody Procedures

The field sampler (to be determined) is personally responsible for the care and custody of the samples until they are transferred or dispatched properly. Field procedures have been designed such that as few people as possible will handle the samples.

All sample containers will be identified by the use of adhesive sample labels (Figure B-1) which will include sample numbers, project identification (i.e., ENSR project number), date/time of collection, preservation, sampler's initials, and type of analysis. The sample numbering system is presented in Section B.3.2 of the QAPP. Sample labels will be completed for each sample using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample label because the pen would not function in freezing weather.

Samples will be accompanied by a properly completed COC form. The sample numbers and locations will be listed on the COC form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents the transfer of custody of samples from the sampler to another person, to the permanent laboratory, or to/from a secure storage location. ENSR SOP No. 1007Pines – Chain-of-Custody Procedures (Appendix B of the SAP) includes additional information. An example COC form is presented as Figure B-2.

All sample shipments will be accompanied by the COC record identifying the contents. The original record will accompany the shipment, and the pink and yellow copies will be retained by the sampler and placed in the project files.

Samples will be properly packaged on ice at 4 ± 2°C for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed custody record enclosed in and secured to the inside top of each sample box or cooler. Shipping containers will be locked and secured with strapping tape and custody seals for shipment to the laboratory. The custody seals will be attached to the front right and back left of the cooler and covered with clear plastic tape after being signed by field personnel. The cooler will be strapped shut with strapping tape in at least two locations. ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples (Appendix B of the SAP) includes a detailed description of these procedures.

If the samples are sent by common carrier, the waybill will be retained as part of the permanent documentation. Commercial carriers are not required to sign off on the custody forms since the custody forms will be sealed inside the sample cooler and the custody seals will remain intact.

Whenever possible, samples will be transported to the laboratory the same day the samples are collected in the field by overnight carrier.

B3.3.2 Laboratory Custody Procedures

Samples will be received and logged in by a designated sample custodian or his/her designee. Upon sample receipt, the sample custodian will:

- Examine the shipping containers to verify and document that the custody tape is intact;
- Examine all sample containers for damage;
- Determine if the temperature required for the requested testing program has been maintained during shipment and document the temperature on the COC form;
- Compare samples received against those listed on the COC;
- Verify that sample holding times have not been exceeded;
- Examine all shipping records for accuracy and completeness;
- Determine sample pH (if applicable) and record on COC;
- Sign and date the COC immediately (if shipment is accepted) and attach the waybill;
- Note any problems associated with the coolers and/or samples on the cooler receipt form and notify the Laboratory Project Manager, who will be responsible for contacting the client;

- Attach laboratory sample container labels with unique laboratory identification and test; and
- Place the samples in the proper laboratory storage.

Following receipt, samples will be logged in according to the following procedure:

- The samples will be entered into the laboratory information management system (LIMS). At a minimum, the following information will be entered: project name or identification, unique sample numbers (both client and internal laboratory), type of sample, required tests, date and time of laboratory receipt of samples, and field ID provided by field personnel.
- The appropriate laboratory personnel will be notified of sample arrival.
- The completed COC, waybills, and any additional documentation will be placed in the project file.

Specific details of laboratory custody procedures for sample receiving, sample identification, sample control, record retention, and data purging to the final evidence file are described in the laboratory SOPs (Attachment A).

B4 Analytical Methods

Non-radionuclide samples will be analyzed by:

Columbia Analytical Services
1 Mustard Street
Rochester, NY 14609
585-288-5380
Contact: Janice Jaeger

CAS Rochester will subcontract the PCDDs/PCDF analysis to their Houston, TX facility:

Columbia Analytical Services
10655 Richmond Avenue
Suite 130A
Houston, TX 77042
713-266-1599
Contact: Karen Verschoor

Radionuclide analyses will be performed by:

General Engineering Laboratories, LLC
2040 Savage Road
Charleston, SC 29417
843-769-7385
Contact: Edith Kent

B4.1 Field Analytical Procedures

There are no field analyses associated with the Yard 520 sampling.

B4.2 Laboratory Analytical Procedures

The laboratories named above will implement the project-required SOPs. These laboratory SOPs for sample preparation and analysis are based primarily on SW-846 Third Edition, November 1986 (including all final updates through Final Update III; USEPA, 1997a) and the DOE HASL 300 method (DOE, 1982). These SOPs provide sufficient detail and are specific to the analyses to be performed for this investigation. Attachment A of the QAPP contains the laboratory SOPs. Laboratory Instrument Detection Limits (IDLs) and MDLs are listed in Tables A-3 (PAHs), A-4 (PCDDs/PCDFs), A-5 (radionuclides) and A-6 (metals and sulfur). The CAS Rochester laboratory SOP for performing MDL studies is included in Attachment A-1; no SOP for MDL studies is included for GEL or CAS Houston as MDL studies are not applicable to radionuclide or PCDD/PCDF parameters. A list of the laboratory SOPs included in Attachment A is provided in the Table B-2.

Table B-2 summarizes the analyte groups of interest, appropriate laboratory SOP number, and reference method for the organic and inorganic analytes evaluated in the investigation.

B4.3 List of Project Target Constituents and Detection Limits

A complete listing of project target constituents and reporting limits for each analyte group listed in Table B-2 can be found in Tables A-3 (PAHs), A-4 (PCDDs/PCDFs), A-5 (radionuclies) and A-6 (metals and sulfur) of this QAPP.

B4.4 List of Associated Quality Control Samples

The analytical laboratory SOPs listed in Table B-2 includes a QC section which addresses the minimum QC requirements for the analysis of specific analyte groups. Section B5 of this QAPP contains a complete list of the associated QC samples for every analyte group.

B5 Quality Control

QC is the overall system of technical activities that measure the attributes and performance of a process, item or service against defined standards to verify that they meet the stated requirements. Acceptable limits of performance are defined for each QC check and sample used in the project.

B5.1 Field

QC samples will include equipment blanks, field duplicates, and MS/MSDs. These samples will be collected as described below:

B5.1.1 Equipment Blanks

Equipment blanks will be prepared by routing laboratory grade and organic free water (provided by the laboratory) through non-disposable or non-dedicated sampling equipment after equipment decontamination and before field sample collection. Equipment blanks will be collected for all solid samples collected with non-disposable or non-dedicated equipment and will be collected at a frequency of one per 10 samples collected using a particular type of equipment. Equipment blanks will be analyzed for the same parameters as their associated samples.

B5.1.2 Field Duplicates

Field duplicates will be collected at a frequency of one field duplicate for every 10 or less investigative samples of each medium. Field duplicates will be collected by alternately filling two sets of identical sample containers from the interim container used to collect the sample. All field duplicates will be analyzed for the same parameters as their associated samples. Whenever possible, collection of field duplicate samples will occur at locations where detectable concentrations of target analytes are expected.

B5.1.3 MS/MSDs

MS/MSD or MS/duplicate samples will be collected at a frequency of one for every 20 or less investigative samples. For those samples designated as MS/MSDs or MS/duplicates, sufficient additional volume (based on the individual laboratory's requirements) will be collected.

B5.2 Analytical Quality Control Checks

Each laboratory has a QC program in place to ensure the reliability and validity of the analysis performed at the laboratories. All analytical procedures are documented in writing as SOPs and each SOP includes a QC section which addresses the minimum QC requirements for the procedure. The internal QC checks differ slightly for each individual procedure but in general the QC requirements include the following:

- Blanks (method, reagent/preparation, instrument, calibration);
- MS/MSDs;
- Surrogate spikes;
- Tracers;
- Laboratory duplicates;
- Laboratory control samples (LCSs);
- Internal standard areas;
- Inductively coupled plasma (ICP) interference checks; and
- Serial dilutions.

Table B-3 summarizes the QC for each method.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

This section describes the procedures used to verify that all instruments and equipment are maintained in sound operating condition and in working order when needed.

B6.1 Field Equipment Maintenance

Specific preventative maintenance procedures to be followed for field equipment are based on those recommended by the manufacturer. The GPS will be checked and calibrated daily before use and periodically throughout the day as specified in Section 4.4.1 of the SAP. Critical spare parts will be kept on site to reduce potential downtime. Backup instruments and equipment will be available on site or within 1-day shipment to avoid delays in the field schedule.

B7 Laboratory Instrument Preventative Maintenance

As part of their QA manual, a routine preventative maintenance program is conducted by the laboratories to minimize the occurrence of instrument failure and other system malfunctions. Designated laboratory employees regularly perform routine scheduled maintenance and repair of (or coordinate with the vendor for repair of) all instruments. All maintenance that is performed is documented in the laboratories' operating record. All laboratory instruments are maintained in accordance with manufacturer's specifications. Table B-4 provides the frequency with which components of key analytical instruments will be serviced. Table B-5 provides a summary of the monitoring of laboratory equipment.

B8 Instrument/Equipment Calibration and Frequency

Calibration is required to ensure that field and laboratory analytical systems are operating correctly and functioning at the proper sensitivity to meet established detection limits.

B8.1 Field Instruments

Field instrumentation is limited to the GPS unit. Calibration of this instrument will be performed according to the manufacturer's instructions and Section 4.4.1 of the SAP. All calibration procedures will be documented in the field records. Calibration records will include the date/time of calibration, name of the person performing the calibration, reference standard used, and the results of the calibration.

B8.2 Analytical Instrumentation

Calibration procedures for laboratory instruments will consist of initial calibrations, initial calibration verifications, and continuing calibration verification. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria, and the

conditions that will require recalibration. This information is summarized in Table B-6. The SOPs are included as Attachment A.

The laboratory maintains documentation for each instrument which includes the following information: instrument identification, serial number, date of calibration, analyst, calibration solutions, and the samples associated with these calibrations.

B9 Inspection/Acceptance of Supplies and Consumables

Inspection and acceptance procedures for field materials are discussed in Section B2.4.

The laboratory system of inspection and acceptance of supplies and consumables includes:

- Approval of purchase orders by the Laboratory Director or Section Managers to ensure that materials and supplies of the appropriate quality are ordered.
- Purchasing of supplies, reagents/chemicals, and bottles through established and approved vendors.
- Inspection of items upon receipt for damage, completeness of the order, and conformance to specifications.
- Logging in of each lot of reagents and verifying the quality through batch analysis.

B10 Non-Direct Measurements

The suitability of use of non-direct data (historical reports, maps, literature searches, previously collected analytical data) will be evaluated and limitations potentially placed on its use. Section B10 of the RI/FS QAPP (ENSR, 2005b) presents a summary of the criteria and limitations.

The data necessary to meet the Yard 520 sampling program objectives specified in Section A7 will be generated during the sampling program proposed in the Yard 520 SAP and will come from the following sources:

- Field records (sample locations, sample observations);
- Field measurements (GPS);
- Laboratory results for chemical and radionuclide analyses of soil and CCBs.

The data collected under this QAPP have been designed to be of sufficient quality to meet the program objectives.

B11 Data Management

Data management operations include data recording, validation, transformation, transmittal, reduction, analysis, tracking, storage and retrieval.

All data will be entered into an EQuIS database system. EDDs provided by the laboratories will be in an EQuIS-compatible format that will minimize manipulation of the data.

Upon receipt from the laboratory, hard copy and EDD will be assigned a unique identifier, which allows the data to be tracked from receipt, through validation, to data loading and storage. The electronic data will be imported into the EQuIS database system concurrent with the data validation process. Data qualifiers generated during data validation will be entered manually. Definitions of all qualifiers are maintained within the database structure and electronic versions of the data validation reports are stored in the project files maintained on the network drive. Data collected in the field will also be entered into the system and integrated with laboratory data.

As data are loaded into the system, a variety of quality checks are performed to ensure data integrity. These checks include:

- Audits to ensure that laboratories reported all requested analyses;
- Checks that all analytes are consistently and correctly identified;
- Reviews to ensure that units of measurement are provided and are consistent;
- Queries to determine that any codes used in the database are documented properly;
- Reports to review sample definitions (depths, dates, locations);
- Proofing manually entered data against the hard-copy original; and
- Reports to review groupings of sampling locations and coordinate systems.

Records of the checks are maintained on file.

At a minimum, the database will contain the following fields:

Sample identifier;
Sample location;
Sample media type;
Sampling date;
Analysis date;
Laboratory analysis identifier (test method);
Analyte name;
Concentration value;
Quantitation limits;
Measurement units; and
Data qualifiers.

Data will be loaded into a "temporary" database until data validation is complete, at which time the database will be finalized. Any changes made to the database after finalization will be documented, including a description of the change, date of change, person responsible, and reason for change.

Once all data quality checks are performed, the data will be exported to a variety of formats to meet project needs. Cross-tab tables showing concentrations by sample location will be prepared. Statistical analyses will be performed as required. Data can be accessed by a variety of mapping and visualization tools.

The project database will be maintained on a secure network drive which is backed up regularly. Access to the database will be limited to authorized users and will be controlled by password access. Data will be retained in accordance with the requirements stated in Section A9.1 of this QAPP.

SECTION C – PROJECT ASSESSMENT/OVERSIGHT

C1 Assessment and Response Actions

This section identifies the number, frequency, and type of planned assessment activities that will be performed for the project.

C1.1 Assessments

C1.1.1 Field Sampling Technical System Audit

The USEPA is responsible for the external TSAs of field activities, including field sampling and measurements, for compliance of requirements specified for this project.

The Project QA Officer and/or Field Operations Leader of ENSR will be responsible for periodic internal TSAs to verify that field sampling procedures and field sampling measurements are properly followed. The TSAs will include examination of

- Field sampling records;
- Field measurement results;
- Field instrument operating and calibration records;
- Sample collection, handling, and packaging procedures;
- QA procedures;
- Chain-of-custody; and
- Sample documentation, etc.

An example of the checklist used during the internal field TSAs is included as Figure C-1. Results of internal field TSAs will be documented in the QA reports to management (Section C2).

C1.1.2 Fixed Laboratory Technical System Audits

The USEPA is responsible for the external TSAs of laboratory activities for compliance of requirements specified for this project.

System audits are performed as described in the laboratory QA manual for internal auditing or as required by accreditation authorities.

Laboratory TSAs are conducted at project start up and then periodically as the project progresses, by ENSR or another qualified party, as part of their analytical subcontractor monitoring program. The laboratory TSA includes a review of the following areas:

- QA organization and procedures;
- Personnel training and qualifications;
- Sample log-in procedures;
- Sample storage facilities;
- Analyst technique;
- Adherence to laboratory SOPs and project QAPP;
- Compliance with QA/QC objectives;
- Instrument calibration and maintenance;
- Facility security;
- Bottleware preparation;
- Waste management;
- Data archival;
- Data recording, reduction, review, and reporting; and
- Cleanliness and housekeeping.

An example of the laboratory TSA checklist is included as Figure C-2.

Preliminary results of the systems audit will be discussed with the Laboratory Director, Laboratory Project Manager, and Laboratory QA Manager. A written report that summarizes audit findings and recommends corrective actions will be prepared and submitted to the Laboratory Director for response, and to the ENSR Project Manager. The results of the audit, including resolution of any deficiencies, will be included in the QA reports to management, as described in Section C2.

C1.1.3 Performance Evaluation Sample Assessment

Continuous performance auditing is accomplished through the regular use of LCS, matrix spike samples, duplicate samples, QC samples, proficiency testing, and through continuing calibration verification samples. Federal and State agencies may administer the proficiency testing.

Prior to the initiation of this project, the results of recent (within 6 months of the start of the program) Performance Evaluation (PE) samples analyzed by the laboratories will be reviewed and evaluated to ensure the acceptability of results for the parameters and matrices of interest. In the event that PE results are not current, not acceptable, or are not available for the target parameters, PE samples will be purchased from a commercial vendor and submitted to the laboratories for analysis prior to the start of the analytical program. The results of the PE samples analyzed by CAS and GEL will be reviewed by the ENSR Project QA Officer. Any deficiencies will be communicated to the ENSR Project Manager, the laboratory, and to the USEPA RPM. Corrective actions, which may include internal laboratory actions, the analysis of additional PE samples, or selection of another analytical subcontractor, will be documented in the QA reports to management (Section C2).

C1.1.4 Data Validation Technical System Audits

Data validation and verification will be performed as described in Section D2. In summary, a subset of data received will be subjected to a full data validation. The remainder of the data will receive a limited data validation. Data will be qualified and the results of the validation will be summarized in a validation memo. Each data validation technical systems audit will be reviewed by a validator other than the one performing the validation. This review will verify that the analytical deliverable package was complete and that any missing information requested from the laboratory was supplied, that validation worksheets were filled out accurately and completely, that validation actions were consistent with the validation guidelines established for this program and/or best professional judgment, and that the validation reports and data qualifiers accurately reflect the validation actions as documented on the worksheets.

C1.1.5 Data Package Technical System Audits

Audits of analytical data packages will be conducted for 100% of the packages received as part of the data validation process (Section D1). The review will include an evaluation of the package to ensure that (1) all required deliverables are provided, (2) each package contains the information necessary to reproduce the reported results, and (3) the QC acceptance criteria specified in the QAPP were met. Any deficiencies will be communicated to the laboratory and documented in the data validation reports.

C1.1.6 Management System Review (MSR)

On a quarterly basis, at a minimum, all projects within ENSR are reviewed. The review includes the following elements:

- Progress towards completion of the scope of work;
- Schedule versus approved plan;
- Costs and invoicing versus approved plan, including adherence to purchasing policy;
- Project task structure and associated budgets;
- Senior review assignments and documentation;
- Compliance with hard copy and electronic file management requirements;
- Client relationship development; and
- Future needs.

Documentation of the review will be maintained with the project files.

C1.2 Assessment Findings and Corrective Action Responses

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out-of-limit QC performance that can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation, and data assessment. All corrective action proposed and implemented should be documented in the QA reports to management (Section C2). Corrective action should only be implemented after approval by the ENSR Project Manager, or their designee.

C1.2.1 Field Corrective Action

Corrective action in the field may be needed when the sample frequency is changed (i.e., more/fewer samples, sample locations other than those specified in the QAPP, etc.), or when sampling procedures and/or field analytical procedures require modification, etc. due to unexpected conditions. The field team may identify the need for corrective action. The Field Operations Leader will approve the corrective action and notify the Project Manager. The Project Manager will approve the corrective measure. The Field Operations Leader will ensure that the field team implements the corrective action. Refer to ENSR No. SOP 100Pines - Field Change Order Procedures (Appendix B of the SAP) for further discussion of field corrective actions.

Corrective action resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The QA auditor will identify deficiencies and recommend corrective action to the Field Operations Leader. The Field Operations Leader and field team will perform implementation of corrective actions. Corrective action will be documented in QA reports to the project management team (Section C2).

Corrective actions will be implemented and documented in the field record book. Documentation will include:

- A description of the circumstances that initiated the corrective action;
- The action taken in response;
- The final resolution;
- Any necessary approvals; and
- Effectiveness of corrective action.

No staff member will initiate corrective action without prior communication of findings through the proper channels.

If at any time a corrective action issue is identified which directly impacts the project DQOs, the USEPA RPM will be notified.

C1.2.2 Laboratory Corrective Action

Corrective action in the laboratory is specified in laboratory SOPs and may occur prior to, during, and after initial analyses. A number of conditions such as broken sample containers, multiple phases, low/high pH readings, and potentially high concentration samples may be identified during sample log-in or analysis. Following consultation with laboratory analysts and supervisory personnel, it may be necessary for the Laboratory QA Manager to approve the implementation of corrective action. If the nonconformance causes project objectives not to be achieved, the ENSR Project QA Officer will be notified, who will in turn notify the ENSR Project Manager, who will communicate with the Respondent Project Managers and other members of the project team, as necessary. The USEPA RPM will also be notified in those cases where the nonconformance affects the achievement of the project DQOs.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action files, and in the narrative data report generated by the laboratory. If the corrective action does not rectify the situation, the laboratory will contact the ENSR Project QA Officer, who will determine the action to be taken and inform the appropriate personnel.

C1.2.3 Corrective Action During Data Validation and Data Assessment

The need for corrective action may be identified during either data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory. These actions are dependent upon the ability to mobilize the field team and whether the data to be collected are necessary to meet the required QA objectives. If the data validator or data assessor identifies a corrective action situation that impacts the achievement of the project objectives, the ENSR Project Manager will be responsible for informing the appropriate personnel, including the USEPA RPM.

C2 Reports to Management

QA reports will be prepared by the ENSR Project QA Officer and submitted on an as-needed basis to the ENSR Project Manager. QA reports will document any problems identified during the sampling and analysis programs and the corrective measures taken in response. The QA reports will include:

- All results of field and laboratory audits;
- Problems noted and actions taken during data validation and assessment; and

- Significant QA/QC problems, recommended corrective actions, and the outcome of corrective actions.

A summary of QA issues, audit findings, and significant nonconformances will be included in the status reports to the USEPA. A complete listing and description of all documents and reports that will be maintained in the project files is included in Section A9 of this QAPP.

SECTION D – DATA VALIDATION AND USABILITY

This element details the QA activities that will be performed to ensure that the collected data are scientifically defensible, properly documented, of known quality, and meet project objectives. Two steps are completed to ensure that project data quality needs are met:

- Data Verification/Validation
- Data Usability Assessment

D1 Data Review, Verification, and Validation

All data generated through field activities or through the analytical program, will be reduced and validated prior to reporting. No data will be disseminated until it has been subjected to the procedures summarized below.

D1.1 Field Data Review

The field data verification includes verification of sampling design, sample collection procedures and sample handling. Field data will be reviewed daily by the Field Operations Leader to ensure that the records are complete, accurate, and legible and to verify that the sampling procedures are in accordance with the protocols specified in the SAP and QAPP (refer to Section D2.1 for the specific elements reviewed).

D1.2 Internal Laboratory Review

Prior to the release of any data from the laboratory, the data will be reviewed and approved by laboratory personnel. The review will consist of a tiered approach (Section D2.2) that will include reviews by the person performing the work, by a qualified peer, and by supervisory and/or QA personnel.

D1.3 Validation of Analytical Data

Analytical data validation includes the verification and validation of analytical procedures, QC, calibration, and data reduction. Validation of the laboratory deliverables will be performed by ENSR. One hundred percent of the analytical data will receive validation, either as full or limited validation.

Ten percent of the data will be subjected to full validation and the remainder will receive limited validation. The ten percent of data selected for full validation will be representative of all matrices and analyses. It is expected that full validation will occur early in the validation process to identify any potential systematic problem and then will be performed periodically as needed.

For full validation, the data will be reviewed for the following, where applicable to the method:

- Completeness of deliverable;
- Technical holding times and sample preservation;
- Laboratory and field blank contamination;
- Surrogate recoveries;
- Tracer recoveries;
- Field and laboratory duplicates;
- MS/MSD recoveries and RPDs;
- Post-digestion spike recoveries;
- LCS recoveries;
- Initial and continuing calibrations;
- Instrument tuning,
- Internal standard performance,
- ICP serial dilution results;
- ICP interference check sample results; and
- Calculation and transcription verifications (i.e., verifying summary data against raw data).

Limited validation will be limited to information presented on summary forms and will include the following:

- Completeness of deliverable;
- Technical holding times and sample preservation;

- Laboratory and field blank contamination;
- Initial and continuing calibrations;
- Surrogate recoveries;
- Tracer recoveries;
- Field and laboratory duplicates;
- MS/MSD recoveries and RPDs; and
- LCS recoveries.

The discovery of significant anomalies or discrepancies during validation using the summary forms may result in an in-depth review of the raw data and the incorporation of additional review elements into the validation of all data.

D2 Validation and Verification Methods

D2.1 Field Data Verification

Field records will be reviewed by the Field Operations Leader to ensure that:

- Logbooks and standardized forms have been filled out completely and that the information recorded accurately reflects the activities that were performed.
- Records are legible and in accordance with good recordkeeping practices, i.e., entries are signed and dated, data are not obliterated, changes are initialed, dated, and explained.
- Sample collection, handling, preservation, storage, and shipping procedures were conducted in accordance with the protocols described in the SAP and QAPP, and that any deviations were documented and approved by the appropriate personnel.

D2.2 Laboratory Data Verification

Prior to being released as final, laboratory data will proceed through a tiered review process. Data verification starts with the analyst who performs a 100 percent review of the data to ensure the work was done correctly the first time. The data reduction and initial verification process must ensure that:

- Sample preparation and analysis information is correct and complete;
- Analytical results are correct and complete;
- Reporting limits are correct;
- The appropriate SOPs have been followed and are identified in the project records;
- Proper documentation procedures have been followed; and
- All nonconformances have been documented.

Following the completion of the initial verification by the analyst performing the data reduction, a systematic check of the data will be performed by an experienced peer or supervisor. This check will be performed to ensure that initial review has been completed correctly and thoroughly and will include a review of:

- Adherence to the requested analytical method SOP;
- Correctness of numerical input when computer programs are used (checked randomly);
- Correct identification and quantitation of constituents with appropriate qualifiers;
- Numerical correctness of calculations and formulas (checked randomly);
- Acceptability of QC data;
- Documentation that instruments were operating according to method specifications (calibrations, performance checks, etc.);
- Documentation of dilution factors, standard concentrations, etc.; and
- Sample holding time assessment.

A third-level review will be performed by the Laboratory Project Manager before results are submitted to clients. This review serves to verify the completeness of the data report and to ensure that project requirements are met for the analyses performed. A narrative to accompany the final report will be prepared by the Laboratory Project Manager.

D2.3 Validation of Analytical Deliverables

Validation will be performed as described in Section D.1.3 of the QAPP using the following documents in conjunction with ENSR data validation protocols (Attachment B):

- *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (USEPA, 2004),
- *Region 5, Standard Operating Procedure for Validation of CLP Organic Data* (USEPA, 1997b)
- *Contract Laboratory Program National Functional Guidelines for Organic Data Review* (USEPA, 1999),
- *Evaluation of Radiochemical Data Usability* (DOE, 1997); and
- *Contract Laboratory Program, National Functional Guidelines for Chlorinated Dioxin/Furan Data Review* (USEPA, 2002).

All guidelines will be modified to reflect any differences in analytical methodologies. Acceptance/rejection criteria will be the project-specific criteria defined in Section A.7 of this QAPP or the method criteria, whichever is more stringent.

Upon completion of the validation, a report will be prepared. This report will summarize the samples reviewed, elements reviewed, any nonconformances with the established criteria, and validation actions (including application of data qualifiers). Data qualifiers will be consistent with the USEPA guidelines as shown below:

- J - The result is an estimated quantity; the associated numerical value is the approximate concentration of the analyte in the sample.
- J+ - the result is an estimated quantity, but the result may be biased high (this qualifier will be used only for metals data).
- J- – The result is an estimated quantity, but the result may be biased low (this qualifier will be used only for metals data).
- UJ - The analyte was not detected above the sample reporting limit; and the reporting limit is approximate.

- U - The analyte was analyzed for, but was not detected above the sample reporting limit.
- R – The data are unusable. The sample result is rejected due to serious deficiencies. The presence or absence of the analyte cannot be verified.

D2.4 Verification during Data Management

Data provided electronically used to facilitate data handling will be verified against the hard copy data report during data validation.

D3 Usability/Reconciliation with Data Quality Objectives

This element describes how the verified/validated project data will reconcile with the project DQOs, how data quality issues will be addressed and how limitations on the use of the data will be reported and handled. The purpose of this section is to indicate the methods by which it will be ensured that the data collected for this investigation falls in line with the DQOs as described in Sections A.7 of this QAPP. To meet these DQOs, a combination of statistical procedures and qualitative evaluations will be used to check the quality of the data. These procedures will be used by the laboratory, in generating the data, and by the Data Validator, in the evaluation of the data for ultimate use in accordance with the RI/FS Work Plan (ENSR, 2005b).

The data generated must meet the data user's needs as defined in the project DQOs in Sections A.7 of this QAPP. The primary objectives for assessing the usability of the data are to ensure (1) data are representative of conditions in the Area of Investigation; (2) data meet the project reporting limit requirements; and (3) data are of the quality needed in order to meet the overall objective of the RI/FS.

Results for QC samples, including field and laboratory blanks, spikes, and duplicates will be evaluated using the equations described below to determine the validity and usability of the data. In addition, the data will be reviewed for indications of interferences to results caused by sample matrices, contamination during sampling, contamination in the laboratory, and sample preservation and storage anomalies (i.e., sample holding time or analytical instrument problems).

Data will be qualified for precision and accuracy by the Data Validator. The Data Validator will apply the standard data validation qualifiers to data to indicate the level of uncertainty in the associated result. In general, data that are left unqualified, data qualified "U" (non-detected), data qualified "J (+/-)" (detected as an estimated result), and data qualified "UJ" (non-detected at an estimated detection reporting limit) are considered valid and usable for project objectives. Data that are qualified "R"

(rejected), due to severe exceedances of QC requirements, will be considered invalid and unusable for making project decisions.

D3.1 Comparison to Measurement Criteria

D3.1.1 Precision Assessment

The RPD, as a measure of variability between the matrix spike and matrix spike duplicate or sample and matrix duplicate (laboratory duplicates), and field duplicates, will be calculated to compare to precision and representativeness DQOs. The RPD of duplicate measurements is calculated according to the following formula:

$$RPD = \frac{|\text{Result in Sample 1 - Result in Sample 2}|}{\text{Average (Result in Sample 1 and Result in Sample 2)}} \times 100$$

where:

Sample 1 = Initial sample or spiked sample result

Sample 2 = Duplicate sample or duplicate spiked sample result

In the event of precision results that do not meet the measurement performance criteria established for this project the results will be inspected to determine if the reduced precision can be attributed to sampling techniques (field duplicates) or sample contamination (field and laboratory blanks). If precision has been determined to be affected by sampling or contamination the data users must decide how to use data near the project action limits that may be affected. Data of reduced precision might be usable with appropriate acknowledgement of the uncertainty associated with results that are near action levels.

D3.1.2 Accuracy Assessment

Accuracy, as a measure of bias, will be evaluated based on the percent recoveries (%Rs) of the matrix spike sample, matrix spike duplicate sample, LCS, surrogates, internal standards, and initial and continuing calibration check samples. These QC results will be compared to the project measurement performance criteria for accuracy.

The increase in concentration of the analyte observed in the spiked sample, due to the addition of a known quantity of the analyte, compared to the reported value of the same analyte in the unspiked sample determines the %R.

Percent recoveries for spiked samples and QC are determined using the following equation:

$$\%\ R = \frac{(\text{Result in Spiked Sample} - \text{Result in Original Unspiked Sample})}{\text{Known Amount of Spike Added}} \times 100$$

Percent recoveries for LCS are determined using the following equation:

$$\%\ R = \frac{\text{Result for constituent in LCS}}{\text{Verified amount of constituent in LCS from vendor information}} \times 100$$

Additionally, field and laboratory blanks will be used to evaluate whether field or laboratory procedures represent a possible source of contamination in the samples. Unmonitored contamination can allow false positive results to be reported and treated as true sample components when, in fact, they are not. This type of error will adversely affect the accuracy of the reported results. Several types of blanks, including field blanks, method blanks, and instrument blanks, will be used in this project as described in Section B5.B.

Specific DQOs for blanks have been defined for this program in Sections B5.B. In general, the procedure for assessing blank samples for potential contamination is as follows.

- Tabulate blank constituent results.
- Identify blank samples for which constituents are reported above the method detection limits.
- If no constituents are detected above the instrument or method detection limits in any blanks, the associated data are reported unqualified and no blank actions are taken.
- If consitituents are detected above instrument or method detection limits in the blanks, the associated sample consitituent results may be qualified during data validation. This qualification may result in the negation of results at raised reporting limits due to blank actions.

Thus potential false results will be reported with elevated reported limits. These elevated limits will be recognized in the data available for the end user. Bias that does not meet the limits of the measurement criteria objectives will be indicated by the results of LCS, MS, and calibration analyses.

Bias indicated by these measurement criteria objectives will need to be evaluated to determine the effect on the use of the data. High bias on nondetect results, results that are well below action levels, or well over action levels may have little effect on the use of the data. Low bias for results that are well below the action levels or well over the action levels may have little effect on the use of the data. For results near the action levels with a high or low bias or indeterminate bias, the data will need to be reviewed carefully to establish if the data is usable for the intended purposes. Sample reanalysis, analysis of archived material, and/or recollection of the sample may be appropriate depending on criticalness of the missing data, logistical constraints, cost, and schedule.

D3.1.3 Completeness Assessment

Completeness is the ratio of the number of valid sample results to the total number of results planned for collection. The goal of this program is to generate valid, usable data. However, in environmental sampling and analysis, some data may be lost due to sampling location logistics, field or laboratory errors, or matrix effects that may cause the rejection of results for some consitituents. The overall completeness goal of collection of valid data is 90% for the field and 95% for analytical data. The Data Validator will assess the completeness of the overall data generation against the project goals of a minimum of 90% as valid and usable results. Valid and usable results are defined as those that are not rejected during validation (e.g., due to severe holding time or spike recovery noncompliances) or during the overall assessment (e.g., improper sampling technique). Following completion of the sampling, analysis, and data validation, the percent completeness will be calculated and compared to the project objectives stated in Section A7.2 using the following equation.

$$\% \text{ Completeness} = \frac{\text{Number of valid/usable results obtained}}{\text{Number of valid/usable results planned}} \times 100$$

If this goal is not met, data gaps may exist that will require evaluation to determine the effect on the intended use of the data. Sample reanalysis, analysis of archived material, and/or recollection of the sample may be appropriate depending on criticalness of the missing data logistical constraints, cost, and schedule.

D3.1.4 Sensitivity

Sensitivity is evaluated by verifying that laboratory reporting limits meet the target reporting limits stated in Tables A-3 through A-6. The failure to calibrate with a standard at the laboratory reporting limit or the presence of excessive dilutions may result in elevated detection limits. The effect of these

elevated limits will need to be reviewed in light of the historical data and project action levels to determine if adequate information is available to satisfy the DQOs.

D3.1.5 Representativeness

Representativeness 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.

Measures to Ensure Representativeness of Field Data

Representativeness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the SAP and QAPP are followed and that proper sampling techniques are used. In designing the sampling program, media of interest have been specified.

Measures to Ensure Representativeness of Laboratory Data

Representativeness in the laboratory is ensured by using the proper analytical procedures, appropriate methods, meeting sample holding times, and analyzing and assessing field duplicate samples. The sampling network was designed to provide data representative of the Area of Investigation. During development of this network, consideration was given to past facility processes, existing analytical data, physical setting and processes, and media of interest. The rationale of the sampling network is discussed in detail in Section 2.0 of the SAP.

D3.2 Overall Assessment of Environmental Data

Data assessment will involve data evaluation and usability to determine if the data collected are of the appropriate quality, quantity, and representativeness to the project decision. This evaluation will be performed by the Project Manager in concert with other users of the data. The QC results associated with each analytical parameter for each matrix type will be compared to the objectives presented in this QAPP. Data generated in association with QC results meeting these objectives and/or the data validation criteria will be considered usable. Data that does not meet the objectives and/or the data validation criteria might still be usable. This assessment may require various statistical procedures to establish outliers, correlations between data sets, adequate sampling location coverage, etc., in order to assess the effect of qualification or rejection of data. The effect of the qualification of data or loss of data deemed unacceptable for use, for whatever reason, will be discussed and decisions made on corrective action for potential data gaps.

Figure A-1 Project Organization Chart

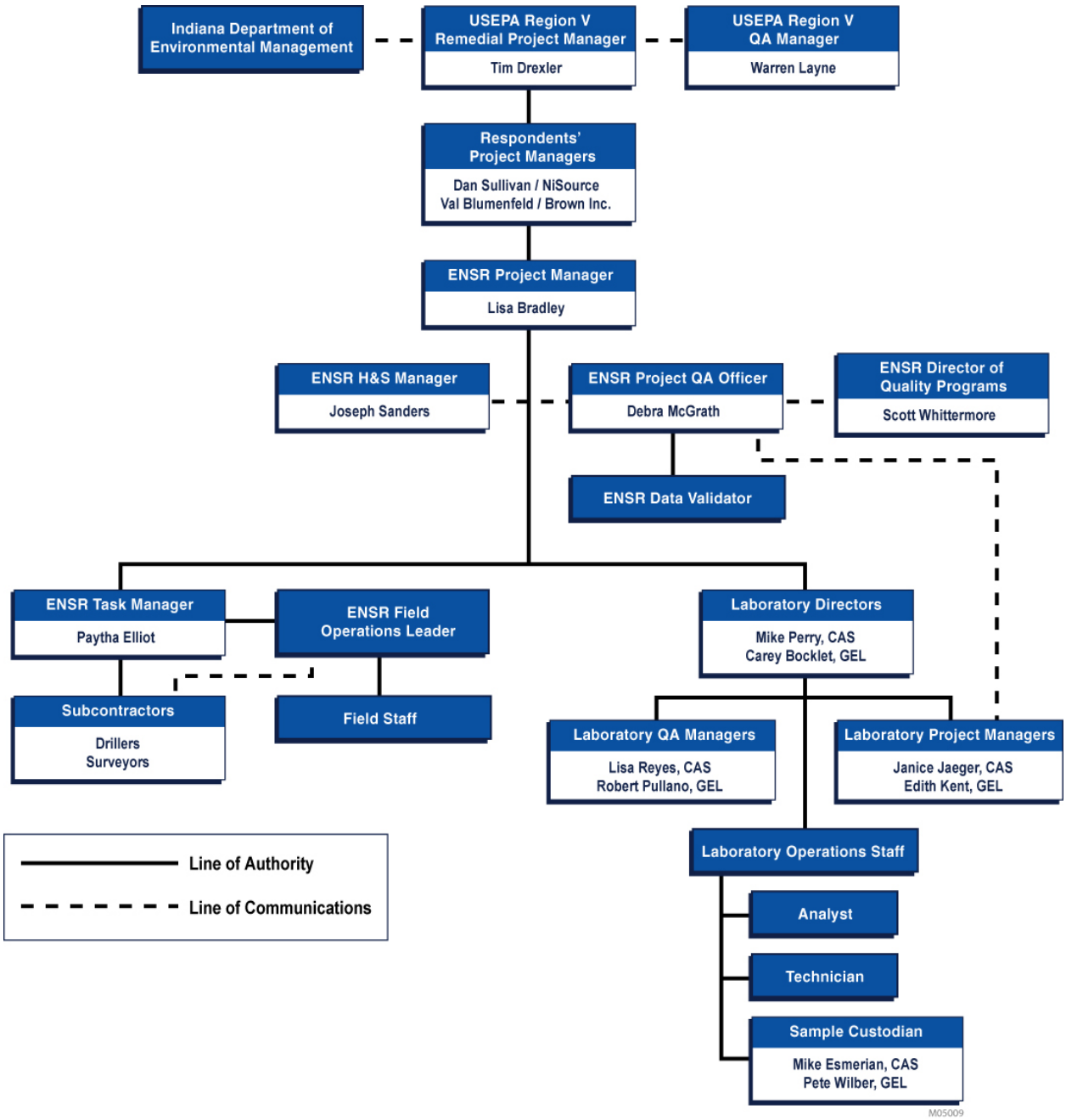

Figure B-1 Example of Sample Label

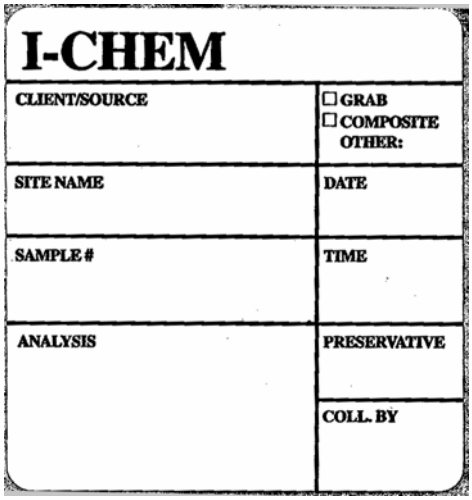

Figure B-2 Example Chain-of-Custody Record

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ENSR — **CHAIN OF CUSTODY RECORD** — Page ____ of ____

Client/Project Name:	Project Location:	Analysis Requested
Project Number:	Field Logbook No.:	
Sampler: (Print Name) /Affiliation:	Chain of Custody Tape No.:	
Signature:	Send Results/Report to:	

Field Sample No./ Identification	Date	Time	Grab	Comp	Sample Container (Size/Mat'l)	Sample Type (Liquid, Sludge, Etc.)	Preservative	Field Filtered							Lab I.D.	Remarks

Relinquished by: (Print Name)	Date:	Received by: (Print Name)	Date:	Analytical Laboratory (Destination):
Signature:	Time:	Signature:	Time:	ENSR 4303 W. LaPorte Ave. Fort Collins, CO 80521 (970) 416-0916
Relinquished by: (Print Name)	Date:	Received by: (Print Name)	Date:	
Signature:	Time:	Signature:	Time:	
Relinquished by: (Print Name)	Date:	Received by: (Print Name)	Date:	
Signature:	Time:	Signature:	Time:	Serial No.

Figure C-1 Example of Internal Field TSA Checklist

Project: **Site Location:** **Auditor:**	
1. Was project-specific training held?	
2. Are copies of project plan (SAP, QAPP) on site and available to personnel?	
3. Are samples being collected in accordance with the project plan?	
4. Do the numbers and locations of samples conform to the project plan?	
5. Are sample locations staked or otherwise marked?	
6. Are samples labeled in accordance with the project plan?	
7. Is equipment decontamination in accordance with the project plan?	
8. Is field instrumentation being operated and calibrated in accordance with the project plan?	
9. Are samples being preserved and containerized in accordance with the project plan?	
10. Are QC samples in accordance with the types, collection procedures, and frequencies specified in the project plan?	
11. Are chain-of-custody procedures and documents in conformance with the project plan?	
12. Are field records complete, accurate, up-to-date, and in conformance to good recordkeeping procedures?	
13. Are modifications to the project plan being communicated, approved, and documented appropriately?	
Additional Comments:	
Auditor:	**Date:**

Figure C-2 Example of Laboratory Audit Checklist

Project: **Facility Location:** **Auditor:**	
Is there a written QA Program Plan/Manual?	
Is there a designated QA Officer?	
Are facilities and equipment adequate to perform the analyses of interest?	
Review procedures and engineering controls for minimizing cross contamination.	
Review most recent interlaboratory PE sample results and recent Agency audits.	
Review SOP system. Review techniques for conformance to approved SOPs.	
Are personnel qualified and trained? Is there a formal training program and are records of training and proficiency maintained?	
Is there a designated sample custodian? Is there a sample inspection checklist? Are sample log-in procedures defined in an SOP?	
Is the laboratory area secure?	
Review internal chain-of-custody procedures.	
Are instruments operated and calibrated in accordance with SOPs? Are records of calibration maintained?	
Is equipment maintained according to written protocols? Are routine and non-routine maintenance procedures documented?	
Are samples being analyzed in conformance to the cited methods?	
Are QC samples and checks being performed at the frequencies stated in the cited methods?	
Are records complete, accurate, up-to-date, and in conformance to good recordkeeping procedures?	
How are project-specific requirements communicated to the bench level?	
Review data reduction, review, and reporting processes.	
Review data archival process (paper and electronic).	
Review audit and corrective action program.	
Additional Comments:	
Auditor:	**Date:**

Table A-1 Sample Summary

Matrix	Field Parameters	Analytical Parameters	Number of Samples	Field Duplicates	Equip. Rinsate Blanks	MS/MSD	Total by Matrix
CCBs	None	PCDDs/PCDFs, PAHs, radionuclides	10	1	1	1 pair	14
Surface Soil	None	TAL metals, boron, molybdenum, silicon, sulfur, PCDDs/PCDFs, PAHs, radionuclides	25	3	2 (if any non-disosable equipment is used)	2 pairs	34

TAL – Target Analyte List
PAHs – Polycyclic Aromatic Hydrocarbons
PCDDs/PCDFs - Polychlorinated Dibenzodioxins/Polychlorinated Dibenzofurans
MS/MSD – Matrix Spike/Matrix Spike Duplicate
CCB – Coal Combustion Byproduct

Table A-2 Laboratory Parameters by Sample Medium

Parameter	Media	
	Soil	CCBs
Metals (TAL) plus boron, molybdenum, and silicon	X	
PAHs	X	X
PCDDs/PCDFs	X	X
Radionuclides	X	X
Sulfur	X	
Notes: Specific analytes are listed in Tables A-3 through A-6		

Table A-3 Target Analytes, Reporting Limits, and Data Quality Levels for PAHs in Soil and CCBs

Parameter	CAS No.	MDL[1] (mg/kg)	RL[1] (mg/kg)	Ecological DQL[2] (mg/kg)	Human Health DQL[3] (mg/kg)	Selected DQL[4] (mg/kg)
2-Methylnaphthalene	91-57-6	0.0010	0.0066	3.24	56[5]	3.24
Acenaphthene	83-32-9	0.00076	0.0066	68.2	3,700	68.2
Acenaphthylene	208-96-8	0.00096	0.0066	682	3,700[6]	682
Anthracene	120-12-7	0.001	0.0066	1,480	22,000	1,480
Benz[a]anthracene	56-55-3	0.0016	0.0066	5.21	0.62	0.62
Benzo(g,h,i)perylene	191-24-2	0.0022	0.0066	119	2,300[7]	119
Benzo[a]pyrene	50-32-8	0.0014	0.0066	1.52	0.062	0.062
Benzo[b]fluoranthene	205-99-2	0.0019	0.0066	59.8	0.62	0.62
Benzo[k]fluoranthene	207-08-9	0.0015	0.0066	1.52[8]	6.2	1.52
Chrysene	218-01-9	0.00089	0.0066	1.52[8]	62	1.52
Dibenz[ah]anthracene	53-70-3	0.0021	0.0066	18.4	0.062	0.062
Fluoranthene	206-44-0	0.0028	0.0066	122	2,300	122
Fluorene	86-73-7	0.0080	0.0066	122	2,700	122
Indeno[1,2,3-cd]pyrene	193-39-5	0.0023	0.0066	109	0.62	0.62
Naphthalene	91-20-3	0.0011	0.0066	0.0994	56	0.0994
Phenanthrene	85-01-8	0.00081	0.0066	3.24[9]	22,000[10]	3.24
Pyrene	129-00-0	0.0018	0.0066	1.52[8]	2,300	1.52

Notes:
[1] Laboratory RLs and MDLs are on an "as-received" basis. Actual dry weight limits will vary based on percent moisture of the samples. MDLs are updated periodically; the current MDLs at the time of analyses will be used.
[2] USEPA Region 5 Ecological Screening Level for soil. Updated August 22, 2003. (http:/www.epa.gov/reg5rcra/ca/ESL.pdf).
[3] USEPA Region 9 PRG table. October 2004. Value for residential soil.
[4] Lower of PRG/ESL
[5] No PRG available. Due to structural similarities, the value for naphthalene was used.
[6] No PRG available. Due to structural similarities, the value for acenaphthene was used.
[7] No PRG available. Due to structural similarities, the value for pyrene was used.
[8] No ESL available. Due to structural similarities, the value for benzo(a)pyrene was used.
[9] No ESL available. Due to structural similarities, the value for 2-methylnaphthalene used.
[10] No PRG available. Due to structural similarities, the value for anthracene was used.
CAS – Chemical Abstracts Service
DQL – Data Quality Level.
ESL – Ecological Screening Level
MDL – Method Detection Limit
PAH – Polynuclear Aromatic Hydrocarbon
PRG – Preliminary Remedial Goal
RL – Reporting Limit

Table A-4 Target Analytes, Reporting Limits, and Data Quality Levels for PCDDs/PCDFs in Soil and CCBs

Parameter	CAS No.	MDL[1] (mg/kg)	RL[1] (mg/kg)	Ecological DQL[2] (mg/kg)	Human Health DQL[3] (mg/kg)	Selected DQL[4] (mg/kg)
2,3,7,8-TetraCDD	1746-01-6	5.7E-07	1.0E-06	1.99E-07	0.001	1.99E-07
1,2,3,7,8-PentaCDD	40321-76-4	8.1E-07	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,4,7,8-HexaCDD	39227-28-6	1.06E-06	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,6,7,8-HexaCDD	57653-85-7	9.5E-07	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,7,8,9-HexaCDD	19408-74-3	1.00E-06	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,4,6,7,8-HeptaCDD	35822-39-4	1.12E-06	2.5E-06	1.99E-07	0.001	1.99E-07
OctaCDD	3268-87-9	1.54E-06	5.0E-06	1.99E-07	0.001	1.99E-07
2,3,7,8-TetraCDF	51207-31-9	5.0E-07	1.0E-06	1.99E-07	0.001	1.99E-07
1,2,3,7,8-PentaCDF	57117-41-6	6.7E-07	2.5E-06	1.99E-07	0.001	1.99E-07
2,3,4,7,8-PentaCDF	57117-31-4	4.2E-07	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,4,7,8-HexaCDF	70648-26-9	1.78E-06	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,6,7,8-HexaCDF	57117-44-9	9.1E-07	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,7,8,9-HexaCDF	72918-21-9	7.7E-07	2.5E-06	1.99E-07	0.001	1.99E-07
2,3,4,6,7,8-HexaCDF	60851-34-5	1.18E-06	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,4,6,7,8-HeptaCDF	67562-39-4	6.1E-07	2.5E-06	1.99E-07	0.001	1.99E-07
1,2,3,4,7,8,9-HeptaCDF	55673-89-7	6.1E-07	2.5E-06	1.99E-07	0.001	1.99E-07
OctaCDF	39001-02-0	2.97E-06	5.0E-06	1.99E-07	0.001	1.99E-07

Notes:
[1] Laboratory RLs and MDLs are on an "as-received" basis. Actual dry weight limits will vary based on percent moisture of the samples. MDLs are sample-specific and will vary.
[2] USEPA Region 5 Ecological Screening Level for soil. Updated August 22, 2003. (http:/www.epa.gov/reg5rcra/ca/ESL.pdf). Value for 2,3,7,8-TetraCDD.
[3] USEPA. 1998. Approach for Addressing Dioxin in Soil at CERCLA and RCRA Sites. Value for dioxins [OSWER Directive 9200.4-26].
[4] Lower of human health DQL/ESL.
CAS – Chemical Abstracts Service
CDD – Chlorodibenzodioxin
CDF - Chlorodibenzofuran
DQL – Data Quality Level.
ESL – Ecological Screening Level
MDL – Method Detection Limit
RL – Reporting Limit

Table A-5 Target Analytes, Reporting Limits, and Data Quality Levels for Radionuclides in Soil and CCBs

Isotope	Element (Atomic Number)	MDA[1] (pCi/g)	RL (pCi/g)	Ecological DQL[2] (pCi/g)	Human Health DQL[3] (pCi/g)	Selected DQL[4] (pCi/g)
Ac-227	Actinium (89)	0.16	NA	NA	2.5	2.5
Pa-231	Protactinium (91)	0.5	NA	NA	0.5	0.5
Pb-210	Lead (82)	3	NA	NA	0.3	0.3
Po-210	Polonium (84)	3	NA	NA	38	38
Ra-226	Radium (88)	0.3	NA	50	0.2	0.2
Ra-228	Radium (88)	0.2	NA	40	0.3	0.3
Th-228	Thorium (90)	0.3	NA	NA	24	24
Th-230	Thorium (90)	3	NA	NA	3.5	3.5
Th-232	Thorium (90)	2	NA	2000	3.1	3.1
U-234	Uranium (92)	3	NA	5000	4.0	4.0
U-235	Uranium (92)	0.1	NA	3000	0.2	0.2
U-238	Uranium (92)	0.5	NA	2000	4.5	4.5

Notes:
[1] The actual Minimum Detectable Activity is calculated on a sample by sample basis with each analysis based on a number of factors including sample size, dilution, and count time.
[2] Obtained from *A Graded Approach for Evaluating Radiation Doses to Aquatic and Terrestrial Biota* (DOE, 2002).
[3] Radionuclide Toxicity and Preliminary Remediation Goals (PRGs) for Superfund. August 4, 2004. (http://epa-prgs.ornl.gov/radionuclides/)
[4] Lower of eco/HH DQL.
DOE – Department of Energy
DQL – Data Quality Level.
MDA – Minimum Detectable Activity
NA – Not Applicable
RL – Reporting Limit

Table A-6 Target Analytes, Reporting Limits, and Data Quality Levels for Metals and Sulfur in Soil (page 1 of 2)

Parameter	CAS No.	IDL[1] (mg/kg)	RL[1] (mg/kg)	Ecological DQL[2] (mg/kg)	Human Health DQL[3] (mg/kg)	Selected DQL[4] (mg/kg)
Metals (mg/kg)						
Aluminum	7429-90-5	5.1	10	50	76,000	50
Antimony	7440-36-0	0.29	6	0.29	31	0.29
Arsenic	7440-38-2	0.25	1	5.7	0.39	0.39
Barium	7440-39-3	0.56	2	330	5,400	330
Beryllium	7440-41-7	0.01	0.5	36	150	36
Boron	7440-42-8	1.68	20	0.5	16,000	0.5
Cadmium	7440-43-9	0.07	0.5	0.38	37	0.38
Calcium	7440-70-2	3.76	50	NS	NS	NS
Chromium (total)	7440-47-3	0.06	1	0.4	210	0.4
Cobalt	7440-48-4	0.12	5	13	900	13
Copper	7440-50-8	0.19	2	5.4	3,100	5.4
Iron	7439-89-6	0.05	10	NS	NS	NS
Lead	7439-92-1	0.16	0.5	16	400	16
Magnesium	7439-95-4	3.81	50	NS	NS	NS
Manganese	7439-96-5	0.06	1	500	1,800	500
Mercury	7439-97-6	0.003	0.03	0.1	23	0.1
Molybdenum	7439-97-7	0.17	1	2	390	2
Nickel	7440-02-0	0.19	4	30	1,600	30
Potassium	7440-09-7	7.52	200	NS	NS	NS
Selenium	7782-49-2	0.43	0.5	0.028	390	0.028
Silicon	7631-86-9	6.49	100	NS	NS	NS
Silver	7440-22-4	0.071	1	4.0	390	4.0
Sodium	7440-23-5	5.31	50	NS	NS	NS
Thallium	7440-28-0	0.13	1	0.057	5.2	0.057
Vanadium	7440-62-2	0.15	5	1.6	78	1.6
Zinc	7440-66-6	0.06	2	6.6	23,000	6.6
Other (mg/kg)						
Sulfur	7704-34-9	12.19	20	NS	NS	NS

Notes:
[1] Laboratory RLs and IDLs are on an "as-received" basis. Actual dry weight limits will vary based on percent moisture of the samples. IDLs are updated periodically; the current IDLs at the time of analyses will be used. Arsenic will be reported as nondetect at the IDL in order to achieve the DQL.
[2] Selected according to hierarchy:
(a) EcoSSLs obtained from http://www.epa.gov/ecotox/ecossl/. Lowest available for plant, soil invertebrate, bird, and mammal.
(b) USEPA Region 5 Ecological Screening Level for soil. Updated August 22, 2003. (http:/www.epa.gov/reg5rcra/ca/ESL.pdf).
(c) ORNL screening benchmark for terrestrial plants (Efroymson, et al., 1997); values for earthworms are higher.

Parameter	CAS No.	IDL[1] (mg/kg)	RL[1] (mg/kg)	Ecological DQL[2] (mg/kg)	Human Health DQL[3] (mg/kg)	Selected DQL[4] (mg/kg)

[3] USEPA Region 9 PRG table. October 2004. Value for residential soil.
[4] Lower of Eco/HR DQL.
CAS – Chemical Abstracts Service
DQL – Data Quality Level.
IDL – Instrument Detection Limit
NS – None Specified
RL – Reporting Limit

Table A-7 Quality Control Performance Criteria

Constituent	Blank	Field Duplicate %RPD	LCS % Recovery	Matrix Spike % Recovery[1]	Duplicate % RPD[2]
Method 6010B					
Metals (excluding mercury)	<RL	30	C of A[3]	75-125	20
Method 7471A					
Mercury	<RL	30	C of A[3]	75-125	35
Method 9056					
Sulfur	<RL	30	90-110%	70-130	20
Method 8270C					
PAHs	<RL	50	Current lab limits	Current lab limits	30
Method 8290A					
PCDDs/PCDFs	<5%RL	30	70-130	50-150 (advisory)	30
Method HASL 300 (gamma spectroscopy)					
Radionuclides	<MDA	300	75-125	75-125	20
Method HASL 300 (alpha spectroscopy)					
Radionuclides	<MDA	30	75-125	75-125	20

[1]Criteria apply to both matrix spike and matrix spike duplicate for organic analyses.
[2]Criteria apply to matrix spike/matrix spike duplicates for organic analyses and for laboratory duplicates for the remaining analyses. RPD criteria are doubled when results are less than 5x RL .
[3]C of A – Certificate of Analysis QC limits provided by manufacturer.
LCS – Laboratory Control Sample
NA - Not applicable
RL - Reporting Limit
RPD – Relative Percent Difference
MDA – Minimum Detectable Activity

Table B-1 Summary of Sample Container, Preservation, and Holding Time Requirements

Parameter[1]	Matrix	Container[2]	Preservative	Maximum Holding Time[3]
PCDDs/PCDFs	CCBs and surface soil	1 250-mL glass with Teflon®-lined cap	Cool 4°C	30 days to extraction; 45 days from extraction to analysis
PAHs	CCBs and surface soil	1 250-mL glass with Teflon®-lined cap	Cool 4°C	14 days until extraction; 40 days from extraction to analysis
Radionuclides	CCBs and surface soil	1 1-L amber glass with Teflon®-lined cap	Cool 4°C	Six months to analysis
Metals and sulfur	Surface soil	One wide-mouth 500-mL plastic[4]	Cool 4°C	Six months to analysis; 28 days for mercury and sulfur

[1] Refer to Tables A-3 through A-6 for specific analytes.
[2] Alternative sample containers may be provided by the laboratory under the condition that sufficient sample volume is provided and the data quality objectives are met.
[3]Sample holding time begins at time of collection.
[4]If glass containers are used, they must be certified clean for boron and silicon.

Table B-2 Analytical Methodologies

Analyte Group[1]	Laboratory SOP Number[2]	Equivalent Method Number[3]
PAHs	EXT-3550BPines 8270CSIMPines	USEPA SW-846 Method 3550 USEPA SW-846 Method 8270C
PCDDs/PCDFs	HRMS-8290	USEPA SW-846 Method 8290A
Metals	MET-3050Pines Rev.0 MET-6010Bpines Rev. 1	USEPA SW-846 Method 3050B USEPA SW-846 Method 6010B
Mercury	MET-7471APines	USEPA SW-846 Method 7471A
Thallium	MET-3050B, Rev. 3 MET-GFAA, Rev. 3	USEPA SW-846 Method 3050B USEPA SW-846 Method 7841
Sulfur	MET-ICSPines Rev. 0 GEN-300Pines Rev. 1	USEPA 300.0
Radionuclides by Gamma Spectrometry	GL-RAD-A-013	DOE EML HASL 300
Radionuclides by Alpha Spectrometry	GL-RAD-A-045	DOE EML HASL 300

[1]See Tables A-3 through A-6 for the compounds in each analyte group.
[2]The version of the SOP that is current at the time of sample analysis will be utilized. Any modification to the approved SOP will require USEPA notification and concurrence.
[3]References: refer to Section A10.
DOE – Department of Energy
PAH – Polynuclear Aromatic Hydrocarbon
PCDD – Polychlorinated Dibenzodioxin
PCDF – Polychlorinated Dibenzofuran
SOP – Standard Operating Procedure
USEPA – United States Environmental Protection Agency

Table B-3 Analytical Quality Control Checks (Page 1 of 4)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
PAHs 8270C	Method blanks	One per analytical batch	No target analytes above PQL	Reextraction/reanalysis of entire batch
	Surrogate spikes	Every sample, blank, standard prior to extraction	Per current laboratory control limits	Reextract or flag data
	MS/MSD samples	One pair per analytical batch	Per current laboratory control limits	Check LCS, reanalyze, flag results
	LCS	One per analytical batch	Per current laboratory control limits	Reextraction/reanalysis of entire batch
	GC/MS tuning	At beginning of each 12 hour shift	Control criteria listed in SOP	Recalibrate instrument until control criteria are met
	Internal standards	Every sample, blank, standard, prior to analysis	Area within 50-200% and RT within 0.5 min of IS in associated calibration standard	Reanalyze sample if no interference present
PCDDs/PCDFs 8290A	Method blanks	One per analytical batch	<5% MRL	Reextraction/reanalysis of entire batch
	MS/MSD samples	One pair per analytical batch	Not required by method 50-150% advisory	If recovery of labeled standards is outside criteria, reextract to confirm matrix interferences
	LCS/LCSD	One pair per analytical batch	RPD <30 70-130%R	Reextraction/reanalysis of entire batch
	GC/MS tuning	At beginning and end of each 12 hour shift	Control criteria listed in SOP	Recalibrate instrument until control criteria are met
	Internal standards	Every sample, blank, standard prior to analysis	40-135% for all 2,3,7,8-substituted internal standards	Evaluate matrix effects. If called for, reextract samples using smaller sample amount.
	Mass resolution check	At beginning and end of each 12 hour shift	Must meet 10,000 resolving power	Reanalysis of entire batch
	GC column performance check	At beginning of each 12 hour shift	2,3,7,8TCDD must be <25% other congeners	Cannot begin run until criteria are met

Table B-3 Analytical Quality Control Checks (Page 2 of 4)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Metals 6010B	Reagent/prep/ ICBK blanks	One per preparation batch	No analytes above RL	Repreparation/reanalysis of entire prep batch
	MS samples	One per preparation batch	75-125% R	Analyze post-digestion spike
	Duplicate samples	One per preparation batch	RPD < 20	Check analytical system, flag results
	LCS	One per preparation batch	Vendor limits	Repreparation/reanalysis of entire prep batch
	Dilution test	One per preparation batch	Within 10% of original sample results	Flag results
	Interference check	Beginning of each analytical run	20% of true values	Recalibrate and reanalyze any sample with interfering elements
Mercury 7471A	Reagent/prep blanks	One per analytical batch of 20 samples or less	Not detected above MRL	Repreparation/reanalysis of entire batch
	MS samples	One per analytical batch of 20 samples or less	75-125%R (lab limits)	Repreparation/reanalysis of entire batch
	Duplicate samples	One per analytical batch of 20 samples or less	RPD <20	Check analytical system, flag results
	LCS	One per analytical batch of 20 samples or less	ERA Vendor listed limits.	Repreparation/reanalysis of entire batch
Thallium 7841	Reagent/prep blanks	One per analytical batch of 20 samples or less	Not detected above MRL	Repreparation/reanalysis of entire batch
	MS samples	One per analytical batch of 20 samples or less	75-125%R (lab limits)	Repreparation/reanalysis of entire batch
	Duplicate samples	One per analytical batch of 20 samples or less	RPD <20	Check analytical system, flag results
	LCS	One per analytical batch of 20 samples or less	ERA Vendor listed limits.	Repreparation/reanalysis of entire batch

Table B-3 Analytical Quality Control Checks (Page 3 of 4)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Sulfur 300.0	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	Control limits listed in Table A-5.	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	Control limits listed in Table A-5.	Repreparation/reanalysis of entire batch
Radionuclides HASL 300 Alpha spectrometry	Method blanks	One per analytical batch	Not detected above MDA	Repreparation/reanalysis of entire batch
	MS/MSD samples	One per analytical batch	75-125% R	Reanalyze samples with recoveries outside limits
	Duplicate samples	One per analytical batch	RPD <20 RPD<100 if activity <5x MDA RPD NA if activity <MDA	Check analytical system, flag results
	Tracers	Every field sample, QC sample, blank	20-120%R	Reanalyze samples with yields outside limits
	LCS	One per preparation batch	75-125% R	Repreparation/reanalysis of entire batch
Radionuclides HASL 300 Gamma spectrometry	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS/MSD samples	One per preparation batch	75-125% R	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20 RPD<100 if activity <5x MDA RPD NA if activity <MDA	Check analytical system, flag results
	LCS	One per preparation batch	75-125% R	Repreparation/reanalysis of entire batch

Table B-3 Analytical Quality Control Checks (Page 4 of 4)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Silica 370.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per batch of 10	81-122 %R	Check LCS, flag results
	CCBK	Every 10 and ending	Not detected above RL	Repreparation/reanalysis of entire batch
	Duplicate samples	One per preparation batch of 10	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	90-118 %R	Repreparation/reanalysis of entire batch

1 = Preparation Batch defined as maximum of 20 field samples of a similar matrix unless otherwise specified.

MS/MSD = Matrix Spike/Matrix Spike Duplicate

RL = Reporting Limit

%R = Percent Recovery

LCS = Laboratory Control Sample

RPD = Relative Percent Difference

MDA = Minimum Detectable Activity

CCBK = Continuing Calibration Blank

ICBK = Initial Calibration Blank

Table B-4 Maintenance Procedures and Schedule for Analytical Instruments (Page 1 of 2)

Instrument	Spare Parts	Activity	Frequency
GC/MS (SW-846 Method 8270C and 8290A)	Septa Carrier gas Filters Columns	Maintenance includes but not limited to: Change septum Check carrier gas, column flow and/or inlet pressure Change carrier gas Change gas filters Change GC column Clean MS source Monitor vacuum Leak-check septum Check gas flow Cut capillary column Replace liner	 Monthly/as needed As needed As needed As needed As needed/poor sensitivity As needed/poor sensitivity Daily As needed As needed As needed Daily
ICP (SW-846 Method 6010B)	Gases O-rings Tubing	Check gases Check argon tank pressure Check aspiration tubing Check vacuum pump gauge Check cooling water system Check nebulizer Check capillary tubing Check peristaltic pump tubing Check high voltage switch Check exhaust screens Check torch, glassware, aerosol injector tube, bonnet Clean plasma torch assembly Clean nebulizer and drain chamber Clean filters Replace tubing Check o-rings	Daily Daily Daily Daily Daily Daily Daily Daily Daily Daily Daily Monthly or as needed Monthly or as needed Monthly or as needed Monthly or as needed Monthly or as needed
CVAAS (SW-846 Methods 7470A/ 7471A)	Tubing Lamps	Change drying tube Check tubing/change tubing Check gas pressure Check aperture reading Check/change lamp Clean optical cell Lubricate pump	Daily Daily/As needed Daily Daily As needed As needed As needed
GFAAS (SW-846 Method 7841)	Tubing Lamps	Change drying tube Check tubing/change tubing Check gas pressure Check aperture reading Check/change lamp Clean optical cell Lubricate pump	Daily Daily/As needed Daily Daily As needed As needed As needed

Table B-4 Maintenance Procedures and Schedule for Analytical Instruments (Page 2 of 2)

Instrument	Spare Parts	Activity	Frequency
Ion Chromatograph Method (300.0)		Rinse IC pump and valves Lubricate pump	Weekly Every 6 months
Gamma Spectrometer (HASL 300)		Energy and FWHM calibration Efficiency calibration Instrument Check Background Liquid Nitrogen Fill Software Backups Filter Cleaning	Annual Annual Daily Weekly Weekly Monthly Quarterly
Alpha Spectrometer (HASL 300)		Pulser Check Efficiency Calibration (Energy, FWHM, efficiency) Background Check Software Backup Vacuum Pump Oil Changed Filter Cleaning	Daily Monthly Weekly Monthly Semi-annually Quarterly

Table B-5 Laboratory Equipment Monitoring

Equipment Type	Activity	Frequency
Ovens	Temperature monitoring Electronics serviced	Daily As needed
Refrigerators	Temperature monitoring Refrigerant system and electronics serviced	Twice daily As needed
Balances	Calibration Manufacturer cleaning and servicing	Daily or before use Annually
High-purity water system	Conductance monitoring	Daily

Table B-6 Analytical Instrument Calibration (Page 1 of 3)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
GC/MS PAHs by SW-846 Method 8270C	Initial: As needed	Minimum of 5 standards	CCC %RSD ≤30
	Continuing: Daily, before sample analysis and every 12 hours	Mid-level standard	CCC %D ≤20 SPCCC RF same as initial
GC/MS PCDDs/PCDFs by SW-846 Method 8290C	Initial: As needed	All 17 native congeners, 12 labeled congeners	SD ±20% native congeners SD ±30% labeled congeners
	WDM and CCal at the beginning of the day	WDM: Two congeners per homologue series; three 2,3,7,8-TCDD congeners Check resolution: HRCC3 at midpoint	WDM: All spiked congeners must be present HRCC3: 20%D native standards 30%D labeled standards
	HRCC3 at end of run or within 12 hours	HRCC3	HRCC3: 25%D native standards 35%D labeled standards
ICP Metals by SW-846 6010B	Initial: Daily	Initial: Per manufacturer's instructions. Minimum of one standard and calibration blank and instrument blank.	Initial: Highest standard within 10% of true value. % RSD 20 < RL
	Continuing: Every 10 samples	Mid-level of each meta and instrument blank	±10% of true value % RSD 20 < RL
	Ending	Mid-level of each metal and instrument blank	±10% of true value % RSD 20 < RL

Table B-6 Analytical Instrument Calibration (Page 2 of 3)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
CVAAS Mercury by SW-846 7471A	Initial: Daily and/or after recalibration	Six standards plus blank Initial Mid-Level standard	r ≥ 0.995 ICV ±10% of true value
	Continuing: Every 10 samples	Mid-level standard	±10% of true value of original prepared standard
	Ending	Mid-level standard	±10% of original prepared standard
GFAAS Thallium by SW-846 7841	Initial: Daily and/or after recalibration	Initial: Minimum of three standards and calibration blank.	Initial: r > 0.995 ICV ≤ 10% D
	Continuing: One per 10 analyses	Mid-level	±10% of true value of original prepared standard
	Ending	Mid-level standard	±10% of true value of original prepared standard
Silica by Method 370.1	Initial: Daily	8-point calibration plus mid-level plus blank	r ≥ 0.997 ± 10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	± 10% of true value Not > RL
	Ending	Mid-level plus blank	± 10% of true value Not > RL
Ion Chromatograph Sulfur Method 300.0	Initial: Every 6 months or as needed	3 standards plus blank	R ≥ 0.995 ±10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	±10% of true value Not > RL
	Ending	Mid-level plus blank	±10% of true value Not > RL

Table B-6 Analytical Instrument Calibration (Page 3 of 3)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
Gamma spectrometer Radionuclides by Method HASL 300	Initial: Annually or as needed (energy, efficiency, resolution)	Low, medium, and high energy standards	±10% of NIST source
	Check source: Monthly – background check Daily - energy, efficiency, resolution	Low, medium, and high energy standards	±3 standard deviations from control values
Alpha spectrometer Radionuclides by Method HASL 300	Daily Pulser Check (peak centroid, pulser count rate, peak FWHM)	NIST Traceable standards	
	Monthly Efficiency Calibration (energy and efficiency)	NIST Traceable standards	Within 2-3 sigma control limits
	Weekly Background		Within 2-3 sigma control limits

[1]= If criteria are not met, corrective actions as specified in the laboratory SOPs (Attachment A), are taken.
NA = Not Applicable

ATTACHMENT A

LABORATORY STANDARD OPERATING PROCEDURES

ATTACHMENT A-1

COLUMBIA ANALYTICAL SERVICES, INC.

STANDARD OPERATING PROCEDURES

EXT-3550BPines, Rev. 0	**Ultrasonic Extraction of Solids for 8270C SIM Analysis for Indiana Pines**
8270CSIMPines, Rev. 0	**Analysis of PAHs by Gas Chromatography/Mass Spectrometry Using Selective Ion Monitoring (GC/MS/SIM) for Indiana Pines Site**
HRMS-8290, Rev. 5.2	**Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)**
MET-3050Pines, Rev. 0	**Metals Digestion, Soils, Sediments, and Sludge for ICP Analysis for the Pines Indiana Site**
MET-6010BPines, Rev. 1	**Determination of Metals and Trace Elements by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP) for Indiana Pines Site**
MET-7471APines, Rev. 0	**Determination of Mercury in Solid or Semisolid Waste by Cold Vapor Atomic Absorption Spectrometry**
MET-3050B, Rev. 3	**Metals Digestion, Soils, Sediments, and Sludge for ICP and GFAA Analysis**
MET-GFAA, Rev. 3	**Determination of Trace Metals by Graphite Furnace Atomic Absorption Spectrometry (GFAAS)**
MET-ICSPines, Rev. 0	**Total Sulfur for Ion Chromatography for Indiana Pines Site**
GEN-300Pines, Rev. 1	**Determination of Anions Using Ion Chromatography for Indiana Pines Site**
ADM-MDL, Rev. 5	**The Determination of Method Detection Limits**
SMO-GEN, Rev. 2	**Sample Receiving**

STANDARD OPERATING PROCEDURE

for

ULTRASONIC EXTRACTION OF SOLIDS FOR 8270C SIM ANALYSIS FOR INDIANA PINES

SOP No.: EXT-3550BPines

Revision: 0

December 3, 2004

Approved by: _____ Supervisor — Date: 12/6/04

_____ QA Coordinator — Date: 12/3/04

_____ Laboratory Manager — Date: 12/9/04

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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1. SCOPE AND APPLICABILITY

1.1. This SOP uses EPA SW-846 Method 3550B for extracting PAHs from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2. This SOP was modified specifically for PAH analysis by 8270C in SIM mode for the Indiana Pines Site project.

2. METHOD SUMMARY

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is then concentrated and a portion of the concentrate is removed for analysis.

3. DEFINITIONS

3.1. **Extraction batch** – a group of no more than 20 field samples extracted on the same day with the same reagents under the same conditions.

3.2. **Laboratory Control Sample (LCS)** - An aliquot of sodium sulfate to which a known quantity of the method analyte is added in the laboratory. The 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.

3.3. **Matrix** - the predominant material, component, or substrate (e.g., soil, sludge, etc.) of which the sample to be analyzed is composed.

3.4. **Matrix Spike (MS/MSD)** - In the matrix spike analysis, a predetermined quantity of a standard solution of the analytes of interest is added to a sample matrix prior to sample extraction. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recovery is calculated for the analytes detected to measure accuracy. The RPD between the MS and MSD is calculated to measure precision.

3.5. **Method Blank (MB)** – an artificial sample known to be free of the analytes of interest. Used to measure contamination introduced during extraction and analysis.

3.6. **Sample** - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

3.7. **Surrogates (Surrogate Standards)** - an organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process. Surrogate compounds are added to every blank, sample, matrix spike, matrix spike duplicate, LCS,

matrix spike blank, and standard. These are used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

4. HEALTH AND SAFETY WARNINGS

The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. Concentrated sulfuric acid and the 50% sodium hydroxide solution are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible. If eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5. CAUTIONS

- *An open container of sodium sulfate may become contaminated during storage in the laboratory.*
- *Avoid concentrating the sample to less than 1 ml. When the volume of solvent is reduced below 1 ml, analytes may be lost*

6. INTERFERENCES

6.1. 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.

6.2. Interferences coextracted from the samples will vary considerably from source to source.

6.3. Phthalate esters contaminate may types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

7. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8. EQUIPMENT AND SUPPLIES

8.1. Ultrasonic Disrupter - A horn type device equipped with a titanium tip, or a device that will give equivalent performance. The horn should be tuned prior to sample extraction. The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low concentration. Use a 1/2" horn.

8.2. Beakers - 400 ml.

8.3. Vacuum filtration apparatus.

8.3.1. Buchner funnel.

8.3.2. Filter paper - Whatman No. 41 or equivalent.

8.3.3. Side- Arm Flask - 1000 mL Pyrex.

8.4. Erlenmeyer flasks - 250 mL and 500 mL.

8.5. Kuderna-Danish (K-D) apparatus.

8.5.1. Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent).

8.5.2. Evaporation flask - 250 mL and 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with clamps.

8.5.3. Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

8.5.4. Plastic Clips - 19/24 Joint (KT675300-0019 or equivalent).

8.6. Glass boiling beads - 3 mm glass beads.

8.7. Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

8.8. Vials and Caps - 20 mL scintillation vials with screw caps and aluminum foil liner, 2 mL capacity glass with crimp tops for GC auto sampler.

8.9. Pipets - glass volumetric 1 mL or 2 mL.

8.10. 5 inch Pyrex funnel with a small pad of Pyrex glass wool.

8.11. Volumetric flasks - 10 mL and 1 and 2 mL

8.12. Balance - Top loading, capable of accurately weighing to the nearest 0.01g.

8.13. Tongue Depressors - 6 inch standard.

8.14. Oven - drying.

8.15. LabConco RapidVap Evaporation System

- 600mL Sample Tubes – End point Stem 1.5mL
- 8 place rack for 600ml Sample tubes

8.16. Standards, LCS, MS/MSD, and surrogate spiking solutions – concentrations and recipes are discussed in the analytical SOP.

8.17. Sodium sulfate - granular - anhydrous reagent grade, heated at 120°C for 16 hours, and stored in a glass bottle. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no indication is provided.

CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

8.18. Extraction solvent - .Methylene chloride - pesticide quality or equivalent. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no indication is provided. Boiling point 39°C.

8.19. Exchange solvent - .Hexane, - Pesticide quality or equivalent. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no indication is provided. Boiling point 68.7°C.

9. PROCEDURE

9.1. **Calibration and Standardization** – Tune the horn according to manufacturer's instructions prior to sample extraction.

9.2. **Sample Collection**

Purchased, precleaned, certified sample containers should be glass or Teflon, and have screw-caps with Teflon lined septa. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. However, acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples shall be stored at 0-6°C and shipped to the laboratory within 48 hrs.

9.3. Sample Handling and Preservation

Sample collection, preservation, and custody management is in accordance with NELAC 2002 Standard.

Soil samples must be iced or refrigerated at 0-6°C from the time of collection until extraction. Extract samples within 14 days from collection. Store sample extracts in extract coolers at 0-6°C and analyze within 40 days of extraction.

9.4. Sample Preparation

9.4.1. Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

9.4.2. Cut, shred, or otherwise break down gummy, fibrous or clay-like materials to allow mixing and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling of these difficult matrices.

9.4.3. The following step should be performed rapidly to avoid loss of the more volatile extractables: Weigh approximately 30 g of sample into a 400 ml beaker. Record the weigh to the nearest 0.1 g. Add 60 g of sodium sulfate and mix thoroughly. Nonporous or wet samples (gummy or clay type) that do not have a freeflowing sandy texture may be mixed with more sodium sulfate if needed. After addition of sodium sulfate, the sample should be free flowing. Add 1 mL of 1 ppm BN surrogate in methanol to all samples, spikes, LCS, and blanks. Add 1 mL of 1 ppm PAH spike in methanol to the LCS, MS, and MSD. Immediately add 100 mL of Methylene chloride.

9.4.4. Place the bottom surface of the tip of the disrupter horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

9.4.5. Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50%. Do not use microtip probe.

9.4.6. Decant and filter extracts through a Buchner funnel, using Whatman No. 41 filter paper and vacuum filtration, into a sidearm flask.

9.4.7. Repeat the extraction two more times with two additional 100 ml portions of solvent. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent. Keep the solvent extract and discard the sample on the filter.

9.4.8. Dry and Concentrate Extract with LabConco RapidVap Nitrogen Evaporation System

9.4.8.1. Add extract to a 600 mL Sample tube

9.4.8.2. Turn on power switch

9.4.8.3. Set parameters – Input the % Speed, Temperature, Time and Number of Samples to be concentrated. (See users manual for Time, Temperature and Speed Setting Guidelines per volume per solvent.)

9.4.8.4. Turn on Nitrogen gas.

9.4.8.5. Load sample tubes into RapidVap chamber. Close lid and swing both latched over the lid and tighten knobs.

9.4.8.6. Press Run to begin concentration. Be sure to check the samples at the beginning of the program to ensure samples are not rotating so quickly that they are splashing out of the sample tube. If this occurs, press the Stop button and adjust the speed. To resume press Run.

9.4.8.7. Allow samples to evaporate to a final volume of 1 mLs. When the time in the program is complete the instrument will beep and stop. Check sample volume. If additional time is needed, reset program and press Run.

CAUTION: Avoid concentrating the sample to less than 1 ml. When the volume of solvent is reduced below 1 ml, analytes may be lost.

9.4.8.8. The final volume is transferred to a vial with a Teflon lined screw-cap or crimp top, and label appropriately. Store extract in extract cooler at temperature of 0-6°C.

9.4.9. At this point samples are ready to be analyzed for the target analytes using the SOP 8270CSIMPines.

9.5. **Troubleshooting**

9.5.1. Ultrasonic probes - Pitting of the probe tip will occur with use. When the bottom begins to cup, the probe needs to be sent out to be machined. Eventually, the probe will need to be replaced.

9.5.2. Bath / RapidVap temperature should be monitored. It is not to exceed 15-20°C of the boiling point of the solvent being evaporated.

9.6. **Data Acquisition, Calculations, and Data Reduction Requirements**

9.6.1. Be sure all documentation is complete and legible.

9.6.2. All benchsheets shall be maintained in the Extraction log binder for reference. On a routine basis, the benchsheets are bound and archived.

10. DATA AND RECORDS MANAGEMENT

10.1. Responsibilities - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data 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 SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2. Data Review - Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. This checklist is found in SOP 8270CSIMPines.

11. QUALITY CONTROL AND QUALITY ASSURANCE

11.1. Extract a MB, LCS, MS and MSD (or LCSD if there is insufficient volume) for every batch of 20 or fewer samples. These QC samples are subjected to exactly the same analytical procedures as those used on actual samples. QC criteria and corrective action for these and the surrogates are specified in SOP 8270CSIMPines.

12. REFERENCES

"Test Methods For Evaluating Solid Waste Physical/Chemical Methods," USEPA SW-846, December 1996.

Example Extraction Benchsheet

Extraction Tech: ______ Extraction Date: ______ Concentration Tech: ______ 40 Day HT:	Spiked By: ______ Spk Witness: ______	Prep Method: ☐ 3540 ☐ 3550 ☐ 3510 ☐ 3520 ☐ 3580	Key: Color: C = Colorless; Y = Yellow; B = Brown; BL = Black; G = Grey Clarity: CLR = Clear; CDY = Cloudy; OP = Opaque Soils: F = Fine/Sand; M = Medium/Soil; C = Coarse/Rocks	Batch ID:

Client / Sub. #	Sample ID	Initial Wt. (g) or Volume (ml)	Appearance (see key)	Analysis (Test) Requested	pH Check (water only) REC'D pH	BN > 11		Acid < 2		Conc. Date	Final Volume (ml)	Date Complete	Comments / Emulsions
						1	2	1	2				

Spikes:

☐	AE/BN Surrogate	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	BN Surrogate	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	680 Surrogate	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	95-2 Surrogate	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	8270 LCS MIX 1	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	95-2 Spike	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	TANK List Spike	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	Phthalate Spike	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	680 Spike	Amt. ____ml	Conc. ____ppm	Lot# ______
☐	Other:	Amt. ____ml; Conc. ____ppm; Lot# ______		

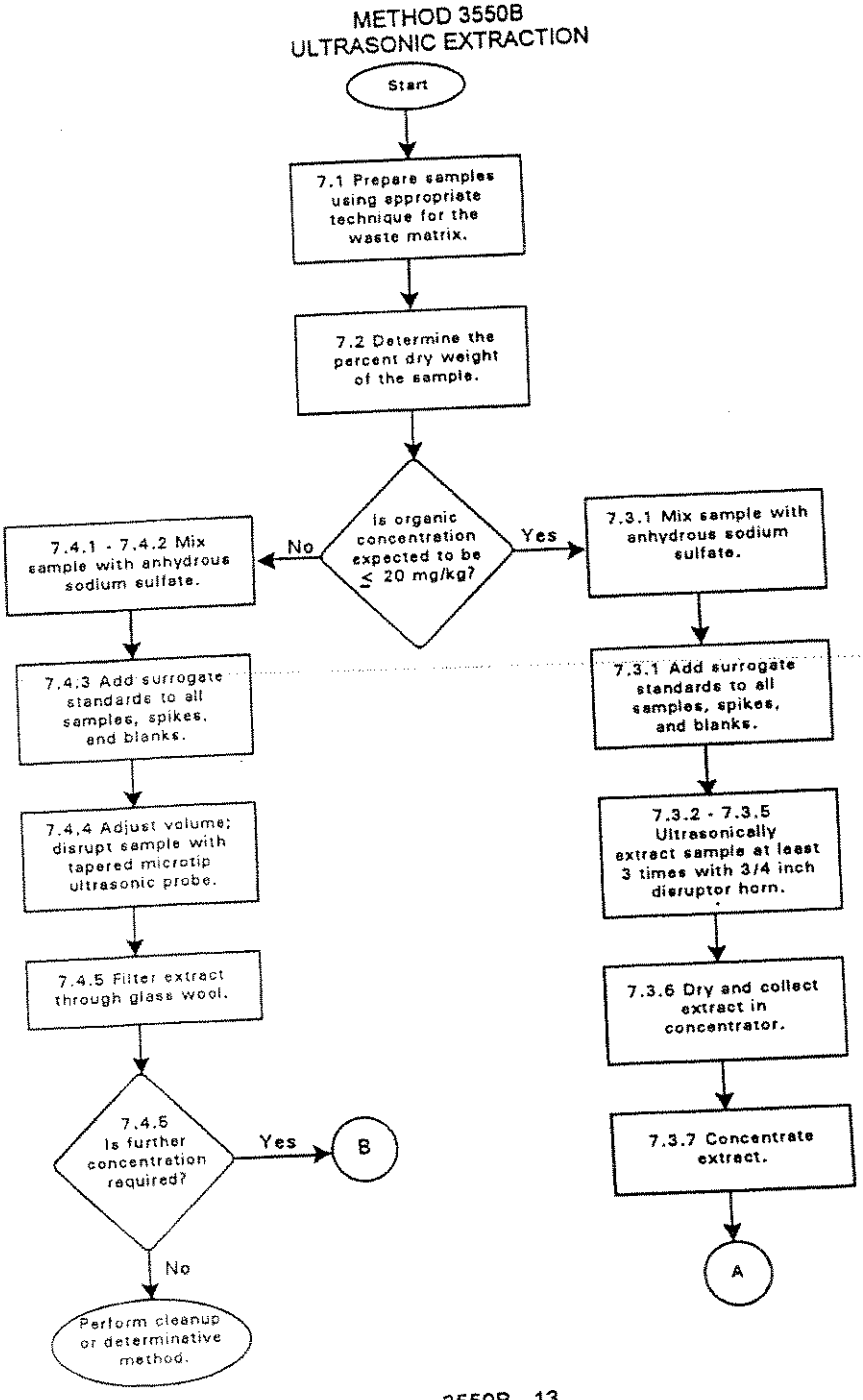
Clean-Ups: ☐ None

☐	3620	Florisil	By/Date ______	Lot# ______
☐	3640	GPC	By/Date ______	Lot# ______
☐	3660	Cu/TBA	By/Date ______	Lot# ______
☐	3665	Acid	By/Date ______	Lot# ______

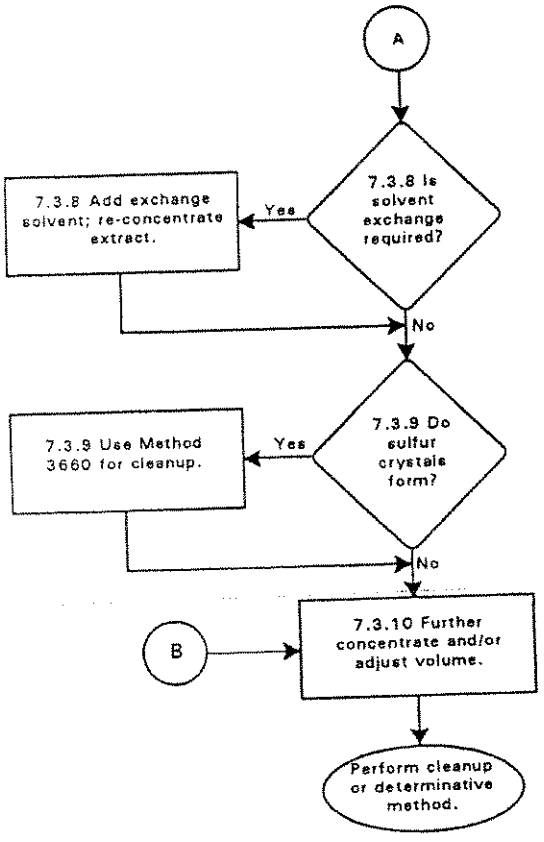
Method Summary:
Continuous Liquid-Liquid @ pH < 2 with 300-500mls MeCl2 for 18 hours.
Start Time: ______ **End Time:** ______

Solvents:

☐ 50:50 Ace:MeCl2 Lot # ______	☐ Hexane Lot# ______	☐ Sulfuric Acid Lot# ______
☐ MeCl2 Lot # ______	☐ Ether Lot# ______	☐ Sodium Hydroxide Lot# ______
☐ Acetone Lot #	☐ Sodium Sulfate Lot#	☐ Other: Lot# ______


METHOD 3550B
ULTRASONIC EXTRACTION
Start
7.1 Prepare samples using appropriate technique for the waste matrix.
7.2 Determine the percent dry weight of the sample.
Is organic concentration expected to be ≤ 20 mg/kg?
No
Yes
7.4.1 - 7.4.2 Mix sample with anhydrous sodium sulfate.
7.4.3 Add surrogate standards to all samples, spikes, and blanks.
7.4.4 Adjust volume; disrupt sample with tapered microtip ultrasonic probe.
7.4.5 Filter extract through glass wool.
7.4.5 Is further concentration required?
Yes
B
No
Perform cleanup or determinative method.
7.3.1 Mix sample with anhydrous sodium sulfate.
7.3.1 Add surrogate standards to all samples, spikes, and blanks.
7.3.2 - 7.3.5 Ultrasonically extract sample at least 3 times with 3/4 inch disruptor horn.
7.3.6 Dry and collect extract in concentrator.
7.3.7 Concentrate extract.
A

METHOD 3550B
continued



STANDARD OPERATING PROCEDURE

for

ANALYSIS OF PAHs BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY USING SELECTIVE ION MONITORING (GC/MS/SIM) FOR INDIANA PINES SITE

SOP Code: 8270CSIMPines

Revision:0

December 21, 2004

Approved by: _____ 12/21/04
Department Manager — Date

_____ 12/21/04
Quality Assurance — Date

_____ 12/21/04
Laboratory Director — Date

1 Mustard Street, Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
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Initials: _____ Date: _____

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1 SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 8270C (in the SIM mode) for the determination of low concentration levels of poly aromatic hydrocarbons(PAHs) in aqueous, soil, sludge, sediment, and various types of waste samples. Table 1 lists the compounds that are routinely determined by this procedure along with their method reporting limits (MRLs) in water and soil matrixes.

This procedure gives gas chromatographic/mass spectrometric (GC/MS) conditions for the detection of parts per billion (ppb) levels of PAHs.

This SOP was specifically modified for the Indiana Pines Site Project.

2 SUMMARY OF METHOD

Samples are extracted with solvent by EPA methodologies. A two μL sample aliquot is injected into the gas chromatograph (GC) by splitless injection. The PAHs are separated by a fused silica capillary column, and the compounds are detected by a mass selective detector (MSD) using the SIM mode. The retention and the ratio of two characteristic ions of each analyte are used for identification. The response of either the primary ion or the secondary ion is used for quantitation.

3 DEFINITIONS

3.1 **Analysis Window** – Samples are analyzed in a set referred to as a "window". The window begins with the injection of the DFTPP tune verification standard. Standards, required QC samples, and samples may be run for 12 hours in this window. A new window must be opened to continue analysis.

3.2 **Retention Time Window:** the time period established within which a target analyte is qualitatively determined to be present in the sample.

3.3 **Initial Calibration** - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the detector to the target compounds.

3.4 **Matrix** - the predominant material, component, or substrate (e.g., surface water, drinking water, etc.) of which the sample to be analyzed is composed.

3.5 **QA/QC Samples**: Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis.

3.5.1 **Laboratory Control Sample** - a matrix spiked sample with compounds representative of the target analytes. This is used to document laboratory performance.

3.5.2 **Matrix Spike/MSD** - an aliquot of sample spiked with a known concentration of target analyte(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.

3.5.3 **Method Blank** - an analyte-free matrix to which all reagents are added in the sample volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the preparation and analytical process.

3.6 **Percent Drift or Difference (%D)** - Used to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference).

3.7 **% Relative Standard Deviation (%RSD):** statistical measure of variation. Used in this method to measure the relative variation of initial calibration standards. Calculated by dividing the standard deviation of the individual calibration factors by the average calibration factor and multiplying by 100 to express as a percentage.

3.8 **Relative Percent Difference (RPD)** – The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.9 **Sample** - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

3.10 **Surrogates** (Surrogate Standards) – an organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process. For semivolatiles, surrogate compounds are added to every blank, sample, matrix spike, matrix spike duplicate, LCS, matrix spike blank, and standard. These are used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

3.11 **Internal Standards** – Internal standards are organic compounds which are similar to the analytes of interest but which are not found in the samples. The chosen internal standards are used to calibrate the instrument's response.

3.12 **Organic Free Reagent Water** - ASTM Type II Deionized Water.

3.13 **Batch** - Samples processed together as a unit, not to exceed 20 investigative samples. See ADM-BATCH for further discussion.

3.14 **Independent (or Initial) Calibration Verification (ICV also known as Reference Check)** - A standard from a different source as the calibration standards used to verify the calibration curve.

3.15 **Continuing Calibration Verification (CCV)** - A standard from the same source as the calibration standards used to verify the curve with each daily run and throughout the run at specified intervals.

3.16 **Method Detection Limit (MDL):** a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.17 **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

3.18 **Neat Stock Standard** - A purchased, single component assayed reference material having a stated purity used to prepare working calibration standards.

4 HEALTH AND SAFETY WARNINGS

4.1 Methylene chloride have been tentatively classified as a known or suspected human or mammalian carcinogen. The toxicity or carcinogenicity of the remaining chemicals used in this method has not been precisely defined. Each compound, mixture of compounds, and surrogates, as well as the samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of gloves (to minimize absorption through the skin) and hoods (to minimize inhalation). Material safety data sheets (MSDS) are available for all these reagents and solvents.

4.2 Samples may contain high concentrations of polynuclear aromatics, amines, phenols, and pesticides/PCBs; therefore, exposure to samples via contact must be minimized. Wear lab coat, gloves, and glasses when handling samples and reagents.

4.3 All applicable safety and compliance guidelines set forth by CAS, and by federal, state, and local regulations must be followed during performance of this procedure. All work must be stopped in the event of known or potential compromise to the health or safety of any CAS employee, and must be reported immediately to a laboratory supervisor.

5 INTERFERENCES

5.1 Sources of interference in this method can be grouped into three broad categories.

5.1.1 Supply: Contaminated solvents, reagents, or GC carrier gas.

5.1.2 Hardware: Contaminated glassware, analytical equipment; e.g., syringe, injection port, column surfaces, and/or detector surfaces.

5.1.3 Matrix: Compounds extracted from the sample to which the detector will respond.

5.2 Interference from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

6 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.

7 EQUIPMENT AND SUPPLIES

7.1 Gas Chromatograph/Mass Spectrometer System (GC/MS)

An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories, including autosampler, analytical column, and carry gas. The capillary column should be directly coupled to the source of the mass spectrometer.

Column - RTx-5Sil MS with Integra guard (or equivalent)
30 m x 0.25 mm ID
0.5 um film thickness
silicone-coated fused capillary

7.2 Mass Spectrometer (MS)

A MS capable of scanning from 35 to 500 amu every second 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 Decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 2 when 50 ng of DFTPP is injected onto the GC/MS system.

7.3 GC/MS Interface

Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

7.4 **In-line Gas Purifier (optional):** Agilent Technologies part no. 5182-9705 (or equivalent) to remove water, oxygen, and hydrocarbons.

7.5 **Microsyringes** - 10, 50, 100, 250, 500, and 1000-µL

7.6 Balance

7.6.1 Top-loading Scale: Capable of weighing to 0.1 g.
7.6.2 Analytical Balance: Capable of weighing to 0.1 mg.

7.7 **Spatula** - Stainless steel.

7.8 **Helium:** High purity grade (99.99%) used as carrier gas for the gas chromatograph.

7.9 **Analyte-free Reagent Water:** Water for which no target analytes are observed at or about the MRL, or the MDL, depending upon the project.

7.10 **Solvents:** acetone, Methylene chloride, methanol, and other appropriate standards that is pesticide grade or better. Purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt when no indication is given.

7.11 **Stock Standards for Initial Calibration and Continuing Calibration Verification Standards** Store all standards at -10-20°C. All stock standards expire upon the manufacturer's indications or one year if no indication is given.

7.11.1 SemiVolatile Internal Standards: 4000 µg/mL in Methylene Chloride, NSI.

7.11.2 8270SIM Stock Standards

7.11.2.1 Ready Stock (CLP surrogates): 200ppm in Methylene Chloride, NSI.

7.11.2.2 1-Methylnaphthalene: 2000 µg/mL in Methylene Chloride, ChemService.

7.11.3 Tuning Mix: 2500 µg/mL in Methylene Chloride, Restek.

7.12 **Intermediate Calibration Standards**

Intermediate Calibration Standards have a 6 months expiration date and must be stored between -10 and -20 ^{0}C.

7.12.1 Semi-volatile Organic Compounds (50 µg/mL in Methylene Chloride): Take 2.50 mL of 200ppm ReadyStock (CLP surrogates) and 0.25 mL of 2000µg/mL 1-Methylnaphthalene standard and dilute to 10 mL with Methylene Chloride.

7.12.2 Semi-volatile Organic Compounds (10 µg/mL in Methylene Chloride): Take 2.0 mL of the 50 ug/mL in Methylene Chloride solution and dilute to 10 mL with Methylene Chloride.

7.13 Working Calibration Standard

The following calibration standards are prepared from the 10 µg/mL intermediate standard to a final volume of 1 mL with Methylene Chloride. These standards expire in 6 months and must be stored between -10 and -20 ^{0}C.

Final Concentration (µg/mL)	Aliquot of 10 ug/mL (µL)	Final Volume (mL)
0.1	10	1
0.2	20	1
0.5	50	1
1.0	100	1
2.0	200	1
5.0	500	1

7.14 Decafluorotriphenylphosphine (DFTPP) Tune Standard

Decafluorotriphenylphosphine Intermediate Standard (25 ppm in Methylene Chloride) - Dilute a 100 uL aliquot of 2500 ppm solution to a 10-mL volumetric flask with Methylene Chloride. This dilution expires in 6 months and must be stored between -10 and -20 ^{0}C.

7.15 Pentafluorotributylamine (PFTBA) - Calibration gas

7.16 Laboratory Control Sample (LCS) and Matrix Spiking Standards –

7.16.1 8270 LCS mix 1 (100 ppm), Supelco - Store at -10-20°C. Standard expires upon the manufacturer's indications or one year if no indication is given.

7.16.2 LCS Working standard solution (1.0 µg/mL) – Take 0.5 mL of 100 ppm 8270LCS mix 1 and dilute to 50 mLs with Methanol. This dilution expires in 6 months and is stored between -10 and -20 ^{0}C.

7.17 ICV standards –

7.17.1 8270/625 Mid-stock (200ppm) in Methylene Chloride, Supelco. Store at -10-20°C. Standard expires upon the manufacturer's indications or 6 months if no indication is given.

7.17.2 Intermediate Solution for ICV (10 µg/mL) Take 0.05 mL of 200ppm 8270/625 Midstock and dilute to 1.0 mL with Methylene Chloride. Expires in 6 months. Store between -10 and -20 ^{0}C.

7.17.3 Working Standard Solution for ICV (1.0 µg/mL) Take 0.10 mL of the intermediate ICV solution and dilute to 1.0 mL with Methylene Chloride. Expires in 6 months. Store between -10 and -20 ^{0}C.

8 PROCEDURE

8.1 Calibration and Standardization

8.1.1 MSD Tuning: Tune the MSD to meet the criteria in Table 2 for a 50 ng injection of DFTPP. Acquire the mass spectrum of DFTPP as follows: Average three scans (the peak apex scan and the scans immediately preceding and following the apex). Alternatively, the apex scan, or the scan preceding the apex, or the scan following the apex can be used. When background subtraction is required, subtract using a single scan no more than 20 scans prior to the elution of DFTPP. Do not use any part of the DFTPP peak to background subtract. Use identical MSD instrument conditions for all subsequent standards, samples, spiked samples, and QC samples associated with a DFTPP analysis. Use the analysis time for the DFTPP to define the start of the 12-hour analysis window.

8.1.2 Initial Calibration (ICAL)
Prior to conducting any sample analyses, prepare a multi-point calibration. See Section 7 for preparation of the Working Calibration Standards. Select a primary and a secondary ion from each analyte for identification. Tabulate the area response of the primary quantitation ion (see Table 3) versus the concentration for each internal standard, analyte, and surrogate. Calculate the response factor (RF) for each analyte and surrogate relative to the associated internal standard using the following formula.

$$RF = (A_X)(C_{IS}) / (A_{IS})(C_X)$$

Where

A_X = Peak area of the analysts or surrogate's characteristic ion;
A_{IS} = Peak area of the associated internal standard's characteristic ion;
C_X = Concentration of the analyte or surrogate in the calibration sample; and
C_{IS} = Concentration of the associated internal standard.

8.1.2.1 Calculate the average response factor, RF_{AVE}, for each analyte and surrogate from RFs of each of the calibration levels.

$$RF_{AVE} = \Sigma RF_i / n$$

8.1.2.2 Calculate the standard deviation (SD) and the percent relative standard deviation (% RSD) for each analyte.

$$\% \ RSD = (SD)(100) / RF_{AVE}$$

8.1.2.3 If the % RSD of any analyte or surrogate is ≤15%, assume linearity over the calibration range. Use the RF_{AVE} for the analyte or surrogate to quantitate sample analytes. Alternatively, calibrate the analytes by linear regression or quadratic regression. If the coefficient corelation of linear or quadratic regression is < 0.990, then corrective action must be taken to eliminate the problem prior to re-attempting calibration. If the calibration criteria are not met, check standards with bad injection and re-analyzed standard. If bad injection is not evident, perform maintenance and calibration. Demonstrate that the calibration is in-control before proceeding with the analysis.

8.1.2.4 Supervisory review and approval of the ICAL is required.

8.1.2.5 Create an ICAL File. Place the following ICAL documents in the file.

- ICAL Checklist filled out and approved
- Sequence report
- DFTPP Tune analysis Report
- Blank analysis Quantitation Report
- Calibration Status Report - Initial
- Response Factor Report
- Data Analysis Parameters Report
- Copy of the calibration curve for any compound that uses a curve (instead on the average RF)
- Quantitation Report for each calibration standard (including manual integration documentation)
- ICV Quantitation Report and Evaluate Continuing Calibration Report
- Calibration Status Report - Final

8.1.3 Initial Calibration Verification: Following the initial calibration, analyze an ICV standard to verify that there are no systematic errors in any of the analyte calibrations. The ICV standard is at a concentration near the midpoint of the calibration curve, but it is made from a source other than the source used for the preparation of the calibration standards. The ICV standard must contain all the analytes that are in the calibration standards. The concentration of each analyte is calculated using the procedure for quantitation determined during the ICAL. The percent recovery for each analyte must be within 70 - 130%. If an analyte's percent recovery is outside the limits, take corrective action to determine why. Some compounds may exceed this criteria and the initial calibration may still be valid. Use professional judgment when evaluating reactive compounds or those exhibiting poor chromatographic behavior.

8.1.4 Continuing Calibration Verification:

8.1.4.1 Check the MSD's tune by injecting 50 ng of DFTPP as described above at the start of a 12-hour analysis window. If the criteria found in Table 2 are met, then continue the check the initial calibration curve by analyzing the CCV. If the first run of the DFTPP fails, retry. If the second run also fails, inspect the system for potential maintenance needs. Take corrective action before attempting to retune.

8.1.4.2 After the tuning criteria have been verified, verify the initial calibration by analyzing a midrange continuing calibration verification (CCV) standard. The 1 ppm level standard is recommended. Compare the results to the ICAL.

- The analytes using RF_{AVE} for quantitation must have a percent difference ≤20%.
- The analytes using an equation for quantitation must have a percent recovery of 80 to 120%.

8.1.4.3 If the tune criteria and the continuing calibration criteria are met, check the retention times of all compounds, surrogates, and internal standards against the initial calibration. If the retention time for any internal standard changes by more than 30 seconds from the retention time from the mid-point standard of the most recent initial calibration, inspect the system for malfunctions and make corrections as required. If the area for any of the internal standards changes by a factor of 2 (-50% to +100%) from the response of the mid-point standard of the most recent initial calibration, make corrections to the system.

8.1.4.4 If the CCV standard analysis meets the continuing calibration verification criteria, begin sample analysis. If the CCV criteria are not met, evaluate if the problem is due to internal standard response, to surrogate response, or to the response of one of the target analytes. If the problem is due to one or more of the internal standards and/or one or more of the surrogates, re-prepare the internal standard/surrogate solution and re-analyze. If the problem persists, perform maintenance. If the results for one or more of the target analytes do not meet criteria for continuing calibration verification, perform maintenance. Demonstration of in-control is required before proceeding with the analysis.

8.2 Sample Collection

8.2.1 Containers used to collect samples are to be purchased precleaned and certified. The sample containers should be 1-liter amber glass with Teflon lined screw-top cap for water and 16 oz. glass jar, or metal sleeve for soil sample.

8.2.2 Sample containers should be filled with care so as to prevent any portion of the sample coming in contact with the sampler's gloves, thus potentially contaminating the sample. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g., if an automatic sampler is used), run reagent water through the sampler and use the rinsate as a field blank.

8.3 Sample Handling and Preservation

8.3.1 Water and soil samples are iced or refrigerated at 0-6 °C in the dark from time of collection until extraction.

8.3.2 Extract water samples within 7 days of collection and analyze the extracts within 40 days of preparation of the extract.

8.3.3 Extract Soil and sludge samples within 14 days of collection and analyze the extract within 40 days of preparation of the extract.

8.4 Sample Preparation

Method Selection: Prepare samples by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510
Soil/sediment	3550

8.5 Sample Analysis

Identify analytes by retention time and ion ratios, using two ions per analyte. Quantitate that compound based on the integrated abundance from the primary or the secondary characteristic ion (see Table 3). Use the internal standard nearest the retention time of that given analyte. Quantify all compounds based on the initial, multi-point calibration using either RF_{AVE} or the calibration equation that was determined during the ICAL.

8.6 Troubleshooting

8.6.1 Carrier Gas Purifier - If in-line purifiers or scrubbers are in place, these purifiers should be changed as recommended by the supplier.

8.6.2 Gas Chromatograph

8.6.2.1 Chromatographic performance can often be improved by clipping off a small portion of the front of the capillary column. The cut needs to be straight and clean (uniform, without fragmentation) by using the proper column cutting tool.

8.6.2.2 Over time, the capillary column will exhibit poorer overall performance as peak resolution deteriorates due to analysis of contaminated samples. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the replace the column. This is especially evident when difficulties are experienced in conjunction with calibration.

8.6.3 Mass Selective Detector (MSD)

8.6.3.1 Tune the MSD as needed to achieve acceptable and consistent performance.

8.6.3.2 Check the foreline pump oil level weekly. Add pump fluid until the oil level in the window is near, but not above, the upper line.

8.6.3.3 Replace the foreline pump oil every six months. This may be done by the chemist or by an authorized service engineer.

8.6.3.4 Check the level of PFTBA in the calibration vial every six months. Refill the vial if necessary.

8.6.3.5 Check the diffusion pump fluid level annually. Replace the fluid if the level is low or dark or cloudy. This may be done by the chemist or by an instrument service person.

8.6.3.6 Clean the ion source as needed, depending upon the performance of the MSD. This may be done by the chemist or by an authorized service engineer.

8.6.3.7 Other maintenance is performed as recommended by Hewlett-Packard.

8.6.4 Maintenance log – Document all Preventive maintenance, as well as instrument repair, in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

8.7 Data Acquisition, Calculations, and Data Reduction Requirements

8.7.1 Introduction: The GC/MS data processing software uses the Hewlett-Packard RTE Integrator to generate the raw data used to calculate each analyte's RF_{AVE} values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all the calibrated analytes in the proper retention times and with the proper characteristic quantitation ions.

8.7.2 Target Analyte Concentrations in Water Samples: The concentration of an analyte, C_X , in a water sample is calculated using the RF_{AVE} as follows.

C_X in µg/L = $(A_X)(C_{IS})(DF) / (A_{IS})(RF_{AVE})$

Where

A_X = Peak area of the analyte's (or surrogate's) characteristic ion;
A_{IS} = Peak area of the associated internal standard's characteristic ion;
C_{IS} = Concentration of the associated internal standard;
RF_{AVE} = Average response factor for analyte from the ICAL; and
DF = Dilution factor, if the sample was diluted prior to analysis. If no dilution was made, DF = 1.

8.7.3 Target Analyte Concentration in Soil Samples The concentration of an analyte, C_X , in a soil sample is calculated using the RF_{AVE} as follows.

Cx in ug/Kg = $(A_X)(C_{IS})(DF) / (A_{IS})(RF_{AVE})(W_S)(D)$

Where

A_X = Peak area of the analyte's (or surrogate's) characteristic ion;
A_{IS} = Peak area of the associated internal standard's characteristic ion;
C_{IS} = Concentration of the associated internal standard;
RF_{AVE} = Average response factor for analyte from the ICAL;
W_S = Weight of sample extracted in gram
D = Percent dry weight of sample ÷ 100 (if the result is to be reported on a dry weight basis; and
DF = Dilution factor

8.8 **Computer Hardware and Software**
IBM-compatible PC with HP Chemstation software including EnviroQuant with Extracted Ion Current Profile (EICP), or equivalent.

9 DATA AND RECORDS MANAGEMENT

9.1 Responsibilities - It is the responsibility of the analyst to perform the analysis according to the instructions in this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are only to be performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

9.2 .Data Review – Data will be reviewed by the instrument analyst and a qualified peer using a Data Review Checklist (attached) and validated by a supervisor.

10 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

10.1 Tune and Calibration: The acceptance criteria for MSD tuning verification, initial calibration, and continuing calibration verification are detailed in the procedure. If tune does not meet criteria, perform target-tune and then re-analyze DFTPP. If tune check with DFTPP is still out-of-control, perform maintenance. Demonstrate that the system is in-control before proceeding with the analysis of CCV standard.

10.2 Internal Standards: The area counts of the internal standards of the initial daily CCV must be within ± 2 times (i.e., -50 % to +100 %) of the responses of the internal standards of the mid-point ICAL standard. Compare the internal standard responses for all analyses in the 12-hour window with the initial daily CCV. Internal standard area counts of subsequent samples and standards must be within ± 2 times (i.e., -50% to +100%) of the responses of the internal standards in the CCV analyzed at the start of the 12-hour window. Internal standards must have RT ± 0.5 min from the ICAL for the CCV and ± 0.5 from the CCV for the samples. CCV internal standard area counts must be –50% to 100% of the initial calibration mid-point standard area counts, otherwise, a new curve is required. Sample internal standard area counts must be –50% to 100% of the CCV area counts. Re-analyze any internal standard outlier unless a matrix interference can be clearly demonstrated by the first analysis. Flag as estimated any associated results from each outlying Internal Standard.

10.3 Surrogate Recoveries

Surrogate compound	**Water Recovery Limits (%)**	**Soil Recovery Limits (%)**
2-Fluorobiphenyl	27-114	23-120
Nitrobenzene –d5	22-124	18-125
Terphenyl- d14	23-139	19-145

If a surrogate fails acceptance, the sample must be evaluated for matrix interferences and "historical results". Reanalyze the sample to confirm the interference. If confirmed, re-extract the sample unless confirmed by MS/MSD or there is insufficient sample volume. If needed contact client and flag the data in the report. If surrogates are diluted more than 10 times, report as "D", diluted below calibration. For package reports, include initial and confirmation analysis results.

10.4 Method Blank The method blank should not have target analytes detected at or above the method reporting limit. If there is MB contamination, determine whether the contamination is from the instrument or due to contamination from the extraction. If the contamination is due to extraction, re-extract the batch with clean glassware or flag the data appropriately.

10.5 Laboratory Control Sample Recoveries

Compound	Water Recovery Limits (%)	Soil Recovery Limits (%)
Acenaphthene	49-116	42-112
Acenaphthylene	45-122	44-114
Anthracene	54-120	49-113
Benzo(a)anthracene	61-116	47-116
Benzo(a)pyrene	60-118	41-122
Benzo(b)fluoranthene	60-116	48-117
Benzo(g,h,i)perylene	50-125	34-126
Benzo(k)fluoranthene	54-120	41-123
Chrysene	60-117	45-117
Dibenzo(a,h)anthracene	31-139	29-129
Fluoranthene	56-121	36-122
Fluorene	48-122	40-113
Indeno(1,2,3-cd)pyrene	50-125	40-122
Naphthalene	39-109	44-101
Phenanthrene	47-128	51-110
Pyrene	60-113	35-128

If the LCS fails acceptance limits for any target compounds, the analyst must evaluate the system and calibration. If no problems are found, then the batch QC must be evaluated to determine what corrective action must be taken. This may involve the Project manager or Department Supervisor. Corrective action will depend on specific project, client, or state agency. The batch shall be re-extracted or the data may be flagged in the final report.

10.6 Matrix Spike Recoveries

Compound	Water Recovery Limits (%)	Soil Recovery Limits (%)
Acenaphthene	49-116	42-112
Acenaphthylene	45-122	44-114
Anthracene	54-120	49-113
Benzo(a)anthracene	61-116	47-116
Benzo(a)pyrene	60-118	41-122
Benzo(b)fluoranthene	60-116	48-117
Benzo(g,h,i)perylene	50-125	34-126
Benzo(k)fluoranthene	54-120	41-123
Chrysene	60-117	45-117
Dibenzo(a,h)anthracene	31-139	29-129
Fluoranthene	56-121	36-122
Fluorene	48-122	40-113
Indeno(1,2,3-cd)pyrene	50-125	40-122
Naphthalene	39-109	44-101
Phenanthrene	47-128	51-110
Pyrene	60-113	35-128

If the matrix spike fails acceptance, the sample must be evaluated for matrix interferences requirements. Evaluate the recovery of the duplicate MS and/or batch LCS. If the LCS is acceptable, continue with the analysis and assume matrix interferences.

11 REFERENCES

11.1 *Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique*, Method 8270C, Revision 3, December 1996 in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, U. S. EPA, SW-846, Final Update III

11.2 *Determinative Chromatographic Separations*, Method 8000B, Revision 2, December 1996 in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, U. S. EPA, SW-846, Final Update III

Table 1
Target Compound List

Compound	MRL for Water (µg/L)	MRL for Soil (µg/Kg)
Acenaphthene	0.2	6.6
Acenaphthylene	0.2	6.6
Anthracene	0.2	6.6
Benzo (a) Anthracene	0.1	3.3
Benzo (a) Pyrene	0.2	6.6
Benzo (b) Fluoranthene	0.2	6.6
Benzo (g,h,I) Perylene	0.2	6.6
Benzo (k) Fluoranthene	0.2	6.6
Chryene	0.2	6.6
Dibenzo (a,h) Anthracene	0.2	6.6
Fluoranthene	0.2	6.6
Fluorene	0.2	6.6
Indeno (1,2,3-cd) Pyrene	0.2	6.6
Naphthalene	0.2	6.6
Phenanthrene	0.2	6.6
Pyrene	0.2	6.6

Table 2
Decafluorotriphenylphosphine Ion Abundance Criteria

Ion Mass (m/z)	Relative Abundance Criteria
51	30 to 60% of m/z 198
68	<2 % of m/z 69
70	<2 % of m/z 69
127	40 to 60 % of m/z 198
197	<1 % of mass 198
198	Base peak, 100 % relative abundance
199	5 to 9% of m/z 198
275	10 to 30 % of m/z 198
365	>1 % of mass 198
441	Present but less than m/z 443
442	>40 % of m/z 198
443	17 to 23 % of m/z 442

Table 3
Characteristic Ions of Target Analytes

Compound	Primary Ion	Secondary Ion(s)
Internal Standards		
Naphthalene-d8	136	68, 108
Acenaphthene-d10	164	162, 160
Phenanthrene-d10	188	94, 80
Chrysene-d12	240	120, 236
Perylene-d12	264	260, 265
Surrogates		
Nitrobenzene-d5	80	82, 54
2-Fluorobiphenyl	172	171
Terphenyl-d14	244	122, 212
Analytes		
Naphthalene	128	127
Acenaphthylene	152	151, 153
Acenaphthene	154	153, 152
Fluorene	166	165, 167
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Fluoranthene	202	101, 203
Pyrene	202	200, 203
Benz(a)anthracene	228	229, 226
Chrysene	228	226, 229
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, 278
Dibenz(a,h)anthracene	278	276, 138
Benzo(g,h,i)perylene	276	138, 277

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GC/MS SEMI-VOLATILES
DATA QUALITY CHECKLIST

Method: _____ Instrument: _____
Analysis Date: _____

Yes	No	NA			Yes	No	NA
☐	☐	☐	1.	Extraction Benchsheet complete?	☐	☐	☐
☐	☐	☐	2.	Holding Times met method requirements?	☐	☐	☐
☐	☐	☐	3.	Instrument Run Log complete?	☐	☐	☐
☐	☐	☐	4.	DFTPP Tune met method requirements?	☐	☐	☐
☐	☐	☐	5.	CCVs acceptable (win, RT, %D)?	☐	☐	☐
☐	☐	☐	6.	Quantitation reports present for all samples,blk,lcs,ms,msd?	☐	☐	☐
☐	☐	☐	7.	Has the analyst initialed and dated each quantitation report?	☐	☐	☐
☐	☐	☐	8.	Are spectral match details for all sample hits present? (packages only)	☐	☐	☐
☐	☐	☐	9.	Graphically cerifies spectral matches for all sample hits? (routine report)	☐	☐	☐
☐	☐	☐	10.	Has current ICAL been used to quantitate all sample results?	☐	☐	☐
☐	☐	☐	11.	Are all analyses within 12-hr window?	☐	☐	☐
☐	☐	☐	12.	Are all Internal standard retention times within 30 sec. of opening CCV?	☐	☐	☐
☐	☐	☐	13.	Are all IS responses within -50% to +100% of opening CCV?	☐	☐	☐
☐	☐	☐	14.	Surrogate recoveries are within QC limits for samples and QC?	☐	☐	☐
☐	☐	☐	15.	Method Blank results <PQL?	☐	☐	☐
☐	☐	☐	16.	LCS recoveries within QC limits?	☐	☐	☐
☐	☐	☐	17.	MS/MSD recoveries within QC limits?	☐	☐	☐
☐	☐	☐		• RPDs between MS/MSD within QC limits?	☐	☐	☐
☐	☐	☐	18.	All sample concentrations within Linear Range?	☐	☐	☐
☐	☐	☐	19.	Dilution factors verified and calculated correctly?	☐	☐	☐
☐	☐	☐	20.	All peak integrations acceptable?	☐	☐	☐
☐	☐	☐	21.	Are all manual integrations flagged, initialed and dated?	☐	☐	☐
☐	☐	☐	22.	Are internal COCs included in package (if applicable)?	☐	☐	☐

Analyst: _____ Peer Review: _____
Date: _____ Date: _____

COMMENTS:
****Comments must be provided for any items noted above as "No"**

Training Plan for Analysis of SVOCs by GC/MS

Procedure:_____

SOP: _____ Revision: _____ Date: _____

Trainee: _____

1. Read SOP — Trainer: ____ Trainee: ____ Date: _____
2. Read appropriate EPA Method — Trainer: ____ Trainee: ____ Date: _____
3. Demonstrated understanding of the scientific basis of the analysis
   Gas chromatography
   Mass spectrometry — Trainer: ____ Trainee: ____ Date: _____
4. Demonstrated familiarity with related SOPs

ADM-BATCHSEQ	ADM-SIGFIG	ADM-DREV
ADM-DATAENTRY	ADM-NCAR	ADM-TRANDOC
ADM-INT	ADM-MDL	

   Trainer: ____ Trainee: ____ Date:_____
5. Observe performance of SOP
   - sample preparation (soil, water, other matrices) and sample loading
   - analytical sequence setup
   - DFTPP tuning evaluation
   - initial calibration and continuing calibration verification
   - sample analysis
   - EnviroQuant use
   - data reduction and reporting

   Trainer: ____ Trainee: ____ Date:_____
6. I have read, understood and agree to perform the most recent version of the SOP:
   Signature:_____ Date:_____
7. Perform SOP with supervision
   - including all items listed in 5. — Trainer: ____ Trainee: ____ Date:_____
8. Independent performance of the SOP
   - including all items listed in 5.
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.

   Trainer: ____ Trainee: ____ Date:_____

STANDARD OPERATING PROCEDURE

ANALYSIS OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND POLYCHLORINATED DIBENZOFURANS BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

SOP Code: HRMS-8290

Revision: 5.2klv

12/07/04

Approved by: Xiangqiu Liang 12/8/04

Xiangqiu Liang, Laboratory Director — Date

Jane Freemyer 12/08/04

Jane Freemyer, Quality Assurance Manager — Date

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Standard Operating Procedure

ANALYSIS OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND POLYCHLORINATED DIBENZOFURANS BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

1.-1 APPLICATION

1.1 This method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) in a variety of environmental matrices and at part-per-trillion to part-per-quadrillion concentrations. The following compounds can be determined by this method:

Analyte	CAS Registry No
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin (PeCDD)	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin (HxCDD)	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin (HpCDD)	35822-46-9
1,2,34,5,6,7,8-Octachlorodibenzo-*p*-dioxin (OCDD)	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	55673-89-7
1,2,3,4,5,6,7,8-Octachlorodibenzofuran (OCDF)	39001-02-0
Total Tetrachlorodibenzo-*p*-dioxin (TCDD)	41902-57-5
Total Pentachlorodibenzo-*p*-dioxin (PeCDD)	36088-22-9
Total Hexachlorodibenzo-*p*-dioxin (HxCDD)	34465-46-8
Total Heptachlorodibenzo-*p*-dioxin (HpCDD)	37871-00-4
Total Tetrachlorodibenzofuran (TCDF)	55722-27-5
Total Pentachlorodibenzofuran (PeCDF)	30402-15-4
Total Hexachlorodibenzofuran (HxCDF)	55684-94-1
Total Heptachlorodibenzofuran (HpCDF)	38998-75-3

1.2 The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based method calibration limits (MCLs), and other pertinent information. Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs – see Table 4) considered within the scope of this method that are greater than ten times the upper MCLs must be analyzed by a protocol designed for such concentration levels, e.g., Method 8280. An optional method for reporting the analytical results using a 2,3,7,8 TCDD toxicity equivalency factor (TEF) is described.

The sensitivity of this method is dependent upon the level of interferences within a given matrix (see Table 1.) The calibration range of the method for a 1L water sample is 10 to 2000ppq for TCDD/TCDF and PeCDD/PeCDF, and 1.0 to 200ppt for a 10g soil, sediment, fly ash, or tissue sample for the same analytes. Analysis of a one tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper MCL. The actual limits of detection and quantitation will differ from the lower MCL, depending on the complexity of the matrix.

1.3 This method is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.4 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed.

2.0 METHOD SUMMARY

2.1 This procedure uses matrix specific extraction, analyte specific cleanup, and HRGC/HRMS analysis techniques.

2.2 If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. A simplified analysis flow chart is presented at the end of this method.

2.3 A specified amount (see Table 1) of soil, sediment, fly ash, water, sludge (including paper pulp), still bottom, fuel oil, chemical reactor residue, fish tissue, or human adipose tissue is spiked with a solution containing specified amounts of each of the nine isotopically labeled PCDDs/PCDFs. The sample is then extracted according to a matrix specific extraction procedure. Aqueous samples that are judged to contain 1 percent or more solids, and solid samples that show an aqueous phase, are filtered. The solid phase (including the filter) and the aqueous phase are extracted separately, and the extracts combined before extract cleanup.

The extraction procedures are:

2.3.1 Toluene: Soxhlet extractions for soil, sediment, fly ash, and paper pulp samples;
2.3.2 Methylene chloride: Jar/Separatory Funnel extraction for water samples;
2.3.3 Toluene: Dean-Stark extraction for fuel oil and chemical samples
2.3.4 Toluene extraction for still bottom samples and sludge samples
2.3.5 Hexane/methylene chloride: Soxhlet extraction for fish tissue samples
2.3.6 Methylene chloride extraction for human adipose tissue samples.
2.3.7 As an option, all solid samples (wet or dry) may be extracted with toluene using a Soxhlet/Dean Stark extraction system. The decision for the selection of an extraction procedure for chemical reactor residue samples is based on the appearance (consistency, viscosity) of the samples.

2.4 The extracts are submitted to a sulfuric acid washing treatment and dried. Following a solvent exchange step, the extracts can be cleaned up by column chromatography on silica gel, alumina or activated carbon.

2.5 The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding 10 to 50µL (depending on the matrix) of a nonane solution containing 50pg/µL of the recovery standards $^{13}C_{12}$ -1,2,3,4-TCDD and $^{13}C_{12}$ -1,2,3,7,8,9-HxCDD. The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners, while the latter is used to determine the percent recoveries of the hexa-, hepta- and octachlorinated PCDD/PCDF congeners.

2.6 One µL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

2.7 The identification of OCDD and nine of the fifteen 2,3,7,8-substituted congeners, for which a $^{13}C_{12}$-labeled standard is available in the sample fortification and recovery standard solutions, is based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous detection of the two most abundant ions in the molecular ion region. The remaining six 2,3,7,8-substituted congeners (i.e., 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standards are available in the sample fortification solution, and all other PCDD/PCDF congeners are identified when their relative retention times fall within their respective PCDD/PCDF retention time windows, as established from the routine calibration data, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to $^{13}C_{12}$ -OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Identification is also based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios.

2.8 Quantitation of the individual congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a multipoint (five points) calibration curve for each homologue, during which each calibration solution is analyzed once.

3.0 DEFINITIONS

3.1. Abbreviations

PCDD	=	Polychlorinated dibenzo-*p*-dioxin
PCDF	=	Polychlorinated dibenzofuran
TCDD	=	Tetrachlorodibenzo-*p*-dioxin
PeCDD	=	Pentachlorodibenzo-*p*-dioxin
HxCDD	=	Hexachlorodibenzo-*p*-dioxin
HpCDD	=	Heptachlorodibenzo-*p*-dioxin
OCDD	=	Octachlorodibenzo-*p*-dioxin
TCDF	=	Tetrachlorodibenzofuran
PeCDF	=	Pentachlorodibenzofuran
HxCDF	=	Hexachlorodibenzofuran
HpCDF	=	Heptachlorodibenzofuran
OCDF	=	Octachlorodibenzofuran
HxCDPE	=	Hexachlorodiphenyl ether
HpCDPE	=	Heptachlorodiphenyl ether
OCDPE	=	Octachlorodiphenyl ether
NCDPE	=	Nonachlorodiphenyl ether
DCDPE	=	Decachlorodiphenyl ether
PFK	=	Perfluorokerosene
CS	=	Cleanup standard
IS	=	Internal standard
RS	=	Recovery standard
HRGC	=	High-resolution gas chromatography
HRMS	=	High-resolution mass spectrometry
TEF	=	Toxicity equivalence factor
TEQ	=	Toxicity equivalent

3.2 Isotope-Labeled Standards

3.2.1 Recovery standards are added to the sample extract immediately before analysis by HRGC/HRMS. Recoveries of the cleanup and internal standards are determined by comparing the peak areas of the cleanup and internal standards with the peak areas of the recovery standards.

3.2.2 The cleanup standard is added to the sample extract prior to initiation of cleanup procedures. Loss of cleanup standard reflects losses occurring during cleanup. Generally, greater losses of cleanup standard occur when exhaustive cleanup techniques are indicated.

3.2.3 Internal standards are added to the sample before extraction. Losses of internal standards reflect losses occurring during both extraction and cleanup. It is difficult to recover the internal standard (and the analytes) from some sample matrices. Severe losses of internal standards may result in impaired detection limits.

3.3 Toxicity Equivalence Factors

3.3.1 Not all of the 17 regulated dioxin/furan isomers have the same degree of toxicity. Toxicity Equivalence Factors (TEF), relative to the most toxic dioxin/furan isomer, 2,3,7,8-TCDD, have been established. The concentration of each 2,3,7,8-congener is multiplied by the appropriate toxicity equivalence factor (TEF). The individual results of these calculations are summed to determine the 2,3,7,8-TCDD toxicity equivalent (TEQ). Table 8

4.0 HEALTH and SAFETY WARNINGS

4.1. This method is to be used only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

4.2 Safety training for working with PCDDs and PCDFs is required prior handling these chemicals.

4.3. Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to self, or to others, of materials known or believed to contain PCDDs or PCDFs.

5.0 CAUTIONS

5.1 Low-level contamination is always a possibility for HRGC/HRMS analysis, due to the chemical properties of dioxins/furans.

5.1.1. When HRGC/HRMS glassware becomes contaminated, it is discarded.
5.1.2 Disposable glassware and material is used whenever possible during extraction and cleanup.

6.0 INTERFERENCES

6.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves.

6.2 The use of high purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

6.3 Interferences coextracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans. These analytes may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the established retention time windows. While cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

6.4 A high-resolution capillary column (60m DB-5, J&W Scientific, or equivalent) is used in this method. However, no single column is known to resolve all isomers. The 60m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity. In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent).

7.0 PERSONNEL QUALIFICATIONS

All analysts must demonstrate proficiency in the method by completing the following Training Plan:

Training Plan for Analysis of Method 8290 by HRMS

SOP File: HRMS-8290 (Rev. 4/01-09-01)

Trainee: _____

1. Read and study SOP — Trainer: ____ Trainee: ____ Date: _____
2. Read Methods 8000B and 8290 — Trainer: ____ Trainee: ____ Date: _____
3. Demonstrated scientific understanding of the analysis — Trainer: ____ Trainee: ____ Date: _____
   Sample preparation
   HR-Gas chromatography
   HR-Mass spectrometry
4. Demonstrated familiarity with related SOPs — Trainer: ____ Trainee: ____ Date: _____
   SOP for Analytical Batches and Analytical Sequences
   SOP for Making Entries into Logbooks and onto Benchsheets
   SOP for Manual Integration of Chromatographic Peaks
   SOP for Significant Figures
   SOP for Nonconformity and Corrective Action Documentation
   SOP for Determination of Method Detection Limits
5. Observe performance of SOP — Trainer: ____ Trainee: ____ Date: _____
   - sample preparation (soil, water, other matrices) and sample loading
   - analytical sequence setup
   - initial calibration and continuing calibration verification
   - sample analysis
   - software introduction
   - data reduction and reporting
6. Perform SOP with supervision — Trainer: ____ Trainee: ____ Date: _____
   - sample preparation (soil, water, other matrices) and sample loading
   - analytical sequence setup
   - initial calibration and continuing calibration verification
   - sample analysis
   - software use
   - data reduction and reporting
7. Independent performance of the SOP — Trainer: ____ Trainee: ____ Date: _____
   - sample preparation (soil, water, other matrices) and sample loading
   - analytical sequence setup
   - initial calibration and continuing calibration verification
   - sample analysis
   -software proficiency
   - data reduction and reporting
   - initial demonstration of competency
   - IPR study

- single blind PE sample

8. Instrument operation and maintenance Trainer: ____ Trainee: ____ Date: _____
   - autosampler
   - gas chromatograph and capillary column installation
   - mass spectrometer
   - data system

8.0 EQUIPMENT AND SUPPLIES

8.1 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS) - The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and capillary columns.

8.1.1 GC Injection Port - The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On column 1µL injections can be used on the 60m DB-5 column. The use of a moving needle injection port is also acceptable. When using the method described in this protocol, a 2µL injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2µL). One-µL injections are allowed; however, laboratories must remain consistent throughout the analyses by using the same injection volume at all times.

8.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Interface – The GC/MS interface components should withstand 350^{o}C. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb
PCDD and PCDF compounds. Vespel or equivalent, ferrules are recommended.

8.1.3 Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley). Figure 4

8.1.4 Data System - A dedicated data system is employed to control the rapid multiple-ion monitoring process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired

during the analyses and stored. Quantitations may be reported based upon computer generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass spectral peak profiles and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should permit the measurement of noise on the base line.

8.2 GC Columns

8.2.1 In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, use of the 60m DB-5 fused silica capillary column is recommended. Minimum acceptance criteria must be demonstrated and documented. At the beginning of each 12 hour period (after mass resolution and GC resolution are demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples. Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60m DB-5 GC column alone. In order to determine the proper concentrations of the individual 2,3,7,8-substituted congeners, the sample extract must be reanalyzed on another GC column that resolves the isomers.

8.2.2 30m DB-225 fused silica capillary column, (J&W Scientific) or equivalent.

8.3 Miscellaneous Equipment and Materials - The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

8.3.1 Nitrogen evaporation apparatus with variable flow rate.

8.3.2 Balances capable of accurately weighing to 0.001g.

8.3.3 Centrifuge.

8.3.4 Water bath, capable of being temperature controlled within $\pm$ 2^{o}C.

8.3.5 Stainless steel or glass container large enough to hold contents of one pint sample container.

8.3.6 250mL polypropylene beaker.

8.3.7 Drying oven.

8.3.8 20mL scintillation vials.

8.3.9 Laboratory hoods.

8.3.10 Pipets, disposable, Pasteur, 150mm long x 5mm ID.

8.3.11 Pipets, disposable, serological, 10mL, for the preparation of the carbon columns.

8.3.12 2mL screw-top vials.

8.3.13 Electric meat grinder with a 3 to 5mm hole size inner plate.

8.3.14 Carbon, 120-440 mesh, activated just before use.

8.3.15 Teflon boiling chips (or equivalent).

NOTE: Teflon boiling chips may float in methylene chloride, may not work in the presence of any water phase, and may be penetrated by nonpolar organic compounds.

8.3.16 6mL and 60mL polypropylene reservoirs.

8.3.17 Frits that fit in the polypropylene reservoirs.

8.3.18 Glass fiber filters, 0.50µm, Whatman GFF, or equivalent.

8.3.19 Dean-Stark trap, 5 or 10mL.

8.3.20 All glass Soxhlet apparatus, 500mL flask.

8.3.21 Soxhlet/Dean Stark extractor (optional), all glass, 500mL flask.

8.3.22 Glass funnels, sized to hold 170mL of liquid.

8.3.23 Desiccator.

8.3.24 2-liter Separatory funnels/Screw top jars

8.3.25 Rotary evaporator with a temperature controlled water bath.

8.3.26 Glass wool.

8.3.27 Extraction jars, glass, 250mL, with teflon lined screw cap.

8.3.28 Volumetric flasks, Class A - 5mL to 100mL.

8.3.29 Auto sampler vials with 150uL inserts.

NOTE: Reuse of glassware should be minimized to avoid the risk of contamination. All glassware that is reused must be scrupulously cleaned as soon as possible after use, according to the following procedure: Rinse glassware with water. Soak glassware overnight in a mixture of equal parts of water, Alconox and RBS-35. Rinse with water and allow drying. Rinse with high purity acetone, toluene, dichloromethane and hexane. Store in a clean environment

8.4 All standards should be logged in and numbered when delivered. Details of all dilutions of standards should also be entered in the PCDD/PCDF Standards Logbook. *Note:* store at room temperature in the dark—do not refrigerate.

8.5 Organic-free reagent water - All references to water in this method refer to organic-free reagent water

8.6 Column Chromatography Reagents

8.7 Carbon 120-440 mesh (Supelco Envi-Carb or equivalent); weigh 0.5g into 20mL scintillation vials and activate overnight at a minimum of 100 C.

8.8 Silica gel, high purity grade, type 60, 70-230 mesh. Activate overnight at a minimum temperature of 120^0C. Store in a glass bottle sealed with Teflon lined screw cap.

8.9 Silica gel impregnated with sodium hydroxide. Add one part (by weight) of 1M NaOH solution to two parts (by weight) silica gel (activated) in a screw cap bottle and mix with a glass rod until free of lumps. Store in desicator in a glass bottle sealed with Teflon lined screw cap.

8.10 Silica gel impregnated with 40 percent (by weight) sulfuric acid. Add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (activated), mix with a glass rod until free of lumps. Store in desiccator in a glass bottle sealed with Teflon lined screw cap.

8.11 Quartz sand.

8.12 Extraction thimbles, 43mm x 123mm.

8.13 Sulfuric acid, concentrated, ACS grade, specific gravity 241.84.

8.14 Sodium chloride, analytical reagent, 5 percent (w/v) in organic-free reagent water.

8.15 Desiccating agent

8.16 Sodium Sulfate (powder, anhydrous), Na_2SO_4.

8.17 Solvents
- 8.17.1 Methylene Chloride. High purity distilled in glass or highest available purity.
- 8.17.2 Hexane. High purity distilled in glass or highest available purity.
- 8.17.3 Methanol. High purity distilled in glass or highest available purity.
- 8.17.4 Nonane. High purity distilled in glass or highest available purity.
- 8.17.5 Toluene. High purity distilled in glass or highest available purity.
- 8.17.6 Tridecane, High purity distilled in glass or highest available purity.
- 8.17.7 Acetone. High purity distilled in glass or highest available purity.

8.18 High-Resolution Concentration Calibration Solutions. Five Nonane solutions containing unlabeled (17) and carbon-labeled (11) PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (1.0 pg/µL) and the highest values for the octachlorinated congeners (1000pg/µL). Table 4

- 8.18.1 Calibration solutions may be obtained from the Environmental Monitoring Systems Laboratory, U.S. EPA Cincinnati, Ohio. However, additional secondary standards must be obtained from commercial sources, and solutions should be prepared in the analyst's laboratory. It is the responsibility of the laboratory to ascertain that the calibration solutions received (or prepared) are indeed at the appropriate concentrations before they are used to analyze samples.

- 8.18.2 Store the concentration calibration solutions in 1mL minivials at room temperature in the dark.

- 7.18.3 Calibration solutions, Set contains one 0.2ml ampule each of HRCC1, HRCC2, HRCC3, HRCC4 and HRCC5 solutions. Table 4

8.19 The Window Defining/GC Column Performance Mix Solution - This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The $^{13}C_{12}$ -2,3,7,8-TCDD and TCDF are also present. Table 6

7.19.1 The three nonspecific TCDD isomers (ng/ml) in this solution used to verify column performance. Table 6

8.20 Internal standard solution- Individual labeled analytes are combined to make an internal compound stock. This stock solution is diluted with Nonane to make internal standard spiking solution. Table 9

8.22 Recovery standard solution- Individual labeled analytes are combined to make a recovery compound stock. This stock solution is diluted with Nonane to make recovery standard spiking solution. Table 9

8.23 Cleanup standard solution- Individual labeled analyte is used to make a stock. This stock solution is diluted with Nonane to make cleanup standard spiking solution

8.24 Matrix spiking solution (natives) - Individual natives analytes are combined to make a matrix reference compound stock. This stock solution is diluted with Nonane to make matrix reference spiking solution. Table 9

9.0 INSTRUMENT CALIBRATION AND STANDARDIZATION

9.1 The total cycle time for data acquisition must be < 1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

9.2 Acquire SIM data for all the ions listed in the five descriptors. Table 5

9.3 Initial Calibration - Initial calibration is required before any samples analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration does not meet the required criteria. All five high-resolution concentration calibration solutions must be used for the initial calibration.

9.4 Tune the instrument with PFK.

9.5 Inject 1µL of the GC column performance check solution and acquire SIM mass spectral data. The total cycle time must be <1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the column performance check criterion was met.

9.6 By using the same GC and MS conditions that produced acceptable results with the column performance check solution, analyze a 1µL portion of each of the five concentration calibration solutions once with the following mass spectrometer operating parameters.

9.7 The ratio of integrated ion current (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series) for all unlabeled calibration standards.

9.8 The ratio of integrated ion current for the ions belonging to the carbon-labeled internal and recovery standards must be within the acceptable control limits.

9.9 For each selected ion current profile (SICP) and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Measurement of S/N is required for any GC peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SICP above the GC peak in question. Figure 3

9.10 Calculate the 17 relative response factors (RF) for unlabeled target analytes [RF(n); n = 1 to 17] relative to their appropriate internal standards and the nine RFs for the labeled $^{13}C_{12}$ internal standards [RF(m); m = 18 to 26)] relative to the recovery standards according to the following formula:

$$RF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n} \qquad RF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{re}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

Where:

A_n^1 and A_n^2 = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDDs/PCDFs.

A_{is}^1 and A_{is}^2 = sum of the integrated ion abundances of the quantitation ions for the labeled internal standard PCDDs/PCDFs.

A_{rs}^1 and A_{rs}^2 = sum of the integrated ion abundances of the quantitation ions the labeled recovery standards.

Q_{is} = quantity of the internal standard injected is (pg)

Q_{rs} = quantity of the recovery standard injected (pg).

Q_n = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RF_n and RF_{is} are dimensionless quantities; the units used to express Q_{is}, Q_{rs} and Q_n must be the same.

9.11 The mean response factor (RF) and the percent relative standard deviation (%RSD) are determined by the following equations

$$\overline{RF_n} = \frac{\sum_{j=1}^{5} RF_{n(j)}}{5}; \qquad \%\text{RSD} = \frac{SDCR}{MVCS}$$

Where:
n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17),and j is the injection number (or calibration solution number; j = 1 to 5).
SDCR= Standard Deviation of the Calibration response
MVCS= Mean Value of the Calibration response

9.12 The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

9.12.1 For congeners that belong to a homologous series with only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the mean RF used will be the same as the mean RF.

NOTE: The calibration solutions do not contain $^{13}C_{12}$ -OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the [M+6] ion of $^{13}C_{12}$-OCDF from the [M+2] ion of OCDD (and [M+4] from $^{13}C_{12}$-OCDF with [M] of OCDD). Therefore, the RF for OCDF is calculated relative to $^{13}C_{12}$ -OCDD.

9.12.2 For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer, the mean RF used for those homologous series will be the mean of the RFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

$$\overline{RF_k} = \frac{1}{t} \sum_{n=1}^{t} RFn$$

where:
k = 27 to 30; with 27 = PeCDF; 28 = HxCDF;
29 = HxCDD; and 30 = HpCDF (Table 11)

t = total number of 2,3,7,8-substituted isomers present in the calibration solutions for each homologous series (e.g., two for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

NOTE: Presumably, the HRGC/HRMS response factors of different isomers within a homologous series are different. However, this analytical protocol will make the assumption that the HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

9.12.3 Relative response factors [RF_m] to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

$$RF_m = \frac{A_{is}^m \times Q_{is}}{Q_{is}^m \times A_{rs}}$$

$$\overline{RF} = 1/5 \sum_{j=1}^{5} \mathrm{RF}m\,(j)$$

m = 18 to 26 (congener type) and j = 1 to 5 (injection number),
A_{is}^m = sum of the integrated ion abundances of the quantitation ions for a given internal standard (m = 18 to 26),
A_{rs} = sum of the integrated ion abundances of the quantitation ions for the appropriate recovery standard,
Q_{rs} , Q_{is}^m = quantities of, respectively, the recovery standard (rs) and a particular internal standard (is = m) injected, (pg),
RF_m = relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from one injection, and RF = calculated mean relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from the five initial calibration injections (j).

9.12.4 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed.

9.12.4.1 The percent relative standard deviations for the mean response factors [RF_n and RF_m] from the 17 unlabeled standards must not exceed $\pm$ 20 percent, and those for the nine labeled reference compounds must not exceed $\pm$ 30 percent.

9.12.4.2 The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be $\geq$ 10.

9.12.4.3 The ion abundance ratios must be within the specified control limits.

NOTE: If the criterion for acceptable calibration is met, the analyte specific RF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RFs will be used for all calculations until the routine calibration criteria are no longer met. At such time, new mean RFs will be calculated from a new set of injections of the calibration solutions.

9.12.5 Routine Calibration (Continuing Calibration Check) – Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12-hour shift. Inject 1µL of the concentration calibration solution HRCC-3 standard. By using the same HRGC/HRMS conditions, determine and document an acceptable calibration.

9.12.6 Criteria for Acceptable Routine Calibration - The following criteria must be met before further analysis is performed.

9.12.6.1 The measured RFs [RF_n for the unlabeled standards] obtained during the routine calibration runs must be within $\pm$ 20 percent of the mean values established during the initial calibration.

9.12.6.2 The measured RFs [RF_m for the labeled standards] obtained during the routine calibration runs must be within $\pm$ 30

percent of the mean values established during the initial calibration.

9.12.6.3 The ion abundance ratios must be within the allowed control limits.

9.12.6.4 If either one these criteria, is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire routine calibration process must be reviewed. It is realized that it may not always be possible to achieve all RF criteria. For example, it has occurred that the RF criteria for $^{13}C_{12}$ -HpCDD and $^{13}C_{12}$ -OCDD were not met, however, the RF values for the corresponding unlabeled compounds were routinely within the criteria established in the method. In these cases, 24 of the 26 RF parameters have met the QC criteria, and the data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must assess the effect on overall data quality as required for the data quality objectives and decide on appropriate action. Corrective action would be in order, for example, if the compounds for which the RF criteria were not met included both the unlabeled and the corresponding internal standard compounds.

NOTE: An initial calibration must be carried out whenever the HRCC-3, the sample fortification, or the recovery standard solution is replaced by a new solution from a different lot.

10.0 SAMPLE COLLECTION

10.1. Samples are typically delivered by a express shipping service or by the client.

11.0 SAMPLE HANDLING AND PRESERVATION

11.1 Samples are logged into the Sample Receiving Logbook, and labeled. A database entry is also made, which triggers the printing of a set of tracking forms.

11.2 Storage and Holding Times - All samples, except fish and adipose tissue samples, must be stored at 4^0C in the dark, extracted within 30 days and completely analyzed within 45 days of extraction. Fish and adipose tissue samples must be stored at -10^0C $\pm 2^0$C in the dark, extracted within 30 days and completely analyzed within 45 days of collection. Whenever samples are analyzed after the holding time expiration date, the results should be considered to be minimum concentrations and should be identified as such.

NOTE: The holding times listed in this method are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times may be as high as a year for certain matrices. Sample extracts, however, should always be analyzed within 45 days of extraction.

11.3. Fish and tissue samples must be shipped on dry ice and arrive at 4 ± 2 degrees C

12.0 SAMPLE PREPARATION AND ANALYSIS

12.1. Before extraction, a visual inspection of a sample is done If it is not homogeneous, the entire contents of the sample container is transferred to a sheet of aluminum foil and then mixed thoroughly with a polystyrene spoon prior to removing an aliquot for analysis.

12.2 If a soil, sediment, or paper pulp sample contains more than 25 percent water, the two phases are separated, the aqueous phase is discarded, and the remaining solid phase is analyzed.

12.2.1 Transfer an estimated 50g aliquot of the sample to a centrifuge tube. Centrifuge for 15 minutes at 1000rpm.

12.2.2. Thoroughly mix the solid with a polystyrene spoon, and weigh out aliquots for analysis and dry weight determination.

12.2.3. Return the remaining sample to the original sample container.

12.3. If a water sample has a solids content greater than or equal to 1 percent, then the solid phase is separated from the aqueous phase, and both phases are extracted separately.

12.3.1. Filter the sample through a 0.5μm filter.

12.3.2. Extract the filter and solids as for a soil sample. Extract the aqueous filtrate as for a water sample.

12.3.3 Combine the two extracts and proceed with the cleanup and analysis.

12.4 Addition of Internal Standard

12.4.1 Use a portion of 10g of the sample to be analyzed. Transfer the sample portion to a tared extraction thimble and determine its weight.

12.4.2 Except for adipose tissue, add 100μL of internal standard solution to the sample(s).

12.4.3 For water samples, mix the internal standard solution with 10.0mL acetone in a pre-labeled scintillation vial and add to the corresponding sample container.

12.5 Extraction of Fish and Tissue

12.5.1 To a tared thimble, add approximately 30g anhydrous sodium sulfate to a 20g portion of a homogeneous fish samples and mix thoroughly with a pasteur pipet. After breaking up any lumps, place the spiked 200 μL of internal standard into the fish/Sodium Sulfate mixture in the Soxhlet apparatus. Add approximately 270mL Hexane/Methylene Chloride (1:1) to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the extracts.

12.5.2 Evaporate the extract to 5-10 mL. Do not allow the extract to go to dryness.

12.5.3 To a tarred 20 mL scintilation vial, transfer exactly one half of the extract. Weigh the scint vial containing the extract, record the weight and allow to dry in a gravity oven overnight before weighing a second time.

12.5.4 Add 500uL tridecane to the 500mL flask.. Concentrate the extract on a rotary evaporator to an apparent volume of 0.5mL.

12.5.5 Add 20mL hexane to the 500mL flask. Again concentrate to 0.5mL, using either a rotary evaporator or by air-drying in the hood.

12.5.6 Add 30mL Hexane and decant the contents of the 500mL flask into a 250mL screw top flask. Rinse the 500mL flask with an additional 30mL portion of hexane in the sonicator and add the rinse to the jar.

12.5.7 Spike with 100 µL cleanup standard and proceed with sulfuric acid clean up.

12.6 Fuel Oil/Chemical

12.6.1 Extract sample by mixing 1g of sample with 60mL hexane in a 250mL jar. Spike with 100 µL internal spiking standard.

12.6.2 The sample extract volume should be in 60 mL hexane. Partition the Hexane extract against approximately 10mL of concentrated sulfuric acid. Shake for 30 seconds. Allow a minimum of 1 hour for separation. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until little color is visible in the acid layer (perform a maximum of four acid washings).

12.6.3 Partition the extract against 20mL of 5 percent (w/v) sodium chloride/HPLC water. Shake for 30 seconds. Allow a minimum 20 minutes for separation. Remove and discard the aqueous layer (bottom).

12.6.4 Add 500uL tridecane to each sample jar and allow to evaporate until near dryness, using a rotary evaporator or by air-drying under the hood. The tridecane will prevent the sample from going to complete dryness. The sample is now ready for column cleanup

12.7 Fly Ash

NOTE: Because of the tendency of fly ash to "fly", all handling steps should be performed in a hood in order to minimize contamination.

12.7.1 Weigh about 10g fly ash to two decimal places in a tared 250 mL extraction jar. Add 100µL internal standard solution to the sample(s). Add 150mL of 1M HCl to the fly ash sample. Seal the jar with the Teflon lined screw cap and shake for 3 hours at room temperature.

12.7.1 Rinse a 0.5um filter with organic-free reagent water. Assemble a Buchner funnel into a 1L flask and place the filter in the funnel. Pour the sample on the filter and filter the fly ash cake with approximately 500mL organic-free reagent water. A disposable filter apparatus can be used.

12.7.2 Place the sample and the filter paper into an extraction thimble. Add 10g anhydrous powdered sodium sulfate.

12.7.3 Extract in a Soxhlet extraction apparatus charged with approximately 270mL toluene for 16 hours using a five cycle/hour schedule.

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

12.7.4 Cool and add 0.5mL tridecane to the 500mL round bottom flask. Concentrate the extract to near dryness on a rotary evaporator at 40-50^{0}C. Add 20mL Hexane and evaporate to near dryness, or alternatively, air-dry under the hood.

12.7.5 Transfer the concentrate to a 250 screw top jar using 20mL Hexane. Rinse the flask in a sonicator with two 20mL portions of hexane and add the rinses to the jar.

12.7.6 The sample is now ready for sulfuric acid clean up.

12.8 Aqueous samples

12.8.1 Allow the sample to come to ambient temperature. Spike 100µL internal standard solution into a 20 mL scintillation vial. Add 10 mL acetone and pour into the appropriate sample jar.

12.8.2 When the sample is judged to contain 1 percent or more solids, the sample must be filtered through a 0.5µm filter. If the suspended solids content is too great to filter through the filter, centrifuge the sample, decant, and then filter the aqueous phase.

12.8.3 Combine the solids from the centrifuge bottle(s) with the particulates on the filter and with the filter itself and proceed with the Soxhlet extraction.

12.8.4 Pour the aqueous filtrate into a 2L screw top jar/or 2L separatory funnel. Add 100mL Methylene Chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Pour the solvent from the sample jar to the 2L jar/or 2L

separatory funnel. Close and shake the 2L jar/or 2L separatory funnel for 3 minutes. Periodic venting is necessary.

12.8.5 Allow the organic layer to separate from the water phase for a minimum of 10minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation (e.g., centrifuge the extract).

12.8.6 Transfer the Methylene Chloride 250mL glass jar.

12.8.7 Repeat the extraction once more with fresh 50mL portions of methylene chloride. Transfer to a 250 mL screw top jar.

12.8.8 After extracting the water sample, pour into a 1L graduated cylinder and record the volume.

12.8.9 If the extract is colorless or has a light tint, add 500 µL tridecane and evaporate to near 500 µL and proceed with the silica gel/carbon column clean up. If the extract has a medium to dark tint, evaporate to near 500 µL (using a rotary evaporator or by air-drying under the hood), and proceed to sulfuric acid clean up. Spike 100 µL of cleanup standard before proceeding with cleanup.

12.9 Soil/Sediment/Paper Pulp

12.9.1 Add approximately 20g anhydrous powdered sodium to an extraction thimble. Tare the thimble. Transfer 10g of sample to the thimble. Spike with internal standard solution.

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. See Tables 15, 16, 17.

12.9.2 Add approximately 270mL toluene to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour.

12.9.3 Cool the extraction apparatus. Add 500 uL tridecane to the flask and concentrate to near dryness on a rotary evaporator at 45- 50°C. Add 20mL Hexane to the flask and evaporate to near dryness, with either a rotary evaporator or by air-drying under the hood.

12.9.4 Transfer the extract to a 250mL screw top jar with 30mL hexane. Rinse

the 500mL flat bottom in a sonicator with an additional 30mL rinse of Hexane and transfer to the screw top jar. Final volume should be approximately 60mL hexane.

12.9.5 If the extract is colorless or has a light tint, add 500 µL tridecane and evaporate to near 500 µL and proceed with the silica gel/carbon column clean up. If the extract has a medium to dark tint, proceed to sulfuric acid clean up.

12.9.6 Transfer approximately 1g of sample into a tarred 20 mL scint vial. Weigh and Record the weight of the vial containing the sample. Place in a gravity oven and allow drying overnight. Re-weigh the dried sample and record the weight.

12.10 Clean up Procedures

All samples must be spiked with 100µL cleanup standard solution before any clean up procedure is performed.

12.10.1 Sulfuric Acid Clean up

12.10.1.1 The sample extract volume should be in 60 mL hexane. Partition the Hexane extract against approximately 10mL of concentrated sulfuric acid. Shake for 30 seconds. Allow a minimum of 1 hour for separation. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until little color is visible in the acid layer (perform a maximum of four acid washings).

12.10.1.2 Partition the extract against 20mL of 5 percent (w/v) sodium chloride/HPLC water. Shake for 30 seconds. Allow a minimum 20 minutes for separation. Remove and discard the aqueous layer (bottom).

12.10.1.3 Add 500uL tridecane to each sample jar and allow to evaporate until near dryness, by air-drying under the hood. The tridecane will prevent the sample from going to complete dryness.

12.10.1.4 The sample is now ready for column cleanup.

12.10.2 Silica/Carbon Column Cleanup

12.10.2.1 Pack a 6mL column as follows: Insert a frit at the bottom of the column. Remove the pre-weighed, activated carbon from the oven, and add approximately 2ml toluene. Cool down is not necessary.

Transfer the slurry to the 6mL column and allow the carbon to settle. Rinse the 20mL vial with addition rinses of toluene until most of the carbon has been transferred. Rinse the column sides of residual carbon. Allow the toluene to completely drain. Insert a frit on top and push down to the top of the carbon. Elute with 5mL dichloromethane then 5mL hexane. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap a wetted column.

12.10.2.2 Pack a 60ml reservoir, with silica gel as follows: Insert a frit and push it to the bottom. Place 1 teaspoon activated neutral silica gel in the column and tap the column gently to settle the silica gel. Add 1 teaspoon sodium hydroxide-impregnated silica gel, 2 teaspoon sulfuric acid-impregnated silica gel, and 1 teaspoon sodium sulfate. Tap the column gently after each addition. Elute with 30mL hexane and stop the flow just before exposure of the top layer of sodium sulfate to air. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap the wetted column.

12.10.2.3 Place the silica gel column on top of the vacuum manifold and the carbon column of the bottom opposite the silica gel column. The column is now ready for loading the sample extract.

12.10.2.4 Transfer the 2mL extract to the silica gel column and allow eluting until the extract level is at the top of the sodium sulfate. A slow vacuum can be used to facilitate the extract into the column.

12.10.2.5 Rinse the flask containing the extract with 5mL hexane and load into the Silica Gel column. Allow eluting until the extract level is at the top of the sodium sulfate. A slow vacuum can be used to facilitate the extract into the column.

12.10.2.6 Slowly add 30mL of Hexane to the Silica Gel column. Add another 30mL, then 20mL more of Hexane when space permits for a total of 80mL.

NOTE: At this point, neither pressure nor vacuum is necessary. Do not adjust the drip rate.

12.10.2.7 Remove the used silica gel column when the drip form the carbon column stops. Reverse the carbon column by placing on top of the

manifold. Elute the column with 5mL Dichloromethane, then 5mL of 1:1 Ethyl Acetate/Hexane.

12.10.2.8 Place a labeled 20mL scintillation vial under the carbon column and elute with a total of approximately 20mL Toluene. Be sure to collect the Toluene. Allow the extract to evaporate to dryness under the fume hood.

12.10.2.9 Add approximately 2mL hexane to the scintillation vial. Vortex and sonicate, then transfer the extract to a clear 2mL screw top vial. Allow evaporation to dryness under the fume hood.

NOTE: If possible, transfer the extract to the labeled autosampler vial when the volume reaches approximately 150µL.

12.10.2.10 Add 160uL Hexane to the 2mL vial. Rinse the sides of the 2mL vial with only the 160uL that was added. Transfer to an appropriately labeled autosampler vial. Allow sample to evaporate to dryness, under the hood.

12.10.2.11 The sample is ready to be spiked with 20uL recovery standard solution.

12.11 Chromatographic/Mass Spectrometric Conditions and Data Acquisition Parameters

12.11.1 Gas Chromatograph
Column coating: DB-5
Film thickness: 0.25µm
Column dimension: 60 m x 0.25mm
Injector temperature: 300^0C
Splitless valve time: 1 min
Interface temperature: 300^0C
Temperature program:

STAGE	INITIAL TEMP, C	INITIAL HOLD TIME, MIN	TEMPERATURE RAMP, C/MIN	FINAL TEMPERATURE C	FINAL HOLD TIME, MIN
1	150	5	35	215	5
2			1.5	230	6
3			7	315	5

12.11.2 Mass Spectrometer

12.11.2.1 The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage-reset time) of one second or less. At a minimum, the ions listed in Table 5 for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection (Table 6) of the molecular ions M and M+2 for $^{13}C_{12}$-HxCDF and $^{13}C_{12}$-HpCDF rather than $^{13}M+2$ and $^{13}M+4$ (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

NOTE: At the option of the analyst, the tetra- and pentachlorinated dioxins and furans can be combined into a single descriptor.

12.11.2.2 The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in Table 5. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). Fig.4 By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the Low Mass and High Mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors.

12.12 Analysis

12.12.1 Remove the sample or blank extract from storage. With a stream of dry, purified nitrogen, reduce the extract volume to dryness.

12.12.12 Inject a 1µL aliquot of the extract into the GC, operated under the conditions that have been established to produce acceptable results with the performance check solution.

12.12.3 Acquire SIM data. Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined. Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run. The analyst may be required to monitor a PFK ion, not as a lock-mass, but as a regular ion, in order to meet this requirement. It is recommended to examine the lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements. Report any discrepancies in the case narrative.

12.12.4 Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.12.4.1Retention Times

12.12.4.1.1 For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD), the retention time (RRT; at maximum peak height) of the sample components must be within -1 to +3 seconds of the isotopically labeled standard.

12.12.4.1.2 For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$ -OCDD as determined from the daily routine calibration results.

12.12.4.1.3 For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution.

12.12.4.1.4 The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach maximum simultaneously ($\pm$ 2 seconds).

12.12.4.1.5 The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$ -TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously ($\pm$ 2 seconds).

NOTE: The analyst is required to verify the presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF in the SICPs of the daily performance checks. Should either one compound be missing, the analyst is required to take corrective action as it may indicate a potential problem with the ability to detect all the PCDDs/PCDFs.

12.12.4.2 Abundance Ratios

12.12.4.2.1 The integrated ion currents for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned. Table 7

12.12.4.3 Signal-to-Noise Ratio

12.12.4.3.1 All ion current intensities must be ≥2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers.

12.12.4.4 Polychlorinated Diphenyl Ether Interferences

12.12.4.4.1 In addition to the above criteria, the identification of a G peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected at the same retention time (± 2 seconds) in the corresponding polychlorinated diphenyl ether channel.

13.0 DATA ANALYSIS AND CALCULATIONS

13.1 For gas chromatographic peaks that have met the criteria, calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RF_n}}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,
A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDDs/PCDFs,
A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,
Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,
W = weight, in g, of the sample (solid or organic liquid), or volume in mL of an aqueous sample, and
$\overline{RF_n}$ = calculated mean relative response factor for the analyte [RF_n with n = 1 to 17]
If the analyte is identified as one of the 2,3,7,8-substituted PCDDs or PCDFs, RF_n is the value calculated using the equation section

13.1.1

However, if it is a non-2,3,7,8-substituted congener, the RF(k) value is calculated using the equation RF(k) = 27 to 30]. Table 11

13.2 Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\% \text{ Recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times RF_n} \times 100$$

where:
A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standard,
A_{rs} = sum of the integrated ion abundances of the quantitation ions for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners,
Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,
Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and
RF_m = calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard. This represents the mean [RF with m = 18 to 26]. (Table 10)

NOTE: For human adipose tissue, adjust the percent recoveries by adding 1 percent to the calculated value to compensate for the 1 percent of the extract diverted for the lipid determination.

13.3 If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds exceeds the upper method calibration limits (MCL) listed in Table 1 (e.g., 200 pg/µL for TCDD in soil), the linear range of response versus concentration may have been exceeded, and a second analysis of the sample (using a one tenth aliquot) should be undertaken. The volumes of the internal and recovery standard solutions should remain the same as described for the sample preparation. For the other congeners (including OCDD), however, report the measured concentration and indicate that the value exceeds the MCL.

13.4 If a smaller sample size would not be representative of the entire sample, one of the following options is recommended:

(1) Re-extract an additional aliquot of sufficient size to insure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Prior to GC/MS analysis, dilute the sample so that it has a concentration of internal standard equivalent to that present in the calibration standard. Then, analyze the diluted extract.

(2) Re-extract an additional aliquot of sufficient size to insure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Immediately following extraction, transfer the sample to a volumetric flask and dilute to known volume. Remove an appropriate aliquot and proceed with cleanup and analysis.

(3) Use the original analysis data to quantitate the internal standard recoveries. Respike the original extract (note that no additional cleanup is necessary) with 100 times the usual quantity of internal standards. Dilute the re-spiked extract by a factor of 100. Reanalyze the diluted sample using the internal standard recoveries calculated from the initial analysis to correct the results for losses during isolation and cleanup.

13.5 The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report. If an isomer is not detected, use zero (0) in this calculation.

13.6 Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

13.6.1 Samples giving a response for both quantitation ions that are less than 2.5 times the background level.

13.6.2 Use the expression for EDL (specific 2,3,7,8-substituted PCDD/PCDF) below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF (i.e., S/N $\leq$ 2.5). The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (those congeners that do not have a $^{13}C_{12}$-labeled standard), multiplying that noise height by 2.5,

and relating the product to an estimated concentration that would produce that peak height.

Use the formula:

$$EDL = \frac{2.5 \times H_x \times Q_{is}}{H_{is} \times W \times \overline{RF_n}}$$

where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.
H_x = sum of the height of the noise level for each quantitation ion for the unlabeled PCDDs/PCDFs
H_{is} = sum of the height of the signal level for each quantitation ion for the labeled internal standard.

13.6.3 Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions.

13.6.4 When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria, calculate the "Estimated Maximum Possible Concentration" (EMPC), except that A should represent the sum of the x area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

13.6.5 The relative percent difference (RPD) of any duplicate sample results are calculated as follows:

$$RPD = \frac{|S1 - S2|}{\frac{(S1 + S2)}{2}} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

13.6.6 The 2,3,7,8-TCDD toxicity equivalents of PCDDs and PCDFs present in the sample are calculated, if requested by the data user, according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Center for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs and to OCDD and OCDF.

(Table 8) The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds. The exclusion of other homologous series such as mono-, di-, and tri-chlorinated dibenzodioxins and dibenzofurans does not mean that they are non-toxic. The above procedure for calculating the 2,3,7,8-TCDD toxicity equivalents is not claimed by the CDWG to be based on a thoroughly established scientific foundation. The procedure, rather, represents a "consensus recommendation on science policy". Since the procedure may be changed in the future, reporting requirements for PCDD and PCDF data would still include the reporting of the analyte concentrations of the PCDD/PCDF congeners.

13.7 Two GC Column TEF Determination

13.7.1 The concentration of 2,3,7,8-TCDD (see note below), is calculated from the analysis of the sample extract on the 60m DB-5 fused silica capillary column. The chromatographic separation between the 2,3,7,8-TCDD and its close eluters (1,2,3,7/1,2,3,8-TCDD and 1,2,3,9-TCDD) must be equal or less than 25 percent valley. Figure 5

13.7.2 The concentration of the 2,3,7,8-TCDF is obtained from the analysis of the sample extract on the 30m DB-225 fused silica capillary column. However, the GC/MS conditions must be altered so that:

(1) only the first three descriptors (i.e., tetra-, penta-, and hexachlorinated congeners) are used;

(2) and the switching time between descriptor 2 (pentachlorinatedcongeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}C_{12}$ - 1,2,3,7,8-PeCDD.

(3) The chromatographic separation between the 2,3,7,8-TCDF and its close eluters (2,3,4,7-TCDF and 1,2,3,9-TCDF) must be equal or less than 25 percent valley. Figure 6

NOTE: The confirmation and quantitation of 2,3,7,8-TCDD may be accomplished on the SP-2330 GC column instead of the DB-5 column.

13.7.3 For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-

noise ratio criteria, respectively. In addition, the retention time identification criterion applies here for congeners for which a carbon-labeled analogue is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions described and the results from the routine calibration run on the SP-2330.

14.0 DATA AND RECORDS MANAGEMENT

14.1 CAS reports the analytical data produced in its laboratories to the client via the certified analytical report. This report typically includes a transmittal letter, a case narrative, client project information, specific test results, quality control data, chain of custody information, and any other project-specific support documentation. The following procedures describe our data reduction, validation and reporting procedures.

14.2 All data is initially reviewed and processed by analysts using appropriate methods (e.g. chromatographic software, instrument printouts, hand calculation, etc.) A file of all raw data is printed, reviewed for completeness and quality criteria against an in-house checklist and signed off by the analyst. The operations manager reviews all reported data against the raw data; validating completeness and quality. The final report data package is then reviewed by the project manager for compliance with previously established project requirements. Typically, all data is reported in the units and MCLs listed in Appendix C.

14.3 Assessment of the analytical data includes a check on data consistency by looking for comparability of duplicate analyses, comparability of previous data from the same sampling location (if available), adherence to accuracy and precision control limits, and anomalous low or high parameter values. The results of this review will be discussed with either the departmental supervisor or lab director for resolution prior to final release of the package.

14.4 Once the data has been checked for accuracy and acceptability, the final report and raw data is forwarded to the lab director or quality assurance coordinator, who further reviews the data package for errors. When the entire data set has been found to be acceptable the lab director signs the report, the report is distributed and the raw data is filed for approximately one year, and then archived. All hard copy and electronic backups are archived in a secured file room for a period of at least 5 years from the date of the final report. It is not unusual to have various clients require 10-year retention of records, therefore, the archivist, project chemist, and possibly the client are consulted prior to destruction of the records.

14.5 The integrity of the data generated in the laboratory is primarily assessed by the analyst, supervisor and project chemist through the use of a variety of measures that may include

reagent blanks, laboratory fortified blanks, duplicates, matrix spikes and QC samples. The numerical criteria for evaluation of these QC samples are listed in Appendix C; these various QC sample analyses are evaluated using the flow diagrams found in Figures 12-1 through 12-9. Other validation measures of the data include a check of the linearity of the calibration curve, an accuracy check of the QC standards and a check of the system sensitivity. Data transcriptions and calculations are also reviewed. Specific calculations used for determining the concentration or value of the measured parameters from the raw data are given in each of the analytical methods or CAS SOPs.

14.6 When an analyst determines that the data has met the data quality objectives (and/or any client-specific data quality objectives) of the method and has qualified any anomalies in a clear, acceptable fashion, the data is validated by the supervisor. Prior to release of the report to the client, the project manager must also review the entire body of data for completeness and to ensure that any and all client-specified objectives were successfully achieved. If required, samples exceeding any established state/federal maximum contaminant level or reportable concentration level, must be reported to the client. A case narrative may be written by the project manager to explain any unusual problems with a specific analysis or sample, client-specific objectives, exceedences, etc... The original raw data, along with a copy of the final report, is archived. CAS maintains control of analytical results by adhering to standard operating procedures and by observing sample custody requirements. All data are calculated and reported in units consistent with project specifications, to enable easy comparison of data from report to report. Typical qualifiers used to flag analytical results are listed in Appendix D.

14.7 A document control system ensures that all documents are accounted for when the project is complete. A service request number is assigned to each project for reporting and filing purposes. This number is associated with each order number (sample).

14.7.1 The archiving system includes all of the following items for each set of analyses performed:

- Chain-of-custody documentation
- Benchsheets describing sample preparation
- Sample analysis sequence
- Analysis benchsheets and instrument printouts
- Chromatograms and peak integration reports for all samples, standards, blanks, spikes and reruns
- Log book ID number for the appropriate standards
- Copies of report submitted to the client
- Copies of Nonconformity and Corrective Action Report (NCAR) forms, if needed

14.7.2 Individual sets of analyses are indexed by analysis date and/or service request number. Since many analyses are performed with computer-based data systems, the final sample concentrations can be automatically calculated. If additional calculations are needed, they are written on the integration report or securely stapled to the chromatogram, if done on a separate sheet.

14.7.3 The archive room is an off-site file room in which files shall be maintained for a period of at least five years (from date of report issue). It is not unusual to have various clients require a 10-year retention of records, therefore, the archivist, project manager, and possibly the client are consulted prior to destruction of the records. The archive cabinet and/or off site storage area is kept locked and access keys are controlled. All documents must be signed out if needed outside of the archive room and returned in a timely manner. A designated archivist monitors filing, incoming, and outgoing data from the archive.

15.0 QUALITY CONTROL AND QUALITY ASSURANCE

15.1 Refer to Chapter One for specific quality control (QC) procedures. Quality control to validate sample extraction is covered in Method 3500. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

15.2 System Performance Criteria - System performance criteria are presented below. The laboratory may use the recommended GC column. It must be documented that all applicable system performance criteria were met before analysis of any sample is performed. Figure 3 provides a typical 12-hour analysis sequence, whereby the response factors and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hour period of operation. A GC column performance check is only required at the beginning of each 12-hour period during which samples are analyzed. An HRGC/HRMS method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch requires more than 12 hours of analyses.

15.2.1 GC Column Performance

15.2.1.1 Inject 1µL of the column performance check solution and acquire selected ion monitoring (SIM) data within a total cycle time of $\leq$ 1 second.

15.2.1.2 The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of $\leq$ 25 percent, where:

$$\text{Valley percent} = \frac{(X)}{(Y)} \times 100$$

x = measured from the 2,3,7,8-closest TCDD eluting isomer, and

y = the peak height of 2,3,7,8-TCDD

NOTE: It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used to determine the eight homologue retention time windows that are used for qualitative and quantitative purposes. All peaks (that includes $^{13}C_{12}$ -2,3,7,8-TCDD) should be labeled and identified on the chromatograms. Furthermore, all first eluters of a homologous series should be labeled with the letter F, and all last eluters of a homologous series should be labeled with the letter L.

Any individual selected ion current profile (SICP) (for the tetras, this would be the SICP for m/z 322 and m/z 304) or the reconstructed homologue ion current (for the tetras, this would correspond to m/z 320 + m/z 322 + m/z 304 + m/z 306) constitutes an acceptable form of data presentation. An SICP for the labeled compounds (e.g., m/z 334 for labeled TCDD) is also required.

15.2.1.3 The retention times for the switching of SIM ions characteristic of one homologous series to the next higher homologous series must be indicated in the SICP. (see Figure 5) Accurate switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds. Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60m DB-5 column. A laboratory with a GC/MS system that is not capable of detecting both congeners (1,2,8,9-TCDD and 1,3,4,6,8-PeCDF) within one analysis must take corrective action. If the recommended column is not used,

then the first and last eluting isomer of each homologue must be determined experimentally on the column which is used, and the appropriate isomers must then be used for window definition and switching times.

15.2.2 Mass Spectrometer Performance

15.2.2.1 Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in downtime for source cleaning.

15.2.2.1 Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which

corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100ppm at m/z 380.9760 (or 0.038amu at that particular mass).

15.3 Quality Control Samples

15.3.1 Performance Evaluation Samples - Included among the samples in all batches may be samples (blind or double blind) containing known amounts of unlabeled 2,3,7,8-substituted PCDDs/PCDFs or other PCDD/PCDF congeners.

15.3.2 Performance Check Solutions

15.3.2.1 At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration. calibration solution, HRCC-3, shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended). If the required criteria are not met, remedial action must be taken before any samples are analyzed.

15.3.2.2 To validate positive sample data, the routine or continuing calibration and the mass resolution check must be performed also at the end of each 12-hour period during which samples are analyzed. Furthermore, an HRGC/HRMS method blank run must be recorded following a calibration run and the first sample run.

15.3.2.3 If the laboratory operates only during one period (shift) each day of 12 hours or less, the GC performance check solution must be analyzed only once (at the beginning of the period) to validate the data acquired during the period. However, the mass resolution and continuing calibration checks must be performed at the beginning as well as at the end of the period.

15.3.2.4 If the laboratory operates during consecutive 12-hour periods (shifts), analysis of the GC performance check solution must be performed at the beginning of each 12-hour period. The mass

resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

15.3.2.5 Results of at least one analysis of the GC column performance check solution and of two mass resolution and continuing calibration checks must be reported with the sample data collected during a 12-hour period.

15.3.2.6 Deviations from criteria specified for the GC performance check or for the mass resolution check invalidate all positive sample data collected between analyses of the performance check solution, and the extracts from those positive samples shall be reanalyzed.

15.3.2.7 If the continuing calibration check performed at the end of a 12-hour period fails by no more than 25 percent RPD for the 17 unlabeled compounds, and 35 percent RPD for the 9 labeled reference compounds, use the mean RFs from the two daily routine calibration runs to compute the analyte concentrations, instead of the RFs obtained from the initial calibration.

15.3.2.8 A new initial calibration (new RFs) is required immediately (within two hours) following the analysis of the samples, whenever the RPD from the end-of-shift routine calibration exceeds 25 percent or 35 percent, respectively. Failure to perform a new initial calibration immediately following the analysis of the samples will automatically require reanalysis of all positive sample extracts analyzed before the failed end-of-shift continuing calibration check.

15.3.3 The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-CIN. However, if not available from the EMSL-CIN, standards can be obtained from other sources, and solutions can be prepared in the laboratory. Concentrations of all solutions containing 2,3,7,8-substituted PCDDs/PCDFs, which are not obtained from the EMSL-CIN, must be verified by comparison with the EPA standard solutions that are available from the EMSL-CIN.

15.3.4 Field Blanks - Each batch of samples usually contains a field blank sample of uncontaminated soil, sediment or water that is to be fortified before analysis. In addition to this field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure the sampling equipment has not contaminated any samples.

15.3.5 Fortified Field Blank

15.3.5.1 Weigh a 10g portion or use 1L (for aqueous samples) of the specified field blank sample and add 100µL of the solution containing the nine internal standards diluted.

15.3.5.2 Add 20µL of the recovery standard solution and analyze a 1µL aliquot of the concentrated extract.

15.3.5.2.1 Calculate the concentration of 2,3,7,8-substituted PCDDs/PCDFs and the percent recovery of the internal standards.

15.3.5.2.2 Extract and analyze a new simulated fortified field blank whenever new lots of solvents or reagents are used for sample extraction or for column chromatographic procedures.

15.3.6 Rinsate Sample

15.3.6.1 The rinsate sample must be fortified like a regular sample.

15.3.6.2 Take a 100mL (+ 0.5mL) portion of the sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add 100µL of the solution containing the nine internal standards.

15.3.6.3 Using a KD apparatus, concentrate to approximately 5mL.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the rinsate.

15.3.6.4 Transfer the 5mL concentrate from the KD concentrator tube in 1mL portions to a 1mL minivial, reducing the volume in the minivial as necessary with a gentle stream of dry nitrogen.

15.3.6.5 Rinse the KD concentrator tube with two 0.5mL portions of hexane and transfer the rinses to the 1mL minivial. Blow down with dry nitrogen as necessary.

15.3.6.6 Just before analysis, add 20µL recovery standard solution and reduce the volume to its final volume, No.column chromatography is required.

15.3.6.7 Analyze an aliquot following the same procedures used to analyze samples.

15.3.6.8 Report percent recovery of the internal standard and the presence of any PCDD/PCDF compounds in µg/L of rinsate solvent.

15.3.7 Duplicate Analyses, if specified by the project instructions:

15.3.7.1 In each batch of samples, locate the sample specified for duplicate analysis, and analyze a second 10g soil or sediment sample portion or 1L water sample, or an appropriate amount of the type of matrix under consideration.

15.3.7.2 The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean). Report all results.

15.3.7.3 Recommended actions to help locate problems:

15.3.7.4 Verify satisfactory instrument performance.

15.3.7.5 If possible, verify that no error was made while weighing the sample portions.

15.3.7.6 Review the analytical procedures with the performing laboratory personnel.

15.3.8 Matrix Spike and Matrix Spike Duplicate

15.3.8.1 Locate the sample for the MS and MSD analyses (the sample may be labeled "double volume").

15.3.8.2 Add an appropriate volume of the matrix spike fortification solution and of the sample fortification solution, adjusting the fortification level.

15.3.8.3 Analyze the MS and MSD samples.

15.3.8.4 The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

15.3.9 Percent Recovery of the Internal Standards

15.3.9.1 For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

NOTE: A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data.

15.4 Identification Criteria

15.4.1 If either one of the identification criteria is not met for a homologous series, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologous series at the calculated detection limit.

15.4.2 If the first initial identification criteria are met, but the criteria appearing are not met, that sample is presumed to contain interfering contaminants. This must be noted on the analytical report form, and the sample should be rerun or the extract reanalyzed.

15.5 Unused portions of samples and sample extracts should be preserved for 90 days after sample receipt to allow further analyses.

15.6 Reuse of glassware is to be minimized to avoid the risk of contamination.

16.0 REFERENCES

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TABLE 1

MATRICES, SAMPLE SIZES, AND METHOD CALIBRATION LIMITS (PARTS PER TRILLIONS)

	Water	Soil Sediment Paper pulp[b]	Fly ash	Fish tissue[c]	Human adipose tissue	Sludges Fuel oil	Still-bottom
Lower MCL[a]	0.01	1.0	1.0	1.0	1.0	5.0	10
Upper MCL[a]	2	200	200	200	200	1000	2000
Weight (g)	1000	10	10	10	2	1	1
IS spiking levels (ppt)	1	100	100	100	100	500	1000
Final extr. vol. (µL)	10-50	10-50	50	10-50	10-50	50	50

[a] For other congeners, multiply the values by 1 for TCDF/TCDD, by 2.5 for PeCDD/PeCDF, HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.
[b] Sample dewatered prior to analysis.
[c] An additional 10g sample is used for determination of lipid content.

TABLE 2

THE FIFTEEN 2,3,7,8-SUBSTITUTE PCDD AND PCDF CONGENERS

PCDD	PCDF
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF

* The 13C-labeled analogue is used as an internal standard
+ The 13C-labeled analogue is used as recovery standard

TABLE 3

ISOMERSOF CHLORINATED DIOXIN AND FURANS AS A FUNCTION OF THE NUMBER OF CHLORINE ATOMS

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2378-Dioxin	Number of Furan Isomers	Number of 2378-furans
1	2	-	4	-
2	10	-	16	-
3	14	-	28	-
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	75	7	135	10

TABLE 4
HIGH RESOLUTION CONCENTRATION CALIBRATION SOLUTIONS

Unlabeled	**Concentrations (pg/uL)**				
Analytes	1	2	3	4	5
2,3,7,8-TCDD	1	2.5	10	50	200
2,3,7,8-TCDF	1	2.5	10	50	200
1,2,3,7,8-PeCDD	2.5	6.25	25	125	500
1,2,3,7,8-PeCDF	2.5	6.25	25	125	500
2,3,4,7,8-PeCDF	2.5	6.25	25	125	500
1,2,3,4,7,8-HxCDD	2.5	6.25	25	125	500
1,2,3,6,7,8-HxCDD	2.5	6.25	25	125	500
1,2,3,7,8,9-HxCDD	2.5	6.25	25	125	500
1,2,3,4,7,8-HxCDF	2.5	6.25	25	125	500
1,2,3,6,7,8-HxCDF	2.5	6.25	25	125	500
1,2,3,7,8,9-HxCDF	2.5	6.25	25	125	500
2,3,4,6,7,8-HxCDF	2.5	6.25	25	125	500
1,2,3,4,6,7,8-HpCDD	2.5	6.25	25	125	500
1,2,3,4,6,7,8-HpCDF	2.5	6.25	25	125	500
1,2,3,4,7,8,9-HpCDF	2.5	6.25	25	125	500
OCDD	5	12.5	50	250	1000
OCDF	5	12.5	50	250	1000
Internal Standards					
13*C*12 – 2,3,7,8 – *TCDD*	50	50	50	50	50
13*C*12 – 2,3,7,8 – *TCDF*	50	50	50	50	50
13*C*12 – 1,2,3,7,8 – *PeCDD*	50	50	50	50	50
13*C*12 – 1,2,3,7,8 – *PeCDF*	50	50	50	50	50
13*C*12 – 1,2,3,6,7,8 – *HxCDD*	125	125	125	125	125
13*C*12 – 1,2,3,4,7,8 – *HxCDF*	125	125	125	125	125
13*C*12 – 1,2,3,4,6,7,8 – *HpCDD*	125	125	125	125	125
13*C*12 – 1,2,3,4,6,7,8 – *HpCDF*	125	125	125	125	125
13*C*12 – *OCDD*	250	250	250	250	250
Recovery Standards					
13*C*12 – 1,2,3,4 – *TCDD*	50	50	50	50	50
13*C*12 – 1,2,3, ,7,8,9 – *HxCDD*	125	125	125	125	125

TABLE 5
IONS MONITORED FOR HRGC/HRMS ANALYSIS OF PCDDS/PCDFS

DESCRIPTOR	EXACT M/Z	M/Z TYPE	ELEMENT COMPOSITION	COMPOUND
1	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF(S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF(S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD(CS)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD(S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD(S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HXCDPE
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PECDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF(S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PECDF(S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_3{}^{37}ClO_2$	PECDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PECDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PECDD(S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PECDD(S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HPCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HXCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HXCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HXCDF(S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HXCDF(S)

TABLE 5 (con't)

DESCRIPTOR	EXACT M/Z	M/Z TYPE	ELEMENT COMPOSITION	COMPOUND
3	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HXCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HXCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HXCDD(S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}C_2lO$	HXCDD(S)
	430.9729	QC	C_9F_{17}	PFK
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_5{}^{37}Cl_2O$	OCDPE
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HPCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HPCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7{}^{37}O$	HPCDF(S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HPCDF(S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HPCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HPCDD
	430.9729	LOCK	C_9F_{17}	PFK
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HPCDD(S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HPCDD(S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
5	441.728	M+2	$C_{12}H^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}H^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}H^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}H^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}H^{35}Cl_7{}^{37}ClO_2$	OCDD(IS)
	471.7750	M+4	$^{13}C_{12}H^{35}Cl_6{}^{37}Cl_2O_2$	OCDD(IS)
	513.6775	M+4	$C_{12}H^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

Nuclidic masses used:

H= 1.007825
C= 12.000000
^{13}C = 13.003355
F= 18.9984
O= 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

PFK= PERFLUROKEROSENE
SS= INTERNAL STANDARD
CS=CLEANUP STANDARD (only one m/z)

TABLE 6

PCDD AND PCDF CONGENERS PRESENT IN THE GC PERFORMANCE EVALUATION SOLUTION AND USED FOR DEFINING THE H GC HOMOLOGUE RETENTION TIME WINDOWS ON A 60-M DB-5 COLUMN

	PCDD Positional Isomer		PCDF Positional Isomers	
# Chlorine Atoms	First Eluters	Last Eluters	First Eluters	Last Eluters
4 [a]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,4,6,7,9/1,2,4,6,8,9	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
7	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,7,8,9
8	1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9	

[a] In addition to these two TCDD isomers, the 1,2,3,4,-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$ – 2,3,7,8-, and 1,2,3,9-TCDD isomers must be present as a check of column resolution

.

TABLE 7

THEORICAL ION ABUNDANCE RATIOS AND THEIR CONTROL LIMITS FOR PCDD AND PCDF

# Chlorine Atoms	Ion Type	Theoretical Abundance Ratio	Control Limits Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 [a]	M/M+2	0.51	0.43	0.59
7 [b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

[a] Used only for $^{13}C_{12}$ – HxCDF (IS)

[b] Used only for $^{13}C_{12}$ – HpCDF (IS)

TABLE 8

2,3,7,8-TCDD TOXICITY EQUIVALENCY FACTORS (TEFs) FOR THE POLYCHLORINATED DIBNZODIOXINS AND DIBENZOFURANS

Analyte	TEF [a]
2,3,7,8-TCDD	1.00
1,2,3,7,8-PeCDD	0.50
1,2,3,6,7,8-HxCDD	0.10
1,2,3,7,8,9-HxCDD	0.10
1,2,3,4,7,8-HxCDD	0.10
1,2,3,4,6,7,8-HpCDD	0.01
1,2,3,4,6,7,8,9-OCDD	0.001
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
1,2,3,4,7,8-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
1,2,3,4,6,7,8,9-OCDF	0.001

[a] Taken from "Interim Procedure for Estimating Risk Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxin and –Dibenzofurans 1989 Update". (EPA/625/3-89/016, March 1989).

TABLE 9
CONCENTRATION OF STOCK AND SPIKING SOLUTION CONTAINING PCDDs/PCDFs

PCDDs/PCDFs	Internal Standard Stock Solution (ng/mL)	Internal Standard Spiking Solution (ng/mL)	MS Stock Fortification Solution (ng/mL)	MS Spiking Fortification Solution (ng/mL)
2,3,7,8-TCDD			100	2
2,3,7,8-TCDF			100	2
1,2,3,7,8-PeCDD			250	5
1,2,3,7,8-PeCDF			250	5
2,3,4,7,8-PeCDF			250	5
1,2,3,4,7,8-HxCDD			250	5
1,2,3,6,7,8-HxCDD			250	5
1,2,3,7,8,9-HxCDD			250	5
1,2,3,4,7,8-HxCDF			250	5
1,2,3,6,7,8-HxCDF			250	5
1,2,3,7,8,9-HxCDF			250	5
2,3,4,6,7,8-HxCDF			250	5
1,2,3,4,6,7,8-HpCDD			250	5
1,2,3,4,6,7,8-HpCDF			250	5
1,2,3,4,7,8,9-HpCDF			250	5
OCDD			500	10
OCDF			500	10
Internal Standard				
$^{13}C_{12}-$2,3,7,8-TCDD	100	10		
$^{13}C_{12}-$2,3,7,8-TCDF	100	10		
$^{13}C_{12}-$1,2,3,78-PeCDD	100	10		
$^{13}C_{12}-$1,2,3,7,8-PeCDF	100	10		
$^{13}C_{12}-$1,2,3,6,7,8-HxCDD	250	25		
$^{13}C_{12}-$1,2,3,4,7,8-HxCDF	250	25		
$^{13}C_{12}-$1,2,3,4,6,7,8-HpCDD	250	25		
$^{13}C_{12}-$1,2,3,4,6,7,8-HpCDF	250	25		
$^{13}C_{12}-$OCDD	500	50		
Cleanup Standard				
$^{37}Cl_4-$2,3,7,8-TCDD		8.0		
Recovery Standard				
$^{13}C_{12}-$1,2,3,4-TCDD		50		
$^{13}C_{12}-$1,2,3,7,8,9-HxCDD		50		

TABLE 10

REFERENCE COMPOUNDS FOR QUANTITATION OF NATIVE AND LABELED PCDDs ANDPCDF

Compound Number	Type	Name	Reference Compound
1	Native	2,3,7,8-TCDD	18
2	Native	1,2,3,7,8-PeCDD	19
3	Native	1,2,3,4,7,8-HxCDD	20
4	Native	1,2,3,4,6,7,8-HxCDD	20
5	Native	1,2,3,7,8,9-HxCDD	20
6	Native	1,2,3,4,6,7,8-HpCDD	21
7	Native	OCDD	22
8	Native	2,3,7,8-TCDF	23
9	Native	1,2,3,7,8-PeCDF	24
10	Native	2,3,4,7,8-PeCDF	24
11	Native	1,2,3,4,7,8-HxCDF	25
12	Native	1,2,3,6,7,8-HxCDF	25
13	Native	1,2,3,7,8,9-HxCDF	25
14	Native	2,3,4,6,7,8-HxCDF	25
15	Native	1,2,3,4,6,7,8-HpCDF	26
16	Native	1,2,3,4,7,8,9-HpCDF	26
17	Native	OCDF	22
18	Internal Standard	^{13}C – 2,3,7,8-TCDD	27
19	Internal Standard	^{13}C – 1,2,3,7,8-PeCDD	27
20	Internal Standard	^{13}C – 1,2,3,6,7,8-HxCDD	28
21	Internal Standard	^{13}C – 1,2,3,6,7,8-HpCDD	28
22	Internal Standard	^{13}C – OCDD	28
23	Internal Standard	^{13}C – 2,3,7,8-TCDF	27
24	Internal Standard	^{13}C – 1,2,3,7,8-PeCDF	27
25	Internal Standard	^{13}C – 1,2,3,4,7,8-HxCDF	28
26	Internal Standard	^{13}C – 1,2,3,4,6,7,8-HpCDF	28
27	Recovery Standard	^{13}C – 1,2,3,4-TCDD	
28	Recovery Standard	^{13}C – 1,2,3,7,8,9-HxCDD	
29	Cleanup Standard	^{37}Cl – 1,2,3,7,8-TCDD	27

TABLE 11
RELATIVE RESPONSE FACTOR [RF (NUMBER)] ATTRIBUITIONS

Number	Specific Congener Name
1	2,3,7,8-TCDD (and total TCDDs)
2	2,3,7,8-TCDF (and total TCDFs)
3	1,2,3,7,8-PeCDD (and total PeCDDs)
4	1,2,3,7,8-PeCDF
5	2,3,4,7,8-PeCDF
6	1,2,3,4,7,8-HxCDD
7	1,2,3,6,7,8-HxCDD
8	1,2,3,7,8,9-HxCDD
9	1,2,3,4,7,8-HxCDF
10	1,2,3,6,7,8-HxCDF
11	1,2,3,7,8,9-HxCDF
12	2,3,4,6,7,8-HxCDF
13	1,2,3,4,6,7,8-HpCDD (and totals HpCDD)
14	1,2,3,4,6,7,8-HpCDF
15	1,2,3,4,7,8,9-HpCDF
16	OCDD
17	OCDF
18	$^{13}C_{12}$ – 2,3,7,8-TCDD
19	$^{13}C_{12}$ – 2,3,7,8-TCDF
20	$^{13}C_{12}$ – 1,2,3,7,8-PeCDD
21	$^{13}C_{12}$ – 1,2,3,7,8-PeCDF
22	$^{13}C_{12}$ – 1,2,3,6,7,8-HxCDD
23	$^{13}C_{12}$ – 1,2,3,4,7,8-HxCDF
24	$^{13}C_{12}$ – 1,2,3,4,6,7,8-HpCDD
25	$^{13}C_{12}$ – 1,2,3,4,6,7,8-HpDf
26	$^{13}C_{12}$ – OCDD
27	Total PeCDFs
28	Total HxCDFs
29	Total HxCDDs
30	Total HpCDFs

FIGURE 1

GENERAL STRUCTURES OF DIBENZO-*p*-DIOXINS (TOP) AND DIBENZOFURANS (BOTTOM)

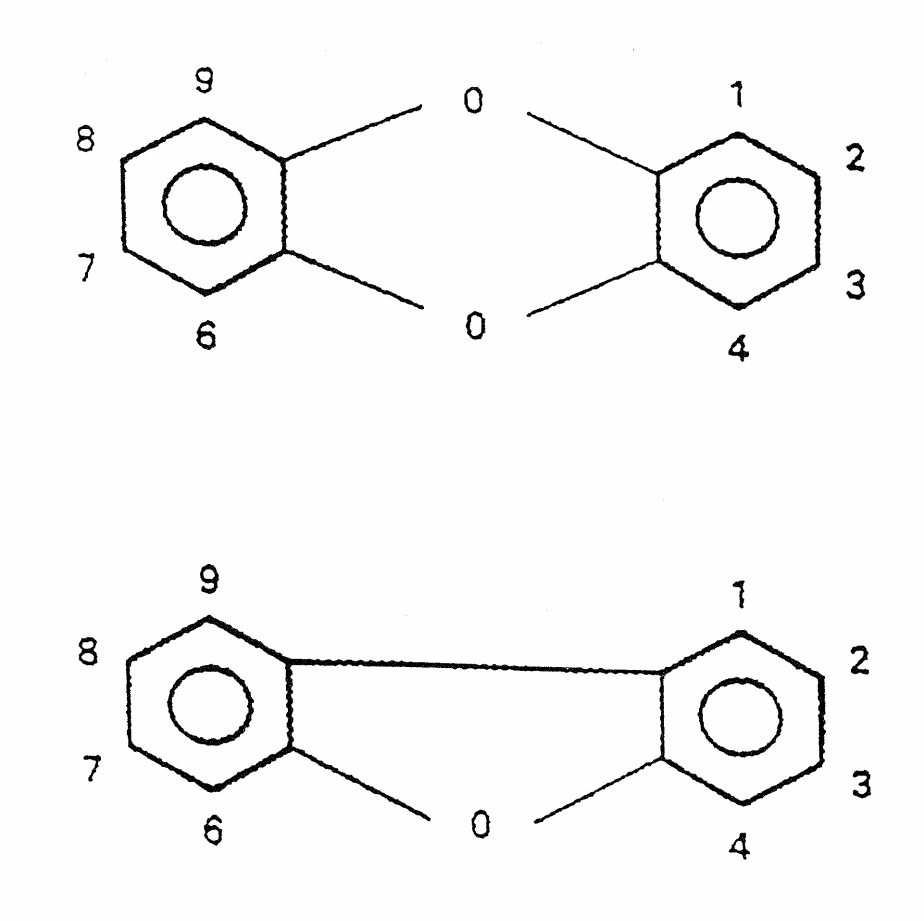


FIGURE 2

TYPICAL 12-HOUR ANALYSIS SEQUENCE OF EVENTS

ANALYTICAL PROCEDURE

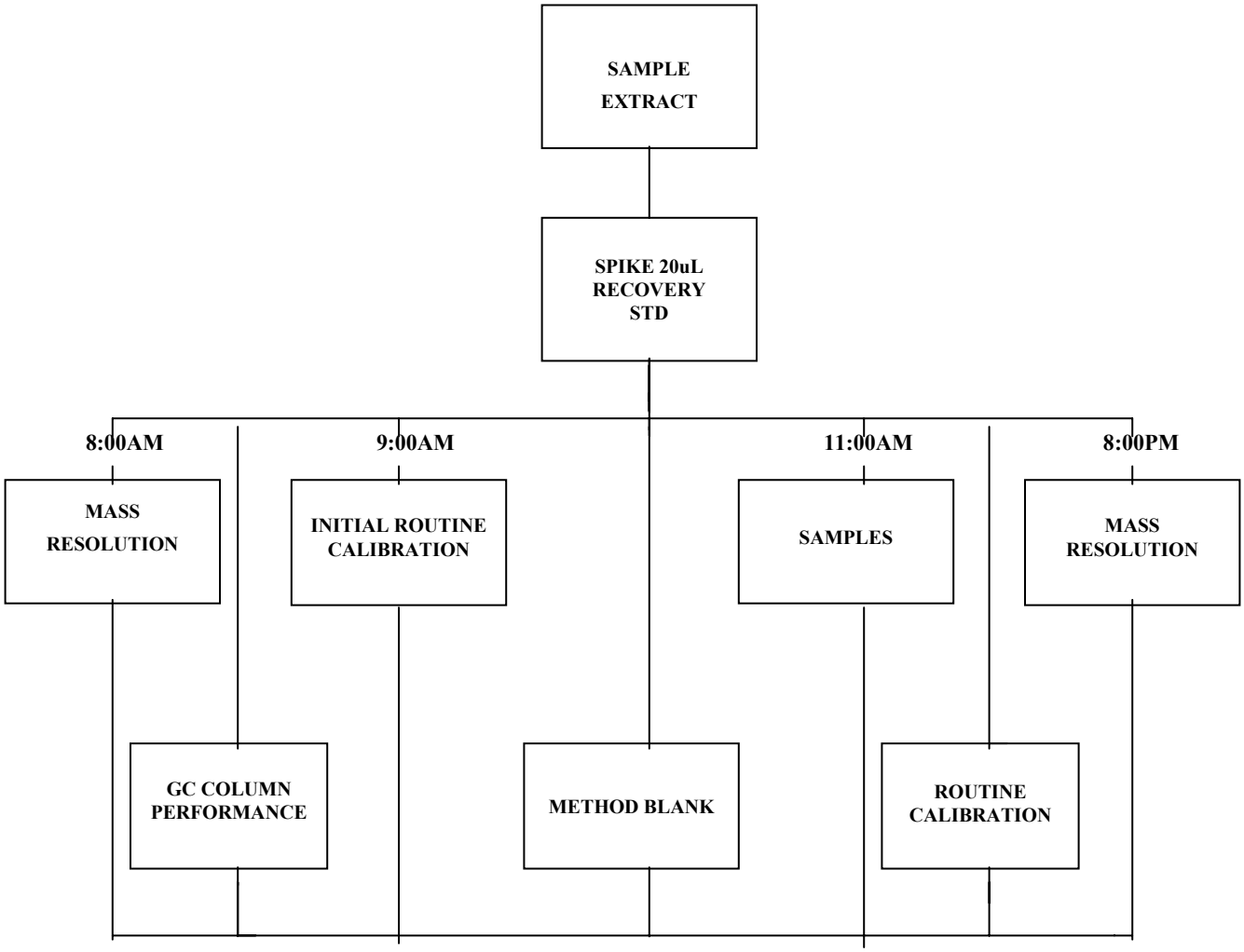
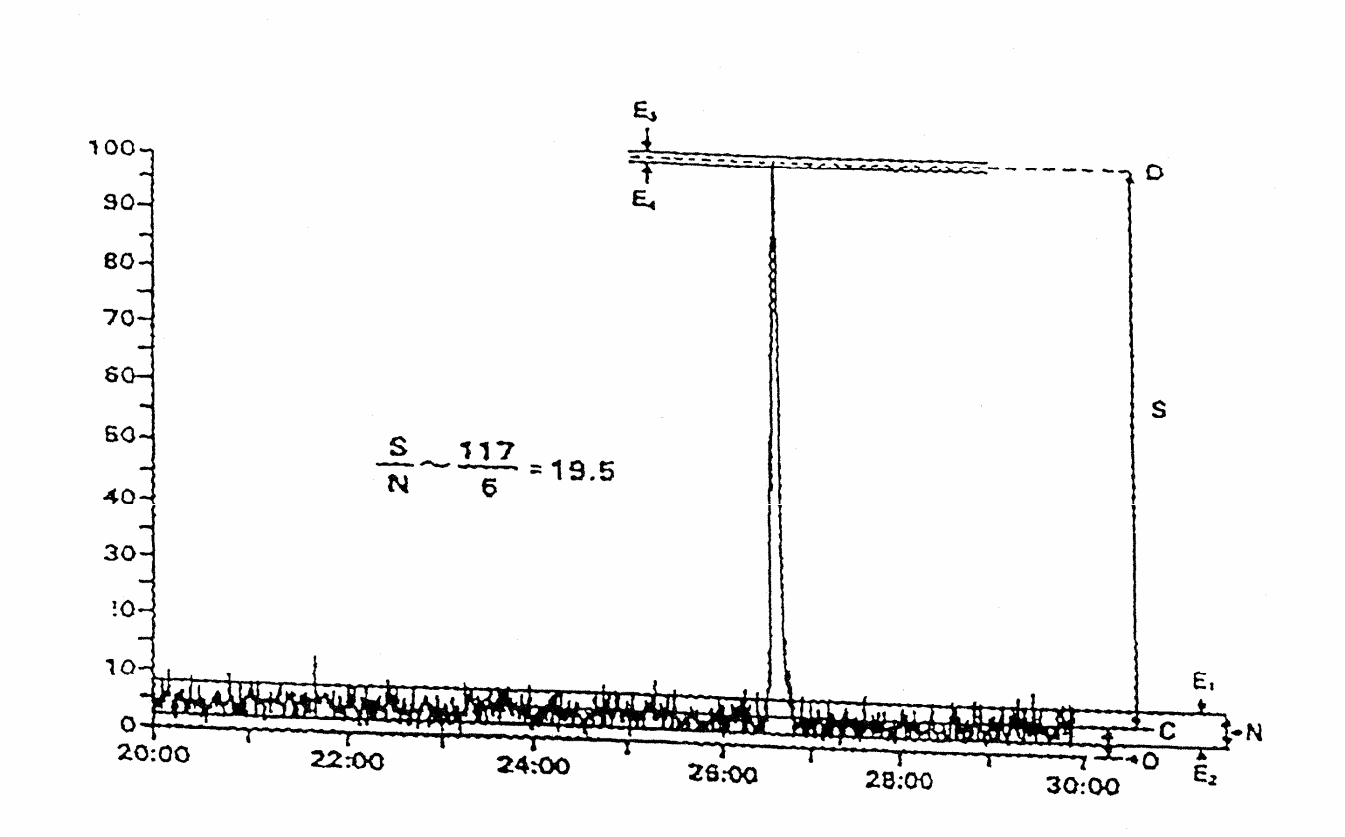


FIGURE 3

MANUAL DETERMINATION OF S/N



The peak height (S) is measured between the mean noise (lines C and D.) These mean signal values are obtained by tracing the line between the baseline average noise extremes, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal.

NOTE: It is imperative that the instrument interface amplifier electronic zero offset be set high enough so that negative going baseline noise is recorded.

FIGURE 4

MASS RESOLUTION CHECK

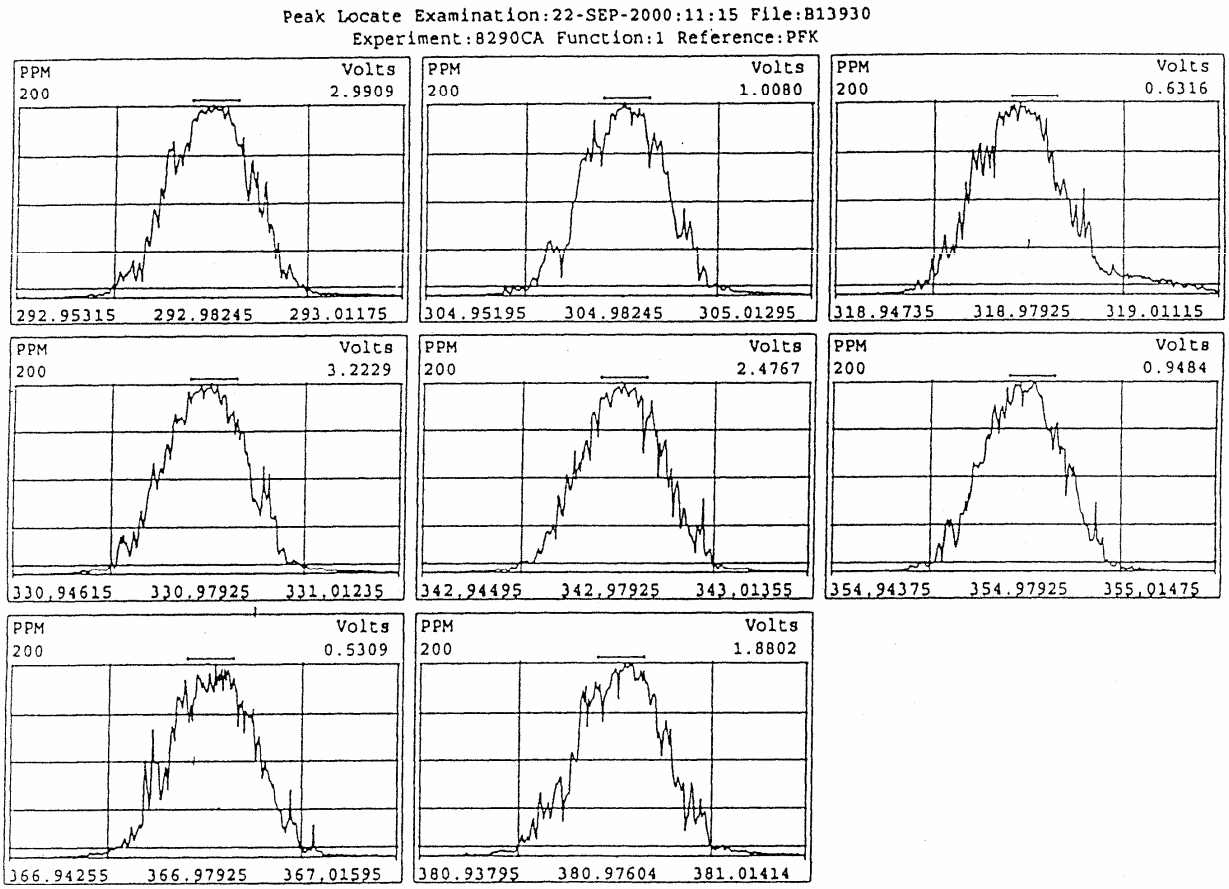


FIGURE 5

DB-5 WINDOW DEFINITION

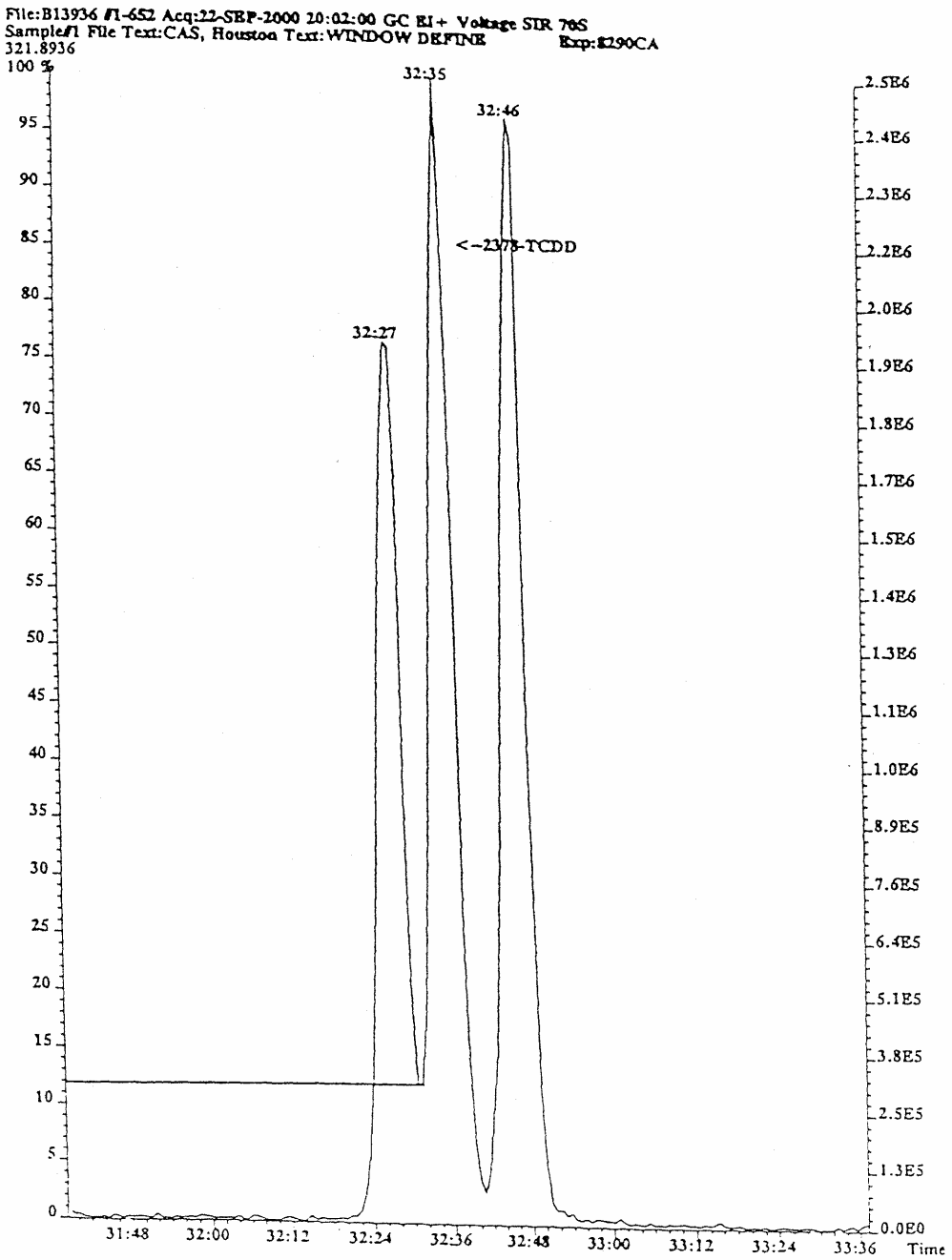


FIGURE 5 (cont.)

DB-5 WINDOW DEFINITION

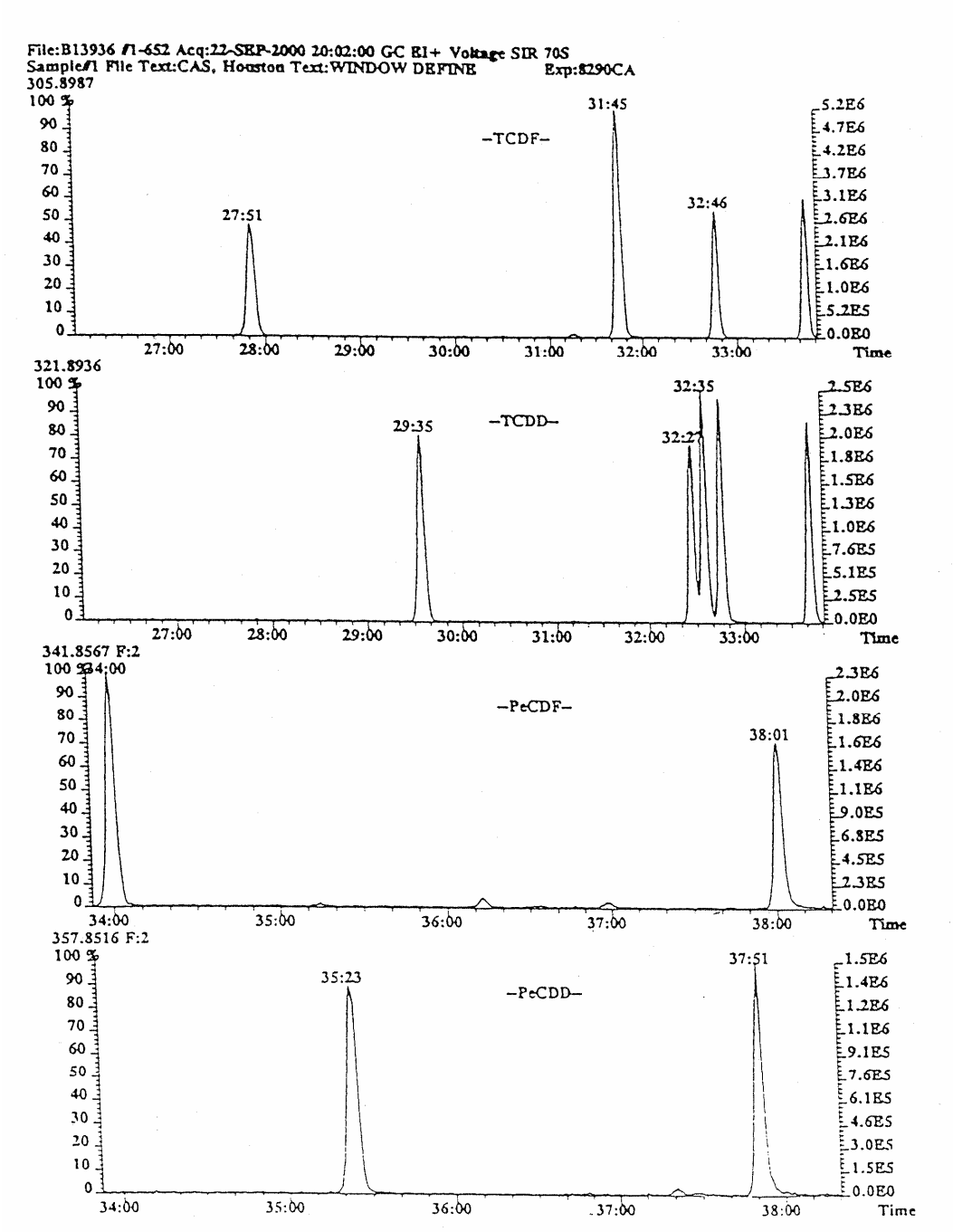


FIGURE 5 (cont.)

DB-5 WINDOW DEFINITION

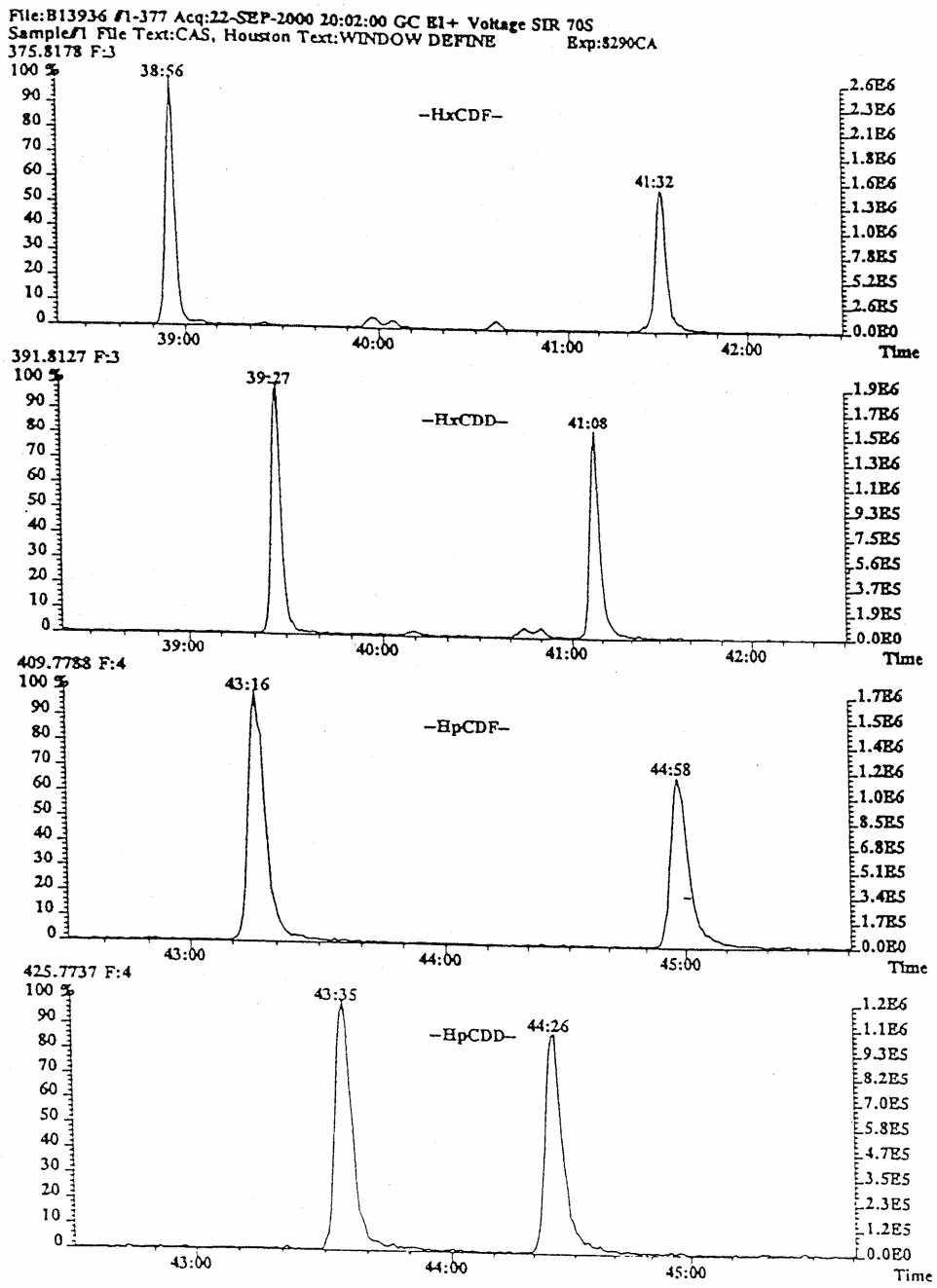
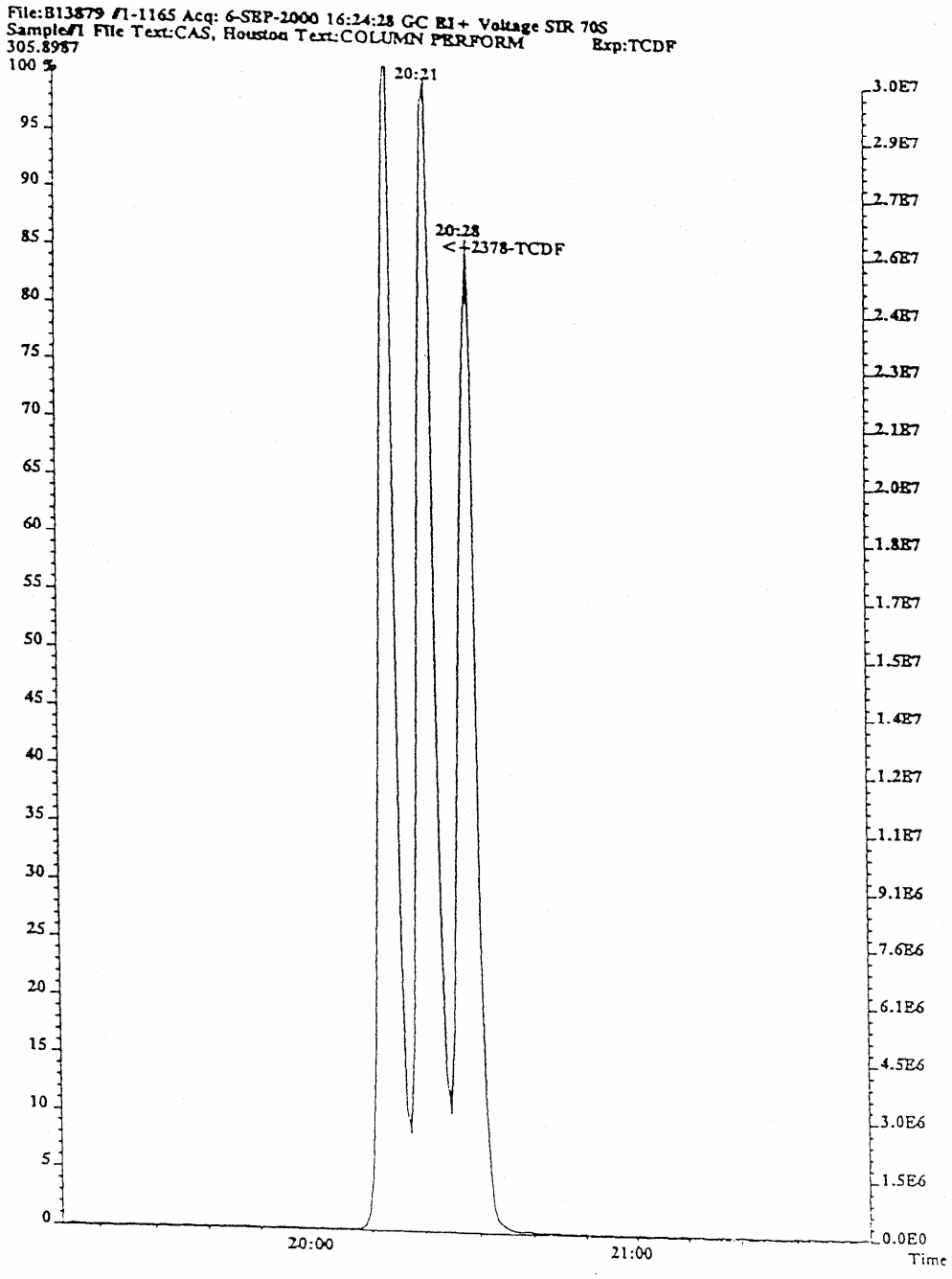


FIGURE 6
DB-225 COLUMN PERFORMANCE



STANDARD OPERATING PROCEDURE

for

METALS DIGESTION, SOILS, SEDIMENTS, AND SLUDGE FOR ICP ANALYSIS FOR INDIANA PINES SITE

SOP No.: MET-3050pines

Revision: 0

September 28, 2004

Approved by: _____ 9/28/04
Supervisor — Date

_____ 9/28/04
QA Coordinator — Date

_____ 9/28/04
Laboratory Manager — Date

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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
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1 SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 3050B for the digestion of soils, sludges, or sediments for analysis by ICP. As stated in the EPA method, "this method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment." This SOP was written specifically for the Indiana Pines Site.

2 SUMMARY OF METHOD

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide. Hydrochloric acid is used as a final reflux acid.

3 DEFINITIONS

3.1 **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 **Laboratory Control Sample Soil (LCSS)** - An aliquot of a soil to which known quantities of the method analytes are added. The LCSS 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.

3.3 **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5 Digestion Batch - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4 HEALTH AND SAFETY WARNINGS

Nitric and Hydrochloric acids are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment including safety glasses (with side shields), gloves, and lab coat shall be worn when handling samples or reagents.

5 CAUTIONS

Antimony is easily lost by volatilization. Do not boil the digestate.

6 INTERFERENCES

Use more sample for those samples with high moisture content to meet detection limits.

7 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8 EQUIPMENT AND SUPPLIES

8.1 Eppendorf Pipettors
8.2 Funnels
8.3 Mortar and pestle
8.4 Tongue depressors
8.5 Filter paper
8.6 Hot Block Digestor with ETR-3200 Controller by Environmental Express, LTD.
8.7 Graduated block digestor cups
8.8 Block Digestor Filters.
8.9 CPI MOD Block Digestor

8.10 Reagent water - ASTM Type II deionized water.

8.11 Concentrated nitric acid (Baker Instra-Analyzed 69-70%): Store at room temperature in the dark in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.12 Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%): Store at room temperature in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.13 Hydrogen peroxide (30%) - H_2O_2. Purchased commercially. Should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature in the original container. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.14 ERA Soil Laboratory Control Sample (LCSS) - Concentrations and Performance Acceptance Limits distributed through vendor. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.15 Metals spiking solutions – Purchased commercially. See Table 1. Store at room temperature. Stocks expire upon manufacturer's indications or 1 year from receipt, whichever is sooner. Solutions prepared from stocks expire 6 months from preparation.

9 PROCEDURES

9.1 Sample Collection – Collect samples in purchased, certified clean glass or plastic.

9.2 Sample Handling and Preservation – Analyze samples within 6 months of sample collection. Store samples in a refrigerator or at room temperature. Sample receiving, handling, storage, and custody procedures are in accordance with NELAC 2002 Standard.

9.3 Sample Preparation

9.3.1 Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

9.3.2 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

9.3.3 Label graduated hot block digestor sample cups with appropriate sample IDs for digestion.

9.3.4 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

9.3.5 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into labeled digestor sample cup. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

9.3.6 Unless otherwise specified by project requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3 and 1.5 mL of 1:1 HCl, cover with reflux cap and reflux for 15 minutes. The sample temperature should be 90-95°C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

9.3.7 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the sample cup.

9.3.8 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

9.3.9 Add 10 mL 1:1 HCL.

9.3.10 Cover and reflux the samples for 15 minutes without boiling. Allow to cool.

9.3.11 Rinse filters with 1:1 nitric acid and DI.

9.3.12 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and reflux cap with DI into the filter. Rinse the filter with DI. Bring to volume with DI. Pour into a labeled B-cup.

9.4 **Sample Analysis** – Give digested samples and a copy of the prep sheet to the ICP analyst. Analyze according to MET-6010Bpines.

9.5 **Troubleshooting** - All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9.6 **Data Acquisition, Calculations and Data Reduction Requirements**

Digestion logs are used to record all sample volumes, spike volumes, etc. The Manufacturer's lot number for the reagents used are added to the digestion log (see attached digestion log benchsheet).

10 DATA AND RECORDS MANAGEMENT

10.1 Responsibilities - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data 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 SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2 Data will be reviewed after ICP analysis according to MET-6010Bpines.

11 QA/QC REQUIREMENTS

11.1 Each day, digest one laboratory control sample (LCS) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use the appropriate solid laboratory control sample (LCSS) for soils analysis.

11.2 Each day, digest one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures.

11.3 Each day, prepare one duplicate and one spiked sample with each digestion batch, or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

11.4 Matrix spikes are prepared by adding the appropriate volume of spiking solution (See Table 1).

11.5 See MET-6010Bpines for applicable QC limits and corrective action.

12 REFERENCES

"Test Methods For Evaluating Solid Waste, Physical/Chemical Methods". EPA SW846, Third Edition, December 1996.

NELAC, 2002 Standard.

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE SOLUTION A			1.00ml Spk A	to Final Vol of 100ml
Metal	*Conc. (ug/mL)*		*Metal*	*Conc. (ug/mL)*
AL	200		**NI**	50
AS	4		**SE**	1
BA	200		**AG**	5
BE	5		**TL**	200
CD	5		**V**	50
CR	20		**ZN**	50
CO	50		**B**	100
CU	25		**CA**	200
FE	100		**MG**	200
PB	50		**NA**	2000
MN	50		**K**	2000

SPIKE SOLUTION B			1.00ml Spk B	to Final Vol of 100ml
Metal	*Conc. (ug/mL)*		*Metal*	*Conc. (ug/mL)*
SB	50		**TI**	50
MO	50		-	-

INDIVIDUAL METALS	0.10ml Spk. to Final Volume of 100ml		INDIVIDUAL METALS	0.5ml Spk. to Final Volume of 100ml
Metal	*Conc. (ug/mL)*		*Metal*	*Conc. (ug/mL)*
SE	1000		**SN**	1000

CAS-Rochester ICP Soil Digestion Log

6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID:

Analyst: _____ Date: _____

Spike Witness / Lot Approval: _____

Batch Temp:

Prep Method: SW846 3050 // CLP

Digest: Initial // Redigest of: _____

Report Type: Routine // ASP // Pkg5

	Submission / Order #	Initial Wgt. (g)	Final Vol (ml)	Initial Color / Texture	Final Color / Clarity	Metals	Spike Vol (ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

Spiking Standards / Reagent Lot #:

Spike A,B: _____ Spike #4: _____

TCLP Spk: _____ TCLP Ba: _____

Se Std: _____ Sn Std: _____

HNO3: _____ HCL: _____

H2O2: _____ LCSS: _____

Color / Clarity Key:

Color: **C** = Colorless ; **Y** = Yellow ; **B** = Brown

BL = Black ; **G** = Grey ; **W** = White

Clarity: **CDY** = Cloudy ; **CLR** = Clear ; **OP** = Opaque

Texture: **F** = Fine ; **M** = Medium ; **CS** = Coarse ; **NAQ** = Non Aqueous

01

Comments: _____

STANDARD OPERATING PROCEDURE

for

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) FOR INDIANA PINES SITE

SOP No.: MET-6010BPINES

Revision: 1

September 29, 2004

Approved by: _____ Department Supervisor — 9/29/04 Date

_____ Laboratory Manager — 9/29/04 Date

_____ QA Coordinator — 9/29/04 Date

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Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
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1. SCOPE AND APPLICABILITY

1.1. This SOP uses EPA SW-846 Method 6010B for the determination of trace elements, including metals, in solution using Inductively coupled plasma-atomic emission spectrometry (ICP-AES). The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. The Method Reporting Limits (MRL) are listed in Table 1. The reported MRL may be adjusted if required for specific project requirements, however, the capability of achieving other reported MRLs must be demonstrated. Results may be reported to the Instrument Detection Limits (IDLs) upon request.

1.3. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

2.1. Samples are digested according to one of the proper metals digestion methods listed in SW-846.

2.2. This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences (discussed later) should also be recognized and appropriate corrections made.

3. DEFINITIONS

3.1. Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

3.2. Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration

3.3. Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification.

3.4. Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength.

3.5. Initial/Continuing Calibration Verification Solution (ICV/CCV) - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6. Internal Standard - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component

3.7. Laboratory Duplicates - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates and indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.8. Laboratory Control Sample (LCS) - An aliquot of to which known quantities of the method analytes are added in the laboratory. The 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.

3.9. Matrix Spike - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.10. Preparation Blank (PB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.11. Linear Range - The concentration range over which the instrument response to an analyte is linear.

3.12. Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.13. Plasma Solution - A solution that is used to determine the optimum height above the work coil for viewing the plasma.

3.14. Interference Check Solution (ICS) - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria.

3.15. Method Reporting Limit Standard (MRL) – Standard prepared with a known concentration of elements to check accuracy at the low end of the curve.

3.16. HLCCV1 – A standard prepared at the bench at a high concentration to encompass the range of the samples being analyzed. This standard is used to assess accuracy at the high end of the linear range.

3.17. HLCCV2 – A standard prepared slightly higher than the calibration range for metals.

3.18. Batch – a group of no more than 20 field samples digested or analyzed together on the same day with the same reagents.

4. HEALTH AND SAFETY WARNINGS

4.1. Corrosives - Because all samples and standards are diluted in 2% HNO_3 and 5% HCl, there is a danger of exposure to corrosives, sufficient care must be taken in handling these solutions. Safety glasses must be worn while preparing and handling the solutions.

4.2. High Voltage - The power unit supplies high voltage to the RF generator which is used to form the plasma. The unit should never be opened. Exposure to high voltage can cause injury or death.

4.3. UV Light - The plasma when lit is a very intense light, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available.

4.4. When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a well ventilated area or fume hood

5. INTERFERENCES

There are several types of interferences by the ICP's: Spectral interferences can be from an overlap of spectral lines, background points or background from line emissions of high concentration elements. Physical interferences are effects associated with the sample introduction process, example high dissolved solids buildup on the nebulizer tip. Chemical interferences caused by the sample matrix itself. IEC's aid in eliminating some of these interferences. IECs are interelement correction factors that the instrument uses to compensate for spectral overlap when analyzing samples with complex spectra. Refer to Method 6010B Section 3.0 or Method 200.7 Section 4.0 for more detail and suggested procedures to correct and adjust the instrument due to interferences.

6. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

7. EQUIPMENT AND SUPPLIES

7.1. ICP- Perkin Elmer Optima 3000XL - Inductively coupled argon plasma emission spectrometer (ICP) equipped with the following:

7.1.1. Computer-controlled emission spectrometer with background correction.

7.1.2. Mass flow controller for argon nebulizer gas supply.

7.1.3. Peristaltic pump.

7.1.4. Autosampler.

7.1.5. Argon gas supply - high purity.

7.2. Volumetric flasks, class A .

7.3. Trace metals grade chemicals shall be used in all tests.

7.3.1. Hydrochloric acid (conc), HCl. Purchased commercially. Store at room temperature. Expires three years from receipt or upon manufacturer's indications, whichever is sooner.

7.3.2. Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker. Store at room temperature. Expires one year from preparation.

7.3.3. Nitric acid (conc), HNO_3. Purchased commercially. Store at room temperature. Expires three years from receipt or upon manufacturer's indications, whichever is sooner.

7.3.4. Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker. Store at room temperature. Expires one year from preparation.

7.4. Reagent Water. All references to water in the method refer to DI Type II water unless otherwise specified. Reagent water will be interference free.

7.5. All standards are prepared from NIST traceable stock standard solutions. Manufacturers expiration dates are used to determine viability of standards. Preparatory procedures for standards and QC solutions vary between instruments due to the working ranges. All preparatory information for the QA/QC samples are provided in Appendix I.

7.5.1. Mixed Calibration Standards are prepared by combining appropriate volumes of the stock solutions in volumetric flasks. Matrix match with the appropriate acid and dilute to 100ml with water. Calibration standards should be verified using a second source quality control sample (LCS, ICV, or CCV). Calibration standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 7 days.

7.5.2. Initial and Continuing Calibration Verification (ICV and CCV) Standards are prepared by combining compatible analytes at concentrations equivalent to the midpoint of their respective calibration curves. The ICV and CCV standards should be prepared from a separate source independent from that used in the calibration standards. ICV / CCV standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 48 hours.

7.5.3. MRL Standards are prepared to contain known concentrations of elements at or near the Method Reporting Limit. MRL standards should be stored in plastic containers with a shelf-life of 6 months.

7.5.4. Interference Check Solutions A and AB are prepared to contain known concentrations of interfering analytes that will provide an adequate test of the correction factors. ICSA / ICSAB standards should be stored in plastic containers with a shelf-life of 6 months.

7.5.5. Laboratory Control Sample and Matrix Spike are purchased as custom mixes stored in plastic containers with a shelf-life of 6 months at the concentrations recommended in the method. Certificates of analysis are attached in Appendix I. Each sample, up to 100 mL, is spiked with 1.0 ml of spike solution.

7.6. Blanks

7.6.1. Method Blanks must contain all the reagents and in the same volumes as used in the preparation of samples. The method blanks must be carried through the complete procedure and contain the same acid concentration in the final solution as the samples.

7.6.2. The Calibration Blank is prepared by acidifying reagent water to the same concentrations of acid found in the standards and samples.

7.7. Reagent Receiving Log

The manufacturer, lot number, standard /reagent name, concentration, date received and expiration date are recorded in a reagent log.

8. PROCEDURE

8.1. Calibration and Standardization

Calibration is accomplished daily using 3 calibration standards and a blank for each element using the internal standard technique. See Sample Analysis section for more information.

8.2. Sample Collection

Containers may be glass or plastic. Samples are cooled with ice to be shipped to the laboratory.

8.3. Sample Handling and Preservation

8.3.1. Solid samples require no preservation prior to analysis other than storage at 0-6°C. Samples are analyzed within 6 months of collection.

8.3.2. Aqueous samples are acid preserved with (1+1) nitric acid to pH <2. Samples are analyzed within 6 months of sample collection.

8.3.3. Samples are checked upon receipt for all the elements listed in the Sample Acceptance Policy found in NELAC 2002 Standard.

8.3.4. For the determination of the dissolved elements, filter the sample through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a well ventilated area or fume hood.

8.3.5. Samples received by the ICP lab as digestates contain nitric and hydrochloric acid. Digestates are stored at room temperature in plastic B-cups.

8.3.6. Following analysis, digestates are stored until all results have been reviewed. Digestates are diluted and disposed of through the sewer system in approximately 90 days after receipt of sample.

8.4. Sample Preparation

8.4.1. Digest samples prior to analysis. Refer to the following Metals Methods found in SW-846:

- 3005A Metals Digestion, Waters, Total Recoverable and Dissolved for ICP
- 3010A Metals Digestion, Waters for ICP
- 3020A Metals Digestion, Waters for GFAA
- 3050B Metals Digestion, Soils, Sediments and Sludges for ICP and GFAA

8.5. Sample Analysis

8.5.1. Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 45 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided in Table 3.

8.5.2. Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data documents the selection criteria of background correction points; linear ranges, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

8.5.3. Turn on power supply for the instrument, computer, printer and light the plasma. Allow instrument to warm-up for 45-60 minutes before operation. The cooling water and the argon are on when the instrument are on.

8.5.4. Profile the instrument on a daily basis, and when maintenance is done to align it optically for both horizontal and vertical optimization in either mode. Aspirate a 10 ppm source of manganese (as recommended by the manufacturer). Choose the Tools menu/Spectrometer Control/Optimize X&Y. The instrument automatically adjusts the torch viewing position for maximum intensity.

8.5.5. Pour the 3 calibration standards, ICV/CCV standards, MRL, ICSA, and ICSAB up to 40 mL in 50 mL centrifuge tubes and add 0.80 mL of the internal standard solution. Pour all other samples, preparation blanks and laboratory control samples up to 10 mL in 15 mL centrifuge tubes and add 0.20 mL of internal standard solution. This gives an apparent concentration of 1.00 mg/L Yttrium. The Yttrium intensity is used by the instrument to ratio the analyte intensity signals for both calibration and quantitation. Cesium is used only as a stabilizer.

8.5.6. Internal standards can be added via pump and mixing block. This technique uses a solution of 10 mg/L Y and 10 mg/L Cs.

8.5.7. Following the calibration, analyze in the following sequence:

- ICV; ICB; MRL; ICSA; ICSAB; CCV; CCB;
- 10 environmental samples (including PBs and LCSs); CCV; CCB; repeat to the end of the run…..
- Last 10 samples; CCV; CCB, MRL, ICSA, ICSAB; HLCCV1; HLCCV2; CCV; CCB.

8.5.8. Rinse the system with the calibration blank solution before the analysis of each sample for one minute.

8.5.9. Samples which exceed the linear range of the instrument must be diluted and reanalyzed.

8.5.10. Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. See Table 2 for approximate wavelengths. See 40 CFR Part136 Appendix B for more information.

8.6. Troubleshooting

8.6.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Most routine maintenance and troubleshooting is performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Record the analytical run filename of the first acceptable run after major maintenance in the maintenance log book. Typical preventive maintenance measures include, but are not limited to, the following items:

- Cleaning the pump tubing as needed
- Empty waste container, as needed
- Cleaning the nebulizer, spray chamber, and torch, as needed
- Replace water and vacuum filters, as needed

8.7. Data Acquisition, Calculations, and Data Reduction Requirements

8.7.1. Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

8.7.2. Sample Calculation (water)

$$\text{Conc. (mg/L)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial volume (L)}}$$

8.7.3. Sample Calculation (soils)

$$\text{Conc. (mg/g)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial mass (g) x Percent Solids expressed as a decimal}}$$

8.7.4. **Matrix Spike Recovery** is calculated to determine accuracy for matrix and blank spikes using the following equation:

$$\text{Accuracy (\%REC)} = \frac{A - B}{C} \times 100$$

Where
A = Analyte total concentration from spiked sample
B = Analyte concentration from unspiked sample
C = Concentration of spike added

8.7.5. **Precision** is measured through the use of replicate sample analyses within the same batch and is expressed as the relative percent difference (RPD) between the replicate measurements.

$$\text{RPD} = \frac{|D1 - D2|}{(D1+D2)/2} \times 100$$

Where
D1 = Original Result
D2 = Duplicate Result

Report each analyte concentration to the proper significant figures in mg/L or µg/L as required.

8.8. Computer Hardware and Software

Each ICP uses a Gateway GP5-233 running the ICP WinLab v.1.42.
Metals Analytical Review and Reporting System (MARRS) v.3.2.44
StarLIMS v.6.11.a

9. DATA AND RECORDS MANAGEMENT

9.1. **Responsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data 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 SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

9.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the ICP analyst. The samples are analyzed for metals of interest using ICP software. The results are transferred to MARRS (for reporting package work) and StarLIMS for validation, reporting, and invoicing.

9.3. Data Review - Data will be reviewed by the ICP analyst and a qualified peer using a Data Review Checklist (attached) and validated by a supervisor.

10. QUALITY CONTROL AND QUALITY ASSURANCE

10.1. Instrument values are based on duplicate readings. Precision between the emission readings shall not exceed 20 %RSD. If RSD values exceed 20%, the sample reanalyzed and reported.

10.2. Preparation Blanks must be analyzed at least one PB with each batch of 20 or fewer samples of the same matrix. PB values must not exceed the MRL. Fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable PB values have been obtained. If detections are greater than the MRL, the batch needs to be redigested if sample concentration is less than 5 times the concentration found in the prep blank. If the sample concentration is less than the MRL the sample does not require redigestion.

10.3. HLCCV1 – High standard used in curve and analyzed once during daily analysis. Should agree within 10% of the true value. If HLCCV1 is > 10% different the analysis is judged to be out of control and the source of the problem should be identified and resolved before continuing analysis.

10.4. HLCCV2 – standard slightly higher than calibration for some metals. Analyzed once during daily analysis. Should agree within 10% of the true value. If out of control, client data above the HLCCV1 should be re-analyzed.

10.5. ICV/CCV - Calibration Verification Standards must immediately follow each calibration, after every tenth sample, and at the end of the sample run. Initial Calibration Verification must verify that the instrument is within 10%. Continuing Calibration Verification standards must confirm the calibration within ±10% throughout the analyses. If the recovery of an analyte falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Recalibrate the instrument.

10.6. The results of the calibration blank (CCB) must be less than the MRL. If not, terminate the analysis, correct the problem, recalibrate, and reanalyze the samples effected.

10.7. Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

10.8. Analyze matrix spiked and duplicate samples at a frequency of one per matrix batch (max. 20 samples). Matrix spiked and duplicate samples are brought through the entire sample preparation and analytical process.

10.8.1. The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix. Sample concentrations greater than four times the spike concentration are not valid and shall not be evaluated. If the matrix spike does not meet these criteria, analyze a Post Digestion Spike.

10.8.2. A control limit of ± 20% RPD shall be used for original and duplicate samples greater than or equal to 5X the CRDL. A control limit of ± the CRDL shall be used if either the sample or duplicate value is less than 5 times the CRDL. CRDL values are given in Table 1.

10.9. Laboratory Control Sample – verify sample preparation and analysis using reagent water spiked with a known amount of analytes of interest. Results should be within ± 20%. Outlying recoveries may indicate loss of analyte due to digestion procedures or laboratory contamination. If an LCS is found to be out of the specified limits, recalibrate and reanalyze. If the LCS remains out of the specified limits, redigestion of the entire batch should occur if the recovery is less than 80%. If the LCS recovery is greater than 120% redigest all positive results (greater than the MRL).

10.10. MRL standard- A standard at or near the MRL is analyzed at the beginning and end of each analytical run but not before the ICV. There are no limits in the 6010B method, but the CAS guideline used is +/- 50% of the true value. If the limits are not met the analysis is stopped and the instrument is recalibrated.

10.11. Interference Check Samples- The ICSA and ICSAB need to be run consecutively at the beginning and end of each analytical run. Results from the ICSA solution shall be monitored for false positive detections of analytes not present in the mix. The analyte recoveries for the AB solution must fall within 20% of the true value otherwise the run must be stopped, recalibrated and reanalyzed unless analytes are not detected in the associated samples or interferent elements are not present.

10.12. Serial Dilution Test If the analyte concentration is sufficiently high (minimally, a factor of 50 times above the IDL), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected and data may be flagged accordingly.

10.13. Post Digestion Spike Addition: Typically if a matrix spike does not yield acceptable results, a post-digestion spike may be added to a portion of a prepared sample, or its dilution, and should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the IDL. If the spike is not recovered within the specified limits, a matrix effect has been confirmed.

10.14. Instrument Performance

- InterElement Correction Factors (IEC) are analyzed annually, or as needed.
- Linear Ranges (LR) are run biannually and must be ±5% of true value.
- Instrument Detection Limits (IDL) are analyzed quarterly, or as needed.
- Method Detection Limits (MDL) are analyzed annually.

11. REFERENCES

- *Test Methods For Evaluating Solid Waste, Physical/Chemical Methods.* USEPA SW-846, 3rd Edition, December 1996.
- *Methods For the Determination of Metals in Environmental Samples Supplement I.* USEPA/600/R-94/111, May 1994.
- 40 CFR Part136 Appendix B
- NELAC 2002 Standard

Metals Instrument Analysis Training Plan

Procedure:_____

SOP:_____ Revision:_____ Date:_____

Trainee:_____

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
   -the chemical and physical principals behind the measurement by the instrument

   Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs

-ADM-BATCHSEQ	-ADM-PCAL	-ADM-SIGFIG
-ADM-DATAENTRY	-ADM-DIL	-ADM-SPSR
-ADM-MDL	-ADM-DREV	-ADM-TRANDOC

   Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
   -standard and reagent prep and documentation – including pipet used
   -instrument power up and warm-up
   -instrument set-up, daily maintenance and checks
   -use and loading of autosampler
   -sample analysis including:
      -calibration
      -sample dilution
      -software command of instrument
      -use of QC samples and QC criteria
      -common troubleshooting
   -instrument logbook use
   -data reduction, reporting, and review

   Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

   Signature:_____ Date:_____

6. Perform SOP with supervision
   - including all items in 4.

   Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
   -all of the item listed in 4
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.

   Trainer:____ Trainee:____ Date:____

TABLE 1

Analyte	*MRL* ***Water*** ***mg/L***	***MRL*** ***Soil*** ***ug/g***	*Typical IDL* ***ug/L***
Silver	0.010	1.00	0.632
Aluminum	0.100	10.0	6.57
Arsenic	0.0100	50.0	6.89
Boron	0.200	20.0	37.3
Barium	0.0200	2.00	12.2
Beryllium	0.0050	0.500	0.26
Calcium	0.500	50.0	167
Cadmium	0.0050	0.500	0.489
Cobalt	0.0500	5.00	3.03
Chromium	0.0100	1.0	1.81
Copper	0.0200	2.00	3.02
Iron	0.100	5.00	44.1
Potassium	2.00	100	857
Lithium	0.200	20.0	23.9
Magnesium	0.500	50.0	124
Manganese	0.0100	1.0	1.78
Molybdenum	0.0250	2.50	3.08
Sodium	0.500	50.0	193
Nickel	0.0400	4.00	3.92
Lead	0.00500	5.00	1.29
Antimony	0.0600	10.0	3.72
Selenium	0.00500	50.0	12.5
Silicon	1.00	100	68.7
Strontium	0.100	10.0	5.38
Tin	0.500	100	15.8
Titanium	0.0500	5.00	3.15
Thallium	0.0100	30.0	7.77
Vanadium	0.0500	5.00	2.74
Zinc	0.0200	1.0	2.47

Table 2

Recommended Wavelengths and Instrument Specifications

Suggested wavelengths are listed below:

Analyte	Wavelength
Ag Silver	328.068
Al Aluminum	308.215
B Boron	249.773
Ba Barium	233.527
Be Beryillium	234.861
Ca Calcium	430.253
Cd Cadmium	226.502
Co Cobalt	228.616
Cr Chromium	267.716
Cu Copper	324.754
Fe Iron	238.863
Li Lithium	610.364
Mg Magnisium	279.079
Mn Manganese	257.610
Mo Molybdenum	202.030
Na Sodium	330.237
Ni Nickel	231.604
Pb Lead	220.353
Sb Antimony	206.833
Si Silicon	252.851
Sn Tin	189.933
Sr Strontium	421.552
Ti Titanium	334.941
V Vanadium	292.402
Zn Zinc	206.191
Y Yittrium	371.030

Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument operating conditions herein are recommended based upon manufacturer's instrument manuals.

Table 3
Operating Conditions

Current Method Operating Conditions are as follows, these conditions may vary to optimize the instrument for different analyses:

Parameter	Radial Plasma	Axial Plasma
Resolution	Fixed	Fixed
Purge Gas Flow	Normal	Normal
Read Time (min/max sec.)	5/20	5/50
Replicates	2	2
Plasma (L/min)	15	15
Aux. (L/min)	0.5	0.3
Nebulizer Flow (L/min)	0.72	0.56
Power (watts)	1300	1450
Viewing Height (mm)	15	15

APPENDIX I

PREPARATION PROCEDURES FOR STANDARDS AND QC

RADIAL OPTIMA #1 CALIBRATION STANDARD #1 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
PQL Std 1	AL		200	0.100	100	0.200	2%HNO3		A				
	BE		5			0.0050	5%HCl		B				
	CO		50			0.0500			C				
	MG		5000			5.00			D				
	SE		5			BELOW			E				
	V		50			0.0500			F				
	SB		60			0.0600			G				
	CD		5			0.0050			H				
	CU		25			0.0250			I				
	MN		15			0.0150			J				
	AG		10			0.0100			K				
	ZN		20			0.0200			L				
	AS		10			BELOW			M				
	CA		5000			5.00			N				
	FE		100			0.100			O				
	NI		40			0.0400			P				
	NA		5000			5.00			Q				
	BA		200			0.200			R				
	CR		10			0.0100			S				
	PB		5			BELOW			T				
	K		5000			5.00			U				
	TL		10			BELOW			V				
PQL Std 2	B		200	0.100		0.200			W				
	MO		25			0.0250			X				
	SN		500			0.500			Y				
	TI		50			0.0500			Z				
Single std	PB	1/10-	100	0.050		0.055			AA				
	AS		1000	0.010		0.110			BB				
	SE		1000	0.010		0.105			CC				
	TL		1000	0.010		0.110			DD				
	SR		1000	0.010		0.100			EE				

RADIAL OPTIMA #1- CALIBRATION STANDARD #3 / HLCCV1 (Standard is prepared weekly or as necessary)
(CALIBRATION STANDARD #2 IS A 1/5 DILUTION OF THIS STANDARD)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 1	CA		5000	4.00	200	100	2%HNO3		A				
	MG		5000			100	5%HCl		B				
	K		5000			100			C				
	NA		5000			100			D				
Cal Std 2	AG		100	2.00		1.00			E				
	CR		100			1.00			F				
	MN		150			1.50			G				
	NI		400			4.00			H				
	ZN		200			2.00			I				
Cal Std 3	AL		2000	2.00		20.0			J				
	BA		2000			20.0			K				
	BE		50			0.500			L				
	CO		500			5.00			M				
	CU		250			2.50			N				
	FE		1000			10.0			O				
	V		500			5.00			P				
Cal Std 4	AS		100	8.00		4.00			Q				
	CD		50			2.00			R				
	PB		50			2.00			S				
	SE		50			2.00			T				
	TL		100			4.00			U				
Single Metals	SB		1000	2.00		10.0			V				
	SN		1000	2.00		10.0			W				
	B		1000	1.00		5.00			X				
	MO		1000	1.00		5.00			Y				
	TI		1000	1.00		5.00			Z				
	SR		1000	1.00		5.00			AA				

RADIAL OPTIMA #1 ICV/CCV STANDARD (Standard is prepared daily.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Pipet ID
Cal Std 1	CA		5000	2.00	200	50.0	2%HNO3 5%HCl		A			
	MG		5000			50.0			B			
	K		5000			50.0			C			
	NA		5000			50.0			D			
Cal Std 2	AG		100	1.00		0.500			E			
	CR		100			0.500			F			
	MN		150			0.750			G			
	NI		400			2.00			H			
	ZN		200			1.00			I			
Cal Std 3	AL		2000	1.00		10.0			J			
	BA		2000			10.0			K			
	BE		50			0.250			L			
	CO		500			2.50			M			
	CU		250			1.25			N			
	FE		1000			5.00			O			
	V		500			2.50			P			
Cal Std 4	AS		100	4.00		2.00			Q			
	CD		50			1.00			R			
	PB		50			1.00			S			
	SE		50			1.00			T			
	TL		100			2.00			U			
Single Elements	SB		1000	1.00		5.00			V			
	SN		1000	1.00		5.00			W			
	B		1000	0.500		2.50			X			
	MO		1000	0.500		2.50			Y			
	TI		1000	0.500		2.50			Z			
	SR		1000	0.500		2.50			AA			

RADIAL OPTIMA #1 - HLCCV2 (Standard is prepared weekly or as necessary.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date
Cal Std 2	AG		100	2.00	100	2.00	2%HNO3	
	CR		100			2.00	5%HCl	
	MN		150			3.00		
	NI		400			8.00		
	ZN		200			4.00		
Cal Std 3	AL		2000	2.00		40.0		
	BA		2000			40.0		
	BE		50			1.00		
	CO		500			10.0		
	CU		250			5.00		
	FE		1000			20.0		
	V		500			10.0		
Single Metals	MO		1000	1.00		10.0		
	PB		1000	~~0.800~~	1.00	10.0		
	TI		1000	1.00		10.0		

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Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
A				
B				
C				
D				
E				
F				
G				
H				
I				
J				
K				
L				
M				
N				
O				
P				
Q				
R				
S				
T				
U				
V				
W				
X				
Y				
Z				

RADIAL OPTIMA #1 CRI STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
CRDL STD		Multi	0.500	500	Multi	5% HCL 2%HNO3		A				
AG		20			0.0200			B				
AS		20			BELOW			C				
BE		10			0.0100			D				
CD		10			0.0100			E				
CR		20			0.0200			F				
CO		100			0.100			G				
CU		50			0.0500			H				
MN		30			0.0300			I				
NI		80			0.0800			J				
PB		6			BELOW			K				
SB		120			0.120			L				
SE		10			BELOW			M				
TL		20			BELOW			N				
V		100			0.100			O				
ZN		40			0.0400			P				
AS		1000	0.050		0.120			Q				
PB		1000	0.050		0.106			R				
SE		1000	0.050		0.110			S				
TL		1000	0.050		0.120			T				

RADIAL OPTIMA #1 ICSAB STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi			A				
AL		5000			500			B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
Int. B Sol'n		Multi	10.0		Multi			F				
AG		100			1.00			G				
BA		50			0.500			H				
BE		50			0.500			I				
CD		100			1.00			J				
CO		50			0.500			K				
CR		50			0.500			L				
CU		50			0.500			M				
MN		50			0.500			N				
NI		100			1.00			O				
PB		100			1.00			P				
V		50			0.500			Q				
ZN		100			1.00			R				
								S				
								T				
								U				

RADIAL OPTIMA #1 MRL STANDARD

	Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Exp. Date	Pipet ID
Cal #1	Ca		5000	0.20	1000	1.00	5% HCL		A				
	K		5000			1.00	2%HNO3		B				
	Mg		5000			1.00			C				
	Na		5000			1.00			D				
Cal #2	Cr		100	0.10		0.0100			E				
	Ag		100			0.0100			F				
	Mn		150			0.0150			G				
	Zn		200			0.0200			H				
	Ni		400			0.0400			I				
Cal #3	Al		2000	0.10		0.200			J				
	Ba		2000			0.200			K				
	Fe		1000			0.100			L				
	Co		500			0.050			M				
	V		500			0.050			N				
	Cu		250			0.025			O				
	Be		50			0.00500			P				
Cal #4	Cd		50	0.10		0.0050			Q				
	As , Tl		100			BELOW			R				
	Pb , Se		50			BELOW			S				
PQL #2	B		200	1.00		0.200			T				
	Mo		25			0.0250			U				
	Sn		500			0.500			V				
	Ti		50			0.050			W				
Single Stds	Sb		1000	0.060		0.060			X				
	Sr		1000	0.100		0.100			Y				
	Tl		1000	0.300		0.310			Z				
	As		1000	0.500		0.510							
	Se		1000	0.500		0.505							
	Pb		1000	0.050		0.055							

AXIAL OPTIMA #2 CALIBRATION STANDARD #1 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
PQL Std 1	AL		200	0.100	100	0.200	2%HNO3		A				
	BE		5			0.0050	5%HCl		B				
	CO		50			0.0500			C				
	MG		5000			5.00			D				
	SE		5			BELOW			E				
	V		50			0.0500			F				
	SB		60			0.0600			G				
	CD		5			BELOW			H				
	CU		25			0.0250			I				
	MN		15			0.0150			J				
	AG		10			0.0100			K				
	ZN		20			0.0200			L				
	AS		10			BELOW			M				
	CA		5000			5.00			N				
	FE		100			0.100			O				
	NI		40			0.0400			P				
	NA		5000			5.00			Q				
	BA		200			0.200			R				
	CR		10			0.0100			S				
	PB		5			BELOW			T				
	K		5000			5.00			U				
	TL		10			BELOW			V				
Cal Std 4	AS		100	0.010		0.0200			W				
	CD		50			0.0100			X				
	SE		50			0.0100			Y				
	PB		50			0.0100			Z				
	TL		100			0.0200			AA				
PQL Std 2	B		200	0.100		0.200			BB				
	MO		25			0.0250			CC				
	SN		500			0.500			DD				
	TI		50			0.0500			EE				

AXIAL OPTIMA #2- CALIBRATION STANDARD #3 / HLCCV1 (Standard is prepared weekly or as necessary)
(CALIBRATION STANDARD #2 IS A 1/5 DILUTION OF THIS STANDARD)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 1	CA		5000	2.00	200	50.0	2%HNO3		A				
	MG		5000			50.0	5%HCl		B				
	K		5000			50.0			C				
	NA		5000			50.0			D				
Cal Std 2	AG		100	2.00		1.00			E				
	CR		100			1.00			F				
	MN		150			1.50			G				
	NI		400			4.00			H				
	ZN		200			2.00			I				
Cal Std 3	AL		2000	2.00		20.0			J				
	BA		2000			20.0			K				
	BE		50			0.500			L				
	CO		500			5.00			M				
	CU		250			2.50			N				
	FE		1000			10.0			O				
	V		500			5.00			P				
Cal Std 4	AS		100	4.00		2.00			Q				
	CD		50			1.00			R				
	PB		50			1.00			S				
	SE		50			1.00			T				
	TL		100			2.00			U				
Single Metals	SB		1000	2.00		10.0			V				
	SN		1000	2.00		10.0			W				
	B		1000	1.00		5.00			X				
	MO		1000	1.00		5.00			Y				
	TI		1000	1.00		5.00			Z				

AXIAL OPTIMA #2 ICV/CCV STANDARD (Standard is prepared daily.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Pipet ID
Cal Std 1	CA		5000	1.00	200	25.0	2%HNO3		A			
	MG		5000			25.0	5%HCl		B			
	K		5000			25.0			C			
	NA		5000			25.0			D			
Cal Std 2	AG		100	1.00		0.500			E			
	CR		100			0.500			F			
	MN		150			0.750			G			
	NI		400			2.00			H			
	ZN		200			1.00			I			
Cal Std 3	AL		2000	1.00		10.0			J			
	BA		2000			10.0			K			
	BE		50			0.250			L			
	CO		500			2.50			M			
	CU		250			1.25			N			
	FE		1000			5.00			O			
	V		500			2.50			P			
Cal Std 4	AS		100	2.00		1.00			Q			
	CD		50			0.500			R			
	PB		50			0.500			S			
	SE		50			0.500			T			
	TL		100			1.00			U			
Single Elements	SB		1000	1.00		5.00			V			
	SN		1000	1.00		5.00			W			
	B		1000	0.500		2.50			X			
	MO		1000	0.500		2.50			Y			
	TI		1000	0.500		2.50			Z			

AXIAL OPTIMA #2- HLCCV2 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 2	AG		100	2.00	100	2.00	2%HNO3		A				
	CR		100			2.00	5%HCl		B				
	MN		150			3.00			C				
	NI		400			8.00			D				
	ZN		200			4.00			E				
Cal Std 3	AL		2000	2.00		40.0			F				
	BA		2000			40.0			G				
	BE		50			1.00			H				
	CO		500			10.0			I				
	CU		250			5.00			J				
	FE		1000			20.0			K				
	V		500			10.0			L				
Cal Std 4	AS		100	4.00		4.00			M				
	CD		50			2.00			N				
	PB		50			below			O				
	SE		50			2.00			P				
	TL		100			4.00			Q				
Single Metals	MO		1000	1.00		10.0			R				
	PB		1000	0.800		10.0			S				
									T				
									U				
									V				
									W				
									X				
									Y				
									Z				

AXIAL OPTIMA #2 CRI STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
CRDL STD		Multi	0.500	500	Multi	5% HCL 2%HNO3		A				
AG		20			0.0200			B				
AS		20			0.0200			C				
BE		10			0.0100			D				
CD		10			0.0100			E				
CR		20			0.0200			F				
CO		100			0.100			G				
CU		50			0.0500			H				
MN		30			0.0300			I				
NI		80			0.0800			J				
PB		6			0.00600			K				
SB		120			0.120			L				
SE		10			0.0100			M				
TL		20			0.0200			N				
V		100			0.100			O				
ZN		40			0.0400			P				
								Q				

ICSA STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi	5% HCL		A				
AL		5000			500	2%HNO3		B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
								F				
								G				
								H				
								I				
								J				
								K				
								L				
								M				
								N				
								O				
								P				
								Q				
								R				
								S				
								T				
								U				
								V				

AXIAL OPTIMA #2 ICSAB STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi			A				
AL		5000			500			B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
Int. B Sol'n		Multi	10.0		Multi			F				
AG		20			0.200			G				
BA		50			0.500			H				
BE		50			0.500			I				
CD		100			1.00			J				
CO		50			0.500			K				
CR		50			0.500			L				
CU		50			0.500			M				
MN		50			0.500			N				
NI		100			1.00			O				
PB		5			0.0500			P				
V		50			0.500			Q				
ZN		100			1.00			R				
AS		10			0.100			S				
SB		60			0.600			T				
SE		5			0.0500			U				
TL		10			0.100			V				

OPTIMA INTERNAL STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Y		1000	50.0	500	100	2% HNO3		A				
Cs		1000	50.0	500	100	5% HCL		B				
								C				
								D				
								E				
								F				
								G				
								H				
								I				
								J				
								K				
								L				
								M				
								N				
								O				
								P				
								Q				
								R				
								S				

AXIAL OPTIMA #2 MRL STANDARD

	Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Exp. Date	Pipet ID
Cal #1	Ca		5000	0.20	1000	1.00	5% HCL		A				
	K		5000			1.00	2%HNO3		B				
	Mg		5000			1.00			C				
	Na		5000			1.00			D				
Cal #2	Cr		100	0.10		0.0100			E				
	Ag		100			0.0100			F				
	Mn		150			0.0150			G				
	Zn		200			0.0200			H				
	Ni		400			0.0400			I				
Cal #3	Al		2000	0.10		0.200			J				
	Ba		2000			0.200			K				
	Fe		1000			0.100			L				
	Co		500			0.050			M				
	V		500			0.050			N				
	Cu		250			0.025			O				
	Be		50			0.00500			P				
Cal #4	Cd		50	0.20		0.0100			Q				
	As , Tl		100			0.0200			R				
	Pb , Se		50			0.0100			S				
PQL #2	B		200	1.00		0.200			T				
	Mo		25			0.0250			U				
	Sn		500			0.500			V				
	Ti		50			0.050			W				
Single Stds	Sb		1000	0.060		0.060			X				
									Y				
									Z				

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MISCELLANEOUS STANDARDS

Type Of Std	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot#	Expiration Date	Pipet ID
Cal Std	1 / MRL	Li Si Sr						SD 9/21/04	A	M1780055W	M1780054U	9/27/04	M17
	Li	M1780053Y	1000	0.050	500	0.100	2% HNO_3 5% HCl	SD 9/23/04	B	M1780055W	M1780054U	10/4/04	M17/M19
	Si	M1780053X	1000	0.500		50ml/10ml Ø1.00			C				
	Sr	M1780051N	1000	0.050		0.100			D				
									E				
Cal 3	HLCCV1				200		2% HNO_3 5% HCl	SD 9/21/04	F	M1780055W	M1780054U	9/27/04	M18
	Li	M1780053Y	1000	2.00		10.0		SD 9/28/04	G	M1780055W	M1780054U	10/4/04	M18
	Si	M1780053X	1000	2.00		10.0			H				
	Sr	M1780051N	1000	1.00		5.00			I				
									J				
HLCCV2					100		2% HNO_3 5% HCl	SD 9/21/04	K	M1780055W	M1780054U	9/27/04	M18
	Li	M1780053Y	1000	2.00		20.0			L				
	Si	M1780053X	1000	2.00		20.0			M				
	Sr	M1780051N	1000	1.00		10.0			N				
									O				
ICV/CCV					200		2% HNO_3 5% HCl	SD 9/21/04	P	M1780055W	M1780054U	9/27/04 50ml/100ml	M18/M19
	Li	M1780053W	1000	1.00		5.00		SD 9/22/04	Q	M1780055W	M1780054U	9/28/04	M18/M19
	Si	M1780053V	1000	1.00		5.00		SD 9/24/04	R	M1780055W	M1780054U	9/25/04	M18/M19
	Sr	M1780050V	1000	0.500		2.50		SD 9/27/04	S	M1780055W	M1780054U	9/28/04	M18/M19
								SD 9/28/04	T	M1780055W	M1780054U	9/29/04	M18/M19
									U				
									V				
									W				

STANDARD OPERATING PROCEDURE

for

DETERMINATION OF MERCURY IN SOLID OR SEMISOLID WASTE BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY FOR INDIANA PINES SITE

SOP No.: MET-7471APines

Revision: 0

September 23, 2004

Approved by: _____ Supervisor — 9/23/04 Date

_____ QA Coordinator — 9/23/04 Date

_____ Laboratory Director — 9/23/04 Date

One Mustard St, Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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1. SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 7471A to determine the concentration of mercury in soils, sediments, bottom deposits and sludge-type materials. The range of the method is 0.2 to 10 ug/L. The range may be extended above or below the normal range by increasing or decreasing the sample size. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

A known portion of a soil sample is transferred to a hot block cup. It is digested in diluted potassium permanganate solution and oxidized for thirty minutes at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured by the conventional cold vapor atomic absorption technique.

3. DEFINITIONS

3.1. **Calibration Blank** - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument.

3.2. **Calibration Standard** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3. **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicate sample indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4. **Laboratory Control Sample (LCS)** - An aliquot of an ERA soil sample with a known concentration. The 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.

3.5. **Matrix Spike (MS)** - An aliquot of an environmental sample to which a known quantity of the method analyte is added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6. **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

3.7. **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear.

3.8. **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.9. **Standard Addition** - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

3.10. **Batch** - Unit of samples prepared together on the same day, not to exceed 20 samples.

4. HEALTH AND SAFETY WARNINGS

The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents.

All contact with mercury should be avoided. Mercury vapor is especially toxic, causing severe respiratory tract damage. Chronic exposure to mercury through any route can produce central nervous system damage. May cause muscle tremors, personality and behavior changes, memory loss, metallic taste, loosening of the teeth, digestive disorders, skin rashes, brain damage and kidney damage. Can cause skin allergies and accumulate in the body. Repeated skin contact can cause the skin to turn gray in color. A suspected reproductive hazard; may damage the developing fetus and decrease fertility in males and females.

5. CAUTIONS

- Because of the extreme sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, care must be taken to avoid extraneous contamination. Sampling devices, sample containers and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

- Samples with high organic content may required additional permanganate. Shake and add additional permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Ensure that equal amounts of permanganate are added to all samples, standards and blanks

6. INTERFERENCES

6.1. Interferences have been reported for soils containing sulfide, chloride, copper and tellurium. Organic compounds, which have broad band UV absorbance (around 253.7 nm), are confirmed interferences. The concentration levels for interferants are difficult to define.

6.2. Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if preformed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as chemical oxygen demand (COD).

7. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in any subject and have successfully completed an Initial Demonstration of Capability after training using the Training Plan Form (found on the CAS Intranet). Training and Demonstration of Capability are in accordance with NELAC 2002 Standard.

8. EQUIPMENT AND SUPPLIES

8.1. Perkin Elmer FIMS - Atomic Absorption Spectrophotometer equipped with a vapor generator, quartz absorption cell and mercury hollow cathode lamp.

8.2. 50mL hot block cups and caps

8.3. 100 mL B-Cups and caps

8.4. Hot Block capable of maintaining a digestion temperature of 90-95°C.

8.5. Pipettes and graduated cylinders.

8.6. Mercury stock solution (1,000 mg/L) - Purchased. Store at room temperature. Dispose per manufacturer's expiration date.

8.7. Intermediate Stock Solution (10 mg/L) - Prepare a 1/100 dilution of the 1000mg/L Stock Solution in a volumetric flask and dilute with DI water. Acidify with 0.5 ml of concentrated HNO_3. Store at room temperature for up to 1 week.

8.8. Working Solution (100 µg/L) - Prepare a 1/100 dilution of the 10mg/L Intermediate Stock Solution in a volumetric flask and dilute with DI water. Acidify with 0.5 ml of concentrated HNO_3. Prepare fresh each day analysis is performed.

8.9. Calibration Standards - Prepare 0, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 ug/L calibration curve. Transfer 0, 0.1, 0.25, 0.5, 1.0, 2.5, 5.0 mL aliquots of the 100 µg/L working solution to a series of labeled hotblock cups. Add the appropriate amount of reagent water to bring each cup to a final volume of 5 ml. Add 5 ml of aqua regia. Loosely cap each cup. Prepare 2 blank standards to ensure sufficient volume for the analysis. The CRDL standard is prepared as the 0.2 standard.

8.10. ASTM Type II water

8.11. Concentrated Nitric Acid – Metals Grade, purchased commercially. Expires as per manufacturer's indications.

8.12. Concentrated Sulfuric Acid – Metals Grade, purchased commercially. Expires as per manufacturer's indications.

8.13. Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

8.14. 5% w/v Potassium Permanganate Solution - Dissolve 50 g of $KMnO_4$ in 1 L of reagent water. Store at room temperature for up to 6 months.

8.15. 12% w/v Sodium chloride-hydroxylamine chloride solution - Dissolve 120 g of NaCl and 120 g of hydroxylamine hydrochloride ($NH_2OH*HCl$) in 1 L of reagent water. (Hydroxylamine sulfate $(NH_2OH)_2$ H_2SO_4 may be used in place of hydroxylamine hydrochloride.) Store at room temperature for up to 6 months.

8.16. 1.1% Stannous chloride + 3% HCl solution - Add 11.0 g of $SnCl_2*2H_2O$ to 1 L of 3% HCl. Prepare daily.

8.17. The calibration blanks (ICB and CCB), prepared daily, must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions.

8.18. The preparation blank (PB) is prepared in the same manner as the calibration blank and is carried through the entire preparation scheme with each batch of samples to be analyzed.

8.19. With each batch of samples to be analyzed, prepare a laboratory control sample (LCS) by weighing a 0.60g portion of an ERA soil standard and place in the bottom of a 50 mL hotblock cup. The LCS must be carried through the entire sample preparation scheme.

8.20. Initial / Continuing Calibration Verification Standard (ICV/CCV) 3.0 ug/L - Prepare an intermediate stock solution and working solution of 10 mg/L and 100 µg/L using a different stock source than the calibration standards. Transfer 1.5 ml of 100 µg/L solution (prepared daily) to a 50 ml hotblock cup. Add 3.5 ml of reagent water and 5 ml of aqua regia. Prepare 2 CCVs to ensure sufficient volume for the analysis.

8.21. The matrix spike sample (MS) is prepared by fortifying a 0.6g sample with 0.5 ml of 100 µg/L CCV standard in a hotblock cup. Carry through the entire digestion and instrument procedure as a routine sample.

9. PROCEDURE

9.1. Calibration and Standardization

Calibration Standards for the initial calibration must be prepared with each daily analysis. A blank and 5 standards is required. The correlation coefficient for each calibration must ≥0.995.

9.2. Sample Collection

Samples are to be collected in purchased, certified clean glass or plastic sample jars.

9.3. Sample Handling and Preservation

9.3.1. Maintain at 0-6°C from receipt until analysis.

9.3.2. Digested and analyze samples within 28 days of collection. Once digested, samples are analyzed as soon as possible.

9.3.3. Sample handling, storage, and custody procedures are in compliance with NELAC 2002 Standard.

9.4. Sample Preparation

9.4.1. Weigh 0.6g portion of a representative sample (approx. 0.2g portions from three areas of the sample) and place in the bottom of a hot block cup. Add 5 ml of reagent water and 5 ml of aqua regia. Loosely cap the sample cup.

9.4.2. Heat in the hotblock for 2 minutes at 95°C. Cool, then add 25 ml of reagent water and 15 ml of 5% potassium permanganate solution. Mix thoroughly and place in the hotblock for 30 minutes at 95°C.

9.4.3. Note: Samples with high organic content may required additional permanganate. Shake and add additional permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Ensure that equal amounts of permanganate are added to all samples, standards and blanks.

9.4.4. Cool and add 3.0 ml of 12% sodium chloride/hydroxylamine hydrochloride solution. Add 25 ml of reagent water and the samples are now ready to be analyzed. The stannous chloride solution is added automatically by the vapor generator.

9.5. Sample Analysis

9.5.1. Analyze the standards and samples using the Perkin Elmer Flow Injection Mercury System. See Operations Manual for details.

9.5.2. Sample concentrations exceeding the Linear Range require sample dilution. Dilutions should be performed so that the instrument concentration will fall in the mid-range of the calibration curve.

9.6. Troubleshooting

All maintenance activities are recorded in a maintenance logbook kept for each instrument. CAS staff performs most routine maintenance and troubleshooting. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Typical preventive maintenance measures include, but are not limited to, the following items:

- Check gases and tubing, daily
- Check optic tubes and filter membrane for moisture before analysis

9.7. Data Acquisition, Calculations, and Data Reduction Requirements

Calculations:

From the prepared calibration curve compute sample values by comparing response with the standard curve. Calculate the mercury concentration in the sample in mg/Kg by using the formula:

mg/Kg = Vol. (ml)/sample Wt(g) **x** 1mg/1000ug **x** 1L/1000ml **x** 1000g/1Kg **x** C **x** dilution

C = concentration of Hg in digestate, in ug/L

9.8. Computer Hardware and Software

- Personal Computer running Perkin Elmer AA Winlab for Window v.2.50
- Metals Analytical Review and Reporting System (MARRS) v.3.2.44
- StarLIMS v.6.11.a

10. DATA AND RECORDS MANAGEMENT

10.1. **Repsonsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data 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 SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the ICP analyst. The samples are analyzed for metals of interest using AA software. The results are transferred to MARRS (for reporting package work) and StarLIMS for validation, reporting, and invoicing.

10.3. **Data Review** – Data will be reviewed by the instrument analyst and a qualified peer using a data review checklist (attached).

11. QUALITY CONTROL AND QUALITY ASSURANCE

11.1. Preparation Blanks must be analyzed at least once per batch of 20 or fewer samples. PB values must not exceed the MRL (method reporting limit). If the PB is out of control, fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable PB values have been obtained.

11.2. Laboratory Control Samples assess laboratory performance against the required control limits. The control limit range is specific for each lot and is recorded on a certificate from the manufacturer. If the recovery of mercury falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Redigestion and analysis is required until acceptable LCS recovery is performed.

11.3. Calibration Verification Standards must immediately follow each calibration, after every tenth sample, and at the end of the sample run. Initial Calibration Verification must verify that the instrument is within ±10%. Continuing Calibration Verification standards must confirm the calibration within ±10% throughout the analyses. If the recovery of mercury falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Reanalysis of any sample(s) associated with the outlying ICV or CCV standards is required. All samples must be bracketed with acceptable ICV and CCV standards.

11.4. Sample Matrix Accuracy and Precision are assessed based upon MS and Duplicated performance. Refer to Appendix C of the Quality Assurance Manual for frequency and QC criteria per method of analysis. If the MS is out of control and the LCS is in control, assume matrix interference and flag the associated data.

11.5. Method Detection Limit (MDL) - A mercury MDL must be determined annually using 7 replicates of a fortified blank solution at a concentration of 2-3 times the estimated detection limit. Practical Quantitation Limits (PQLs) are calculated from the MDL by multiplying the MDL by a factor of at least 3. The PQLs are generally used as CAS Reporting Limits. To determine the MDL, refer to 40 CFR Part 136 Appendix B.

12. REFERENCES

- *Test Methods For Evaluating Solid Waste, Physical/Chemical Methods*. USEPA SW-846, 3rd Edition, September 1994.
- *Methods For the Determination of Metals in Environmental Samples Supplement I.* USEPA/600/R-94/111, May 1994
- EPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, SOW No. ILM04.0.
- Analytical Services Protocol (ASP), New York State Department of Environmental Conservation, December 1995.
- 40 CFR Part 136 Appendix B
- NELAC 2002 Standard.

Columbia Analytical Services

Analysis For: Hg
EPA Method: 7470 / 7471 / 245.1 / 245.5
Analyst: _____
[redacted] Temp: In____/ Out____
Report: Routine / ASP / Pkg.5
Date Prepped: _____
Time In: _____
File Name: _____
Date Analyzed: _____
Time Out: _____

	Client / Submission #	Sample Number	Initial Wgt/Volume (g/ml)	Final Volume (ml)			Client / Submission #	Sample Number	Initial Wgt/Volume (g/ml)	Final Volume (ml)
1						31				
2						32				
3						33				
4						34				
5						35				
6						36				
7						37				
8						38				
9						39				
10						40				
11						41				
12						42				
13						43				
14						44				
15						45				
16						46				
[redacted]						47				
[redacted]						48				
19						49				
20								ICB	100ml DI Water	100
21								Std 0	100ml DI Water	100
22								Std 0.2*	0.20ml of 0.1ppm	100
23								Std 0.5*	0.50ml of 0.1ppm	100
24								Std 1.0*	1.00ml of 0.1ppm	100
25								Std 2.0*	2.00ml of 0.1ppm	100
26								Std 5.0*	5.00ml of 0.1ppm	100
27								Std 10.0*	10.0ml of 0.1ppm	100
28								ICV/CCV**	3.00ml of 0.1ppm	100
29								LCSW/MS**	1.00ml of 0.1ppm	100
30								CRDL*	0.20ml of 0.1ppm	100

Lot # of Reagents Used:

HNO3: _____ H2SO4: _____ HCL: _____ K2S2O8: _____ KMnO4: _____

SnCl2: _____ NaCl: _____ NH2OH-HCL: _____ LCSS CAS Lot#: _____

LCSS ERA Lot#: _____

*Source Standard: (Vendor/Lot #)_____

*(10ppm stock Lot#: _____)

*(0.1ppm working std Lot#: _____)

**ICV Standard: (Vendor/Lot #)_____

**(10ppm stock Lot#: _____)

**(0.1ppm working std Lot#: _____)

Comments/Problems: _____

Batch Name: _____ _____

Metals Instrument Analysis Training Plan

Procedure:_____

SOP:_____ Revision:_____ Date:_____

Trainee:_____

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
-the chemical and physical principals behind the measurement by the instrument

Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs

-ADM-BATCHSEQ	-ADM-PCAL	-ADM-SIGFIG
-ADM-DATAENTRY	-ADM-DIL	-ADM-SPSR
-ADM-MDL	-ADM-DREV	-ADM-TRANDOC

Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
-standard and reagent prep and documentation – including pipet used
-instrument power up and warm-up
-instrument set-up, daily maintenance and checks
-use and loading of autosampler
-sample analysis including:
    -calibration
    -sample dilution
    -software command of instrument
    -use of QC samples and QC criteria
    -common troubleshooting
-instrument logbook use
-data reduction, reporting, and review

Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

Signature:_____ Date:_____

6. Perform SOP with supervision
- including all items in 4.

Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
-all of the item listed in 4
-IDC (4 mid-range standards performed before client samples are analyzed)
-attach IDC certificate, raw data, and summary spreadsheet.

Trainer:____ Trainee:____ Date:____

Columbia Analytical Services, Inc.
An Employee-Owned Company

METALS DEPARTMENT
DATA QUALITY CHECKLIST

Data File:_____ Run Date:_____ Instrument:_____

Methods Used:
ICP- 200.7 // 6010B // ASP/CLP // NIOSH
GFAA- EPA 200 Series // SW846 // ASP/CLP
CVAA- EPA 200 Series // SW846 // ASP/CLP

Batch ID / Metals Reviewed:_____

_____

Yes	No	NA			Yes	No	NA
☐	☐	☐	1.	**Holding Times met method requirements?** ICP / GFAA- 6mths from sampling to analysis Hg- 28 days from sampling to analysis (26 days from VTSR)	☐	☐	☐
☐	☐	☐	2.	**ICAL met method requirements?** Correlation Coefficient > or = 0.995 ICP High Check= 95-105%	☐	☐	☐
☐	☐	☐	3.	**ICV acceptable?** ICP: 200.7= 95-105% ; NIOSH / 6010B / ASP/CLP= 90-110% GFAA: EPA 200 Series / SW846 / ASP/CLP= 90-110% Hg: EPA 200 Series= 95-105% ; SW846 / ASP/CLP= 90-110%	☐	☐	☐
☐	☐	☐	4.	**CCVs acceptable? Analyzed per 10 samples?** ICP: 200.7 / 6010B / ASP/CLP / NIOSH= 90-110% GFAA: EPA 200 Series= 90-110% ; SW846 / ASP/CLP= 80-120% Hg: EPA 200 Series= 90-110% ; SW846 / ASP/CLP= 80-120%	☐	☐	☐
☐	☐	☐	5.	**CCBs accepttable? Analyzed per 10 samples?** Concentrations < RL	☐	☐	☐
☐	☐	☐	6.	**Method Blank results <RL?**	☐	☐	☐
☐	☐	☐	7.	**LCS recoveries within QC limits?** ICP: 200.7= 85-115% ; 6010B / ASP/CLP / NIOSH= 80-120% GFAA: EPA 200 Series= 85-115% ; SW846 / ASP/CLP= 80-120% Hg: EPA 200 Series= 85-115% ; SW846 / ASP/CLP= 80-120% LCSS (soil) Certificate of Analysis QC limits per manufacturer	☐	☐	☐
☐	☐	☐	8.	**All sample concentrations within LR?**	☐	☐	☐
☐	☐	☐	9.	**MS recoveries within QC limits?** ICP: 200.7= 70-130% ; 6010B / ASP/CLP= 75-125% GFAA: EPA 200 Series / SW846 / ASP/CLP= 75-125% Hg: EPA 200 Series= 70-130% ; SW846 / ASP/CLP= 75-125%	☐	☐	☐
☐	☐	☐	10.	**Duplicate RPD within QC limits?** 20% for RPD shall be used for samples > or = 5 times the RL. RL shall be used for samples < 5 times the RL.	☐	☐	☐
☐	☐	☐	11.	**Is GFAA Post Digest Spike within 85-115%?**	☐	☐	☐
☐	☐	☐	12.	**Dilution factors verified and calculated correctly?**	☐	☐	☐
☐	☐	☐	13.	**Bench Sheet complete, initials, date, and time:**	☐	☐	☐
☐	☐	☐		•Are standards and reagents traceable?	☐	☐	☐
☐	☐	☐		•Is unused space on the sheet crossed out?	☐	☐	☐

Analyst:_____ Peer Review:_____
Date:_____ Date:_____

COMMENTS:
**Comments must be provided for any items noted above as "No"

STANDARD OPERATING PROCEDURE

for

METALS DIGESTION,
SOILS, SEDIMENTS, AND SLUDGE FOR ICP AND GFAA ANALYSIS

SOP No.: MET-3050B

Revision: 3

January 15, 2003

Approved by: _____ _____
Supervisor Date

_____ _____
QA Coordinator Date

_____ _____
Laboratory Manager Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

1 SCOPE AND APPLICATION

Method 3050 is an acid digestion procedure used to prepare matrices such as soils, sludges, or sediments for analysis by ICP or graphite furnace atomic absorption.

2 METHOD SUMMARY

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide. Hydrochloric acid is used as a final reflux acid for ICP analyses. Nitric Acid is used as the final reflux acid for most Graphite Furnace analyses.

3 DEFINITIONS

3.1 **Laboratory Duplicates -** Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates and indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 **Laboratory Control Sample Soil (LCSS)** - An aliquot of a soil to which known quantities of the method analytes are added by an outside vendor. The LCSS 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.

3.3 **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 **Preparation Blank (PB) -** An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5 Digestion Batch - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4 INTERFERENCES

4.1 See appropriate analysis SOP for applicable interferences

5 SAFETY

Nitric and Hydrochloric acids are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment including safety glasses (with side shields), gloves, and lab coat shall be worn when handling samples or reagents.

6 SAMPLE COLLECTION, PRESERVATION AND STORAGE

For non-aqueous samples, glass or plastic sample containers are acceptable. Samples are analyzed within 6 months of sample collection. Additional sample handling policies and procedures are in SMO-GEN.

7 APPARATUS AND EQUIPMENT

7.1 250 and 100 mL beakers
7.2 Ribbed watch glasses
7.3 Hot plates
7.4 Graduated cylinders
7.5 Eppendorf Pipettors
7.6 Funnels
7.7 Mortar and pestle
7.8 Tongue depressors
7.9 Filter paper
7.10 Hot Block Digestor with ETR-3200 Controller by Environmental Express, LTD.
7.11 Graduated block digestor ribbed watch glasses
7.12 Block Digestor Filters.
7.13 CPI MOD Block Digestor

8 PREVENTIVE MAINTENANCE

8.1 All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Reagent water - ASTM Type II deionized water. Reagent water must be interference free.

9.2 Concentrated nitric acid (Baker Instra-Analyzed 69-70%): Acid should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature in the dark. Expires per manufacturer's indications or one year from receipt, whichever is sooner.

9.3 Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%): Acid should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature. Expires per manufacturer's indications or one year from receipt, whichever is sooner.

9.4 Hydrogen peroxide (30%) - H_2O_2. Purchased commercially. Should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt, whichever is sooner.

9.5 ERA Soil Laboratory Control Sample (LCSS) - Concentrations and Performance Acceptance Limits distributed through vendor. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt, whichever is sooner.

9.6 Metals spiking solutions – Purchased commercially. See Table 1. Store at room temperature. Stocks expires upon manufacturer's indications or 1 year from receipt, whichever is sooner. Solutions prepared from stocks expire 6 months from preparation.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data 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 SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11 PROCEDURES

11.1 HOT PLATE

11.1.1 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

11.1.2 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into a 250 or 100 mL beaker. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

11.1.3 Unless specified by project or state requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3, cover with a ribbed watch glass and reflux for 15 minutes. The sample temperature should be 90-95°C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

11.1.4 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the beaker.

11.1.5 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

11.1.6 If the sample is being prepared for analysis by ICP, add 10 mL 1:1 HCL. If the sample is being prepared for analysis by Graphite Furnace no HCl is added.

11.1.7 Cover and reflux the ICP samples for 15 minutes without boiling. Allow to cool.

11.1.8 Prepare filters by rinsing with 1:1 nitric acid and DI.

11.1.9 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and watch glass with DI into the filter. Rinse the filter with DI. Bring to volume with DI.

11.2 HOT BLOCK DIGESTOR

11.2.1 Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

11.2.2 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

11.2.3 Label graduated hot block digestor sample cups with appropriate sample IDs for digestion.

11.2.4 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

11.2.5 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into labeled digestor sample cup. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

11.2.6 Unless specified by project or state requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3 and for ICP only add 1.5 mL of 1:1 HCl, cover with reflux cap and reflux for 15 minutes. The sample temperature should be 90-95°C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

11.2.7 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the sample cup.

11.2.8 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

11.2.9 If the sample is being prepared for analysis by ICP, add 10 mL 1:1 HCL. If the sample is being prepared for analysis by Graphite Furnace no HCl is added.

11.2.10 Cover and reflux the ICP samples for 15 minutes without boiling. Allow to cool.

11.2.11 Prepare filters by rinsing with 1:1 nitric acid and DI.

11.2.12 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and reflux cap with DI into the filter. Rinse the filter with DI. Bring to volume with DI. Pour into a labeled B-cup.

12 QA/QC REQUIREMENTS

12.1 Each day, digest one laboratory control sample (LCS) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use the appropriate solid laboratory control sample (LCSS) for soils analysis.

12.2 Each day, digest one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures.

12.3 Each day, prepare one duplicate and one spiked sample with each digestion batch, or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

12.4 Matrix spikes are prepared by adding the appropriate volume of spiking solution (See Table 1).

12.5 See appropriate analysis SOP for applicable QC limits and corrective action.

13 DATA REDUCTION AND REPORTING

13.1 Digestion logs are used to record all sample volumes, spike volumes, etc. The Manufacturer's lot number for the reagents used are added to the digestion log (see attached digestion log benchsheet).

13.2 Reporting and method performance is discussed in the appropriate analysis SOP. Data review is discussed in ADM-DREV.

14 METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

15 WASTE MANAGEMENT AND POLLUTION PREVENTION

15.1 Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis.

15.2 Acidic waste is poured down the drain with copious amounts of water.

15.3 Samples with analyte concentrations exceeding TCLP regulatory limits are disposed of as hazardous waste. Others are dumped down the drain with plenty of water. See SMO-SPLDIS.

16 CORRECTIVE ACTION FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18 REFERENCES

"Test Methods For Evaluating Solid Waste, Physical/Chemical Methods". EPA SW846, Third Edition, December 1996.

19 TRAINING OUTLINE

19.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2 Observe Sample Preparation.

19.3 Participate in the methodology, documentation, and data reduction with guidance.

19.4 Complete a Training Plan Form for the procedure.

19.5 Show Initial Demonstration of Capability (IDC) by independently preparing and digesting four LCSs, or equivalent, according to the test method either concurrently or over a period of days. If recovery is within acceptable limits, complete IDC certification form, and Training Plan forms and file with QA. Continued capability shall be demonstrated annually using PE results, a single blind, or a new 4 replicate study.

20 METHOD MODIFICATIONS

None

21 INSTRUMENT-SPECIFIC ADDENDUM

Not Applicable

22 ATTACHMENTS

Table 1 Spike Concentrations
Digestion Log Benchsheets
SW846 Method 3050 Flow Chart

23 CHANGES FROM PREVIOUS REVISION

- Added Hot Block digestion procedures (11) and associated items to Apparatus and Equipment (7)
- Added sections 14, 16, 17, and 20 for NELAP compliance
- Changed the amount of time to reflux sample from 10-15 minutes to just 15 minutes after the first addition of acid (11).

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE SOLUTION A			1.00ml Spk A	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
AL	200		**NI**	50
AS	4		**SE**	1
BA	200		**AG**	5
BE	5		**TL**	200
CD	5		**V**	50
CR	20		**ZN**	50
CO	50		**B**	100
CU	25		**CA**	200
FE	100		**MG**	200
PB	50		**NA**	2000
MN	50		**K**	2000

SPIKE SOLUTION B			1.00ml Spk B	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SB	50		**TI**	50
MO	50		**-**	-

INDIVIDUAL METALS	0.10ml Spk. to Final Volume of 100ml		**INDIVIDUAL METALS**	0.5ml Spk. to Final Volume of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SE	1000		**SN**	1000

SPIKE #4 Furnace Spike			1.00ml Spk #4	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
AS	4		**SB**	10
PB	2		**TL**	5
SE	1		**CU**	0.5

CAS-Rochester ICP Soil Digestion Log

6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID:

Analyst: _____ **Date:** _____

Spike Witness / Lot Approval: _____

Batch Temp:

Prep Method: SW846 3050 // CLP

Digest: Initial // Redigest of: _____

Report Type: Routine // ASP // Pkg5

	Submission / Order #	Initial Wgt. (g)	Final Vol (ml)	Initial Color / Texture	Final Color / Clarity	Metals	Spike Vol (ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

Spiking Standards / Reagent Lot #:

Spike A,B: _____ Spike #4: _____

TCLP Spk: _____ TCLP Ba: _____

Se Std: _____ Sn Std: _____

HNO3: _____ HCL: _____

H2O2: _____ LCSS: _____

Color / Clarity Key:

Color: **C** = Colorless ; **Y** = Yellow ; **B** = Brown
BL = Black ; **G** = Grey ; **W** = White

Clarity: **CDY** = Cloudy ; **CLR** = Clear ; **OP** = Opaque

Texture: **F** = Fine ; **M** = Medium ; **CS** = Coarse ; **NAQ** = Non Aqueous

01

Comments: _____

CAS-Rochester Furnace Soil Digest Log

Analyst:_____ **Date:**_____ **Spike Witness:**_____ **Approval:**_____

[redacted]od: SW846 3050 // CLP Digest: Initial Digestion // Redigestion of _____

Report: Routine // ASP // Pkg.5 **6010B/846 // 200.7/136 // ASP/CLP**

	Client/ Order #	Initial wgt(g)	Final vol(ml)	Initial Color/Clarity	Final Color/Clarity	Metals	Spike vol(ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
[redacted]							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							
25							
26							

Spiking Standards Lot # or Prep Date:

[redacted] Spike #4_____

[redacted]ent Lot #:

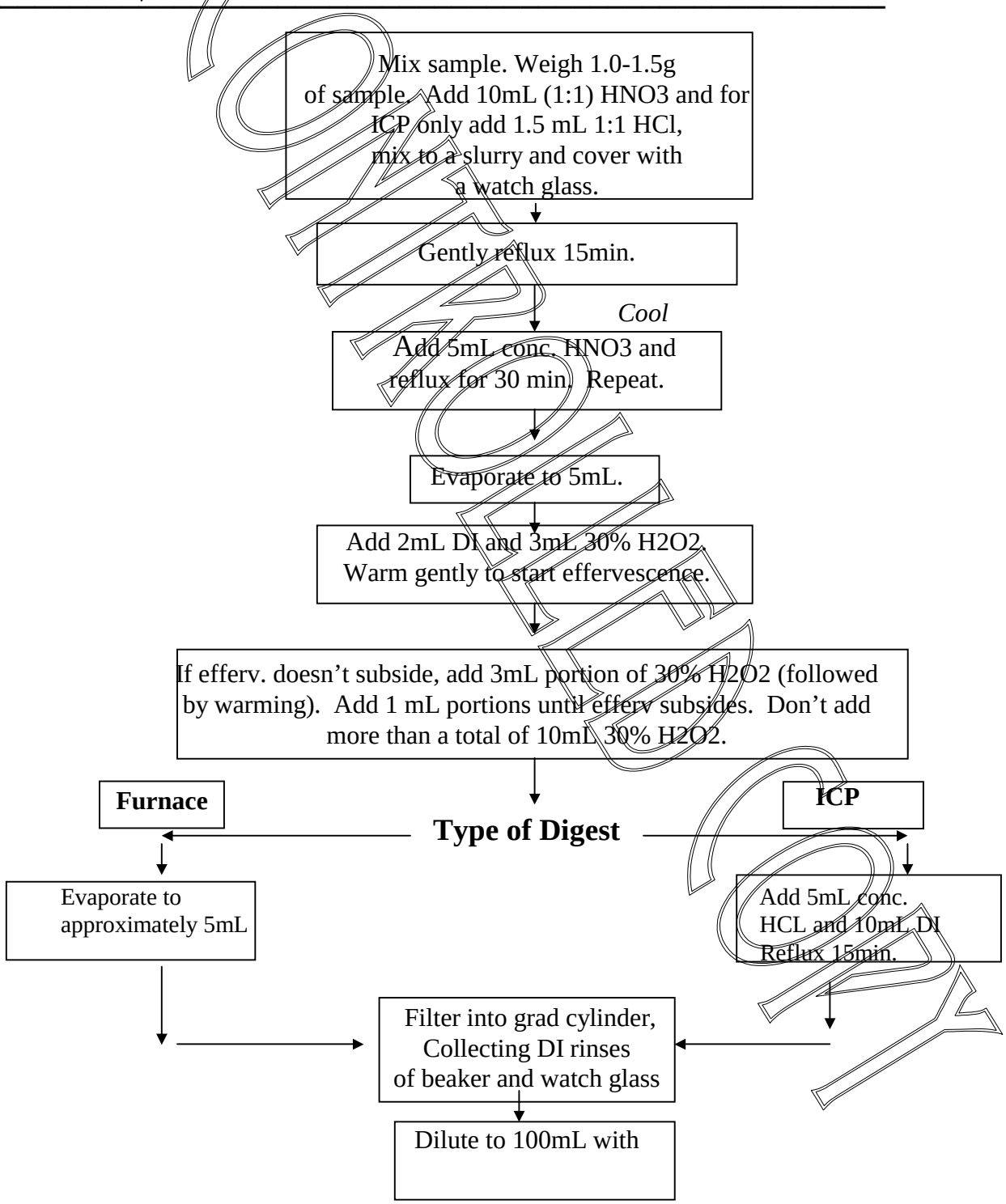
LCSS_____ HNO3_____ H2O2_____

0091

Comments/Problems:_____

SW846 Method 3050
Flow Chart

Non-CLP Soils, Sediments and Sludges



DI water.

STANDARD OPERATING PROCEDURE

DETERMINATION OF TRACE METALS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAA)

SOP Code: MET-GFAA

Revision: 3.0

September 27, 2001

Approved by: _____ Department Manager — 11/1/01 Date

_____ Quality Assurance Coordinator — 11/1/01 Date

_____ Laboratory Director — 11/1/01 Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: DCD Date: 12/20/02
Initials: DCD Date: 12/19/03
Initials: DCD Date: 12/14/04

DOCUMENT CONTROL
NUMBER: MET-002
Initials: ~~9pc~~ Date: 11/2/01

1.0 SCOPE AND APPLICATION

1.1 This procedure describes the procedure for the analysis of soil, sludge and water digestates by graphite furnace atomic absorption (GFAA) spectrometry. Typically, this procedure is applicable to the analytes and EPA methods listed in Table 1. Other elements may be determined when reference is made to the applicable published method. All analytical methods used are in accordance with EPA methods from SW-846 and EPA 200 Series, the EPA Contract Laboratory Program (CLP) statement of work (SOW), and the NYSDEC Analytical Services Program (ASP).

1.2 The Practical Quantitation Limits (PQL) are listed in Table 1. The reported PQL may be adjusted if required for specific project requirements, however, the capability of achieving other reported PQLs must be demonstrated. Results may be reported to the Instrument Detection Limits (IDLs) upon request. IDLs are updated quarterly. The Method Detection Limits (MDLs) are updated annually and are available upon request.

2.0 METHOD SUMMARY

2.1 Prior to analysis, samples must be digested using appropriate sample preparation methods. A representative aliquot of sample is prepared as described in the applicable digestion SOP. Refer to the following Metals Digestion SOPs:

MET-3005A	Metals Digestion, Waters, Total Recoverable and Dissolved for ICP
MET-3010A	Metals Digestion, Waters for ICP
MET-3020A	Metals Digestion, Waters for GFAA
MET-3050B	Metals Digestion, Soils, Sediments and Sludges for ICP and GFAA
MET-CLP	Metals Digestion, Waters and Soils for CLP

2.2 The digestate is analyzed for the element(s) of interest, using GFAA conditions (See Instrument Specifications by Metal Manual in the GFAA lab) for the element to be determined. Absorbance is measured as a function of element concentration.

2.3 For GFAA analyses by CLP procedures, see the applicable CLP SOW or ASP.

3.0 DEFINITIONS

3.1 **Analytical Sequence** - Samples are analyzed in a set referred to as an analytical sequence. The sequence begins with instrument calibration followed by analysis of sample digestates interspersed with analysis of calibration verification standards.

3.2 **Initial Calibration Verification (ICV)** - ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization.

3.3 **Matrix Spike** (MS) - In the matrix spike analysis, predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to sample digestion and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for each of the analytes detected.

3.4 **Duplicate Sample** (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.5 **Method Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

3.6 **Continuing Calibration Verification Standard (CCV)** - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.7 **Instrument Blank (CCB)** - The instrument blank (also called continuing calibration blank) is a volume of blank reagent of composition identical to the digestates. The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

4.0 INTERFERENCES

Interferences are dealt with through the use of matrix modifiers (commonly Ni and Pd) and post digestion spikes. Detailed discussion of interferences may be found in the applicable EPA method.

Interferences from contaminated reagents must be eliminated. The purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the Method Detection Limit.

5.0 SAFETY

Normal precautions as per the CAS EH&S Manual are to be followed. In addition, because acids are used in the procedure, there is a danger of exposure to corrosives. Sufficient care must be taken in handling acidic solutions. Safety glasses must be worn while preparing and handling the solutions. Gloves and a laboratory coat should be worn while handling samples, acids, and sample digestates.

6.0 SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1 Either glass or plastic sample containers may be used.

6.2 All aqueous samples are preserved with nitric acid to a pH of <2.

6.3 Soil and aqueous samples for GFAA analyses by CLP procedures are stored at 0-6 °C. from time of receipt until digestion. Soil and aqueous samples for GFAA analyses by other procedures are stored at ambient temperature from time of receipt until digestion.

6.4 Holding time for samples for GFAA analyses is 6 months (sample collection to digestion).

6.5 Samples are received in the GFAA analysis laboratory as 0.5% nitric acid digestates. Sample digestates are stored in labeled plastic B-cups or Hot Block digestion vessels.

7.0 APPARATUS AND EQUIPMENT

7.1 Graphite furnace atomic absorption spectrophotometer (AAS). See Appendix A for element-specific instrument parameters.

7.2 Hollow Cathode Lamp (HCL) or Electrodeless Discharge Lamp (EDL) for each metal analyzed by this procedure.

7.2.1 Electrodeless Discharge Lamp power supply.

7.3 100-1000uL Eppendorfs

7.4 2 ml Beaker cups compatible with the AAS autosampler.

7.5 Volumetric flasks of suitable precision and accuracy.

8.0 PREVENTIVE MAINTENANCE

All maintenance activities are recorded in a maintenance logbook kept for each instrument. Most routine maintenance and troubleshooting is performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Typical preventive maintenance measures include, but are not limited to, the following items:

- Cleaning the quartz windows
- Changing the graphite tubes

- Cleaning the capillary tube
- Change filter in Separator Trap annually or if necessary
- Inspection and cleaning of electrodes, shroud, and cells as needed.

9.0 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Concentrated Nitric Acid – Metals Grade or higher to eliminate the introduction of contamination above the method detection limit.

9.2 Matrix Modifiers

Palladium Modifier Dilute 10 mls Palladium Nitrate (1%) plus 1.0 ml Magnesuim Nitrate (2%) with 100.0 ml DI. Expires within 6 months at room temperature. Used for arsenic, selenium, and thallium.

Ammonium Dihydrogen Phosphate (purchased) Dilute 1.0 g to 100 mls DI. Expires 6 months at room temperature. Used for lead analysis.

9.3 Standards

9.3.1 1000 ppm Stock Standards (AA Grade) - Commercially available certified solutions.

9.3.2 The GFAA Calibration Stock Standard is made by pipetting the volume of the 1000 ppm As, Pb, Se, and Tl stock standards shown in the table below, plus 0.50 ml of concentrated nitric acid into a 100 ml volumetric flask and diluting to volume with DI water. Prepare Calibration Stock Standard weekly.

Analyte	ml of Stock Std. (1000 ppm)	Add 0.50 ml conc. HNO_3 and dilute to	Final Concentration (mg/L)
Arsenic	0.50	100 ml	5.0
Lead	0.45	100 ml	4.5
Selenium	0.50	100 ml	5.0
Thallium	0.50	100 ml	5.0
Lead - DW	0.30	100 ml	3.0

9.3.3 The GFAA Calibration Working Standard is prepared by diluting 1.0 ml of the GFAA Calibration Stock Standard and 0.5 ml of concentrated nitric acid to 100 ml with DI water. Final concentrations range from 0.030 to 0.050 mg/L. Prepare calibration working standard fresh each day. LMK 8/23/02

insert table > see attached

9.3.4 The GFAA Initial and Continuing Calibration Verification (ICV andCCV) Stock Standard is made by pipetting the volume of the 1000 ppm As, Pb, Se, and Tl

SOP No: MET-GFAA
Rev. 3.0
Addendum LMR 8/23/02

9.3.3 Continued…
"Prepare the calibration working standard fresh each day." This standard is loaded into the autosampler (typically location 38) so that the instrument may auto-dilute the working standard to prepare the calibration standards at four concentration levels intended for the initial curve (blank and 4 standards). The instrument makes the following dilutions according to the analyte being analyzed:

Element	Working Standard (ug/L)	Volume of Working Std. (uL)	Final Volume (uL)	Final Concentration (ug/L)
Arsenic	50	4	20	10
	50	8	20	20
	50	12	20	30
	50	20	20	50
Lead	30	3	30	3
	30	9	30	9
	30	15	30	15
	30	30	30	30
Antimony	50	6	30	10
	50	12	30	20
	50	18	30	30
	50	30	30	50
Selenium	50	3	30	5
	50	9	30	15
	50	18	30	30
	50	30	30	50
Thallium	50	4	20	10
	50	8	20	20
	50	12	20	30
	50	20	20	50
Copper	10	4	20	2
	10	8	20	4
	10	12	20	6
	10	20	20	10

stock standards shown in the table below, plus 0.50 ml of concentrated nitric acid into a 100 ml volumetric flask and diluting to volume with DI water. Prepare the ICV / CCV Stock Standard from a second source, weekly.

Analyte	ml of Stock Std. (1000 ppm)	Add 0.50 ml conc. HNO_3 and dilute to	Final Concentration (mg/L)
Arsenic	0.25	100 ml	2.5
Lead	0.20	100 ml	2.0
Selenium	0.25	100 ml	2.5
Thallium	0.25	100 ml	2.5
Lead - DW	0.14	100 ml	1.4

9.3.5 The GFAA CCV Working Standard is prepared by diluting 1.0 ml of the GFAA CCV Stock Standard and 0.5 ml of concentrated nitric acid to 100 ml with DI water. Final concentrations range from 0.014 to 0.025 mg/L. Prepare CCV working standard fresh each day.

9.3.6 The Continuing Calibration Blank (CCB) is prepared by diluting 5.0 ml of concentrated HNO_3 to 1000 ml with DI water.

10.0 RESPONSIBILITIES

It is the responsibility of the analyst to perform the analysis according to the instructions in this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are only to be performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

11.0 PROCEDURE

11.1 Instrument Operation and Data Acquisition Procedure

11.1.1 Instrument performance specifications are specified in the operations manual located in the GFAA Lab. Refer to these when setting the parameters for acquisition and select the set of parameters applicable to the element being measured. For Arsenic, Lead, Selenium, and Thallium, the gas type is 95% argon-5% hydrogen. The modifiers used are 500 ppm Pd and 500 ppm $Mg(NO_3)_2$.

11.1.4 Turn on computer and instrument. Install appropriate HCL or EDL lamp and turn on by going to the Align Lamps screen. Allow the Hollow Cathode Lamp to warm up atleast 15 minutes and the Electrodeless Discharge Lamp atleast one hour. This warm up time is used to insure maximium optimization is achieved.

11.1.5 Wipe down the autosampler tip before each analysis. Inspect and clean, if necessary, the electrodes, shroud, lens and cells. If the instrument has a fume extractor be sure the Separator Trap is filled with deionized water.

11.1.6 Select Automatic Run and choose the appropriate program for analysis.

11.1.7 Go to Align Lamp screen and optimize lamp alignment.

11.1.8 Insert sample analysis sequence into Instrument Run Log. Create Sample Information File (sample labels) from logbook. Open the Method Editor and go to the Checks page. Assign a post digestion spike to the proper samples by setting parameters where is asks "Perform Recovery Measurements".

11.1.9 Load autosampler wheel with standards, blank, modifier, and sample digestates being analyzed, being sure to identify samples by their autosampler position in the instrument log book.

11.1.10 Start automatic run.

11.1.11 Monitor the analytical run for calibration and sample abnormalities.

11.1.12 Dilutions for samples with results over the calibration range are to be made manually and added to the autosampler.

11.2 Calibration

11.2.1 The analysis begins with the analysis of calibration standards. Analyze an instrument blank and four calibration standards. The correlation coefficient for each calibration shall be checked to determine that the coefficient is equal to or greater than 0.995.

11.2.2 Following calibration, analyze an ICV standard. The resulting value must be within 95-105% of the true value for 200 Series metals and 90-110% of the true value for SW-846 and ASP / CLP4.1. If not, prepare new standards and recalibrate the system.

11.3 Sample Analysis

11.3.1 Following calibration, analyze samples and QC samples in an analytical sequence. Refer to the *SOP for Analytical Batches and Analytical Sequences.*

11.3.2 Prepare and analyze post-digestion spiked samples. For ASP / CLP4.1 analyses, all samples must be post-spiked and analyzed. For routine analyses, one sample per submission / job number is spiked and evaluated. If the spike recovery is outside the control limits of 85-115%, all the samples in the batch are post-spiked and analyzed. If spike recoveries are within the acceptable limits, analysis is continued with no further spiking. If the post-digestion spike is <40% recovery the sample is diluted by a factor of 5-10 and reanalyzed. If the post-digestion spike is between 40-85% and the sample concentration is less than half of the spike the data is reported. For CLP4.1 a "W" flag will be on the Form I when this occurs.

11.3.3 Method of Standard Additions (MSA) analysis is required when an outlying post-digestion spike recovery is between 40-85% or >115% AND the sample absorbance or concentration is less than 50% of the spike. Quantitation is bias to some unknown interference that has been confirmed and dilution and reanalysis does not improve performance, therefore MSA must be performed by analyzing the sample plus 3 spikes at 50, 100, and 150% of the sample concentration (single injection is only required). Plot a linear regression curve of concentration vs. absorbance and quantitate sample concentration from the curve. Refer to the CLP SOW or NYSDEC ASP for proper qualifications of sample data.

12.0 QA/QC REQUIREMENTS

12.1 All GFAA sample analyses shall be performed with duplicate burns and the average reported. Duplicate burns should not exceed 20%RSD to maintain precision throughout the run. If RSD exceeds 20%, reanalyze once; if continues to be >20%, dilute 1:2 and reanalyze to avoid interference.

12.2 The correlation coefficient for each calibration must be equal to or greater than 0.995. The software produces the calibration curve point by point and does not reject a calibration that has a correlation coefficient < 0.995. The run must be stopped by the operator if the correlation coefficient fails.

12.3 Analyze CCV standards and CCBs no less frequently then every ten samples in the analytical sequence.

12.3.1 For CCVs, the resulting value must be 90-110% of the true value for CLP analyses and 80-120% for routine analyses. If not, recalibrate the system and reanalyze samples run since the last acceptable CCV.

12.3.2 For CCBs, the resulting value must be less than the PQL. Check the CCB result for carryover. Re-analyze if the CCB result is above the PQL.

12.4 Each sample preparation batch must have a method blank associated with it. The method blank result should be < PQL. If not, redigest the batch of samples.

12.5 A laboratory control sample (LCS) is digested one per batch, or per 20 samples. The LCS recovery criteria is listed in Appendix C of the Quality Assurance Manual. If the LCS fails the acceptance criteria, redigest the batch of samples.

12.6 Post-digestion spike recovery acceptance limits are 85-115%. If outside these limits for the Preparation Blank stop analysis, correct problem and reanalyze. If routine sample recovery fails all samples in the corresponding submission / job # must be spiked. If post-spike recovery is > 40%, samples may be run by the method of standard additions to prevent further dilution see sections 11.3.2 and 11.3.3.

12.7 A duplicate sample is digested one per batch, or per 20 samples (one per 10 if 200 Series is requested). Frequency and QC criteria are listed in Appendix C of the Quality Assurance Manual. If the RPD is greater than the limit, determine if the sample is non-homogenous. Redigest if necessary, otherwise data may be flagged with a "*" for job specific QC samples.

12.8 A matrix spiked sample is digested one per batch, or per 20 samples. Frequency and QC criteria are listed in Appendix C of the Quality Assurance Manual. If outside acceptance limits, redigest if necessary, otherwise the data may be flagged with a "N" for job specific QC samples. If the sample concentration is >4x the spike level, no action is required.

12.9 Additional QC measures include annual determination of method detection limits. Refer to ADM-MDL for procedure and requirements.

LMR 10/14/02

13.0 DATA REDUCTION AND REPORTING

Refer to ADM-DREV for data review procedures.

13.1 Results for aqueous samples are calculated as follows and are reported in mg/L:

*mg/L (sample) = C * x (Digestion Dilution Factor) x (Post-Digestion Dilution Factor) ÷ 1000*

13.2 Results for soil and solid samples are calculated as follows and are reported in mg/Kg.

$$mg / Kg\ (Sample) = C^{*} \times Post\ Digestion\ Dilution\ Factor \times \frac{Digestion\ Vol.\ (ml)}{Sample\ wt.\ (g)} \times \frac{1mg}{1000g} \times \frac{1L}{1000ml} \times \frac{1000g}{1Kg}$$

where C * is the concentration of the analyte as measured at the instrument in µg/L.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

14.2 Excess, unused sample and testing byproducts are disposed following the procedures in the *SOP for Waste Disposal.*

15.0 REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA SW-846, 3rd Edition; (September 1986) and Updates I (July 1992), II (September 1994), IIA (August 1993), IIB (January 1995), III (December 1996).

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, (Revised March 1993).

Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010 (June 1991) and Supplement I, EPA/600/R-94/111 (May 1994).

EPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, SOW No. ILM04.0.

Analytical Services Protocol (ASP), New York State Department of Environmental Conservation, December 1995.

16.0 TRAINING OUTLINE

16.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry.

16.2 Observe Sample Preparation and Analysis.

16.3 Participate in the methodology, documentation, and data reduction with guidance.

16.4 Instrument Operation and Maintenance, if applicable.

16.5 Demonstrate Competency by performing the analysis independently. Analyze a known proficiency or standard four times to establish Initial Demonstration of Capability. If recovery is

within acceptable limits, complete training form and certificate and file with QA. Continuing Demonstration of Capability is required on an annual basis, refer to ADM-TRANDOC.

17.0 INSTRUMENT-SPECIFIC ADDENDUM

See Operations Manual in GFAA Lab.

18.0 ATTACHMENTS

Table 1 Summary of Parameters, Methodology, and Reporting Limits

19.0 CHANGES FROM PREVIOUS REVISION

- Added reference to the Instrument Specifications per Metal Manual to Section 2.2.
- Changed Independent to Initial in Section 3.2
- Added reference to Hot Block digestion vessels in Section 6.5
- Added EDL Lamp and EDL power supply to Section 7
- Inserted how often the Calibration and ICV / CCV Standard Stocks should be prepared in Section 9.3.2 and 9.3.4
- Sections 11.0, 12.0 of previous SOP were revised to include more detail and referenced Appendix C of Quality Assurance Manual for QC criteria and frequency requirements.
- Deleted all references to analyzing Antimony by GFAA.

Table 1

Parameters, Methodology, and Reporting Limits

Parameter	Methology	Practical Quantitation Limit (PQL)	
		Water (mg/L)	Soil (ug/g)
Arsenic	206.2/7060A/CLP	0.0050	0.50
Lead	239.2/7421	0.0050	0.50
Lead	CLP	0.0030	0.30
Lead in Drinking Water	239.2	0.0010	
Selenium	270.2/7740/CLP	0.0050	0.50
Thallium	279.2/7841/CLP	0.010	1.0

*Contract Laboratory Program (CLP) references refer to ILM04.1 and/or 6010B-CLPM (ASP 1995).

Standard Operating Procedure for Document Control

SOP No.: MET-GFAA

DISTRIBUTION LIST

DOCUMENT CONTROL No.	REVISION NUMBER	ISSUE DATE	RECIPIENT	DATE RETURNED
MET-001	0	7/14/98	M. Perry	11/18/99
~~MET-006~~	UNR 7/14/98			
MET-003	0	7/14/98	C. Kutzer	11/18/99
MET-001	1.0	11/18/99	M. Perry	8/5/99
MET-003	1.0	11/18/99	C. Kutzer	not found 11/2/01
MET-001	2.0	7/30/99	M. Perry	UNR 8/6/19/00
MET-003	2.0	7/30/99	C. Kutzer	11/2/01
MET-002	3.0	11/2/01	L. Reyes	
MET-003	3.0	11/2/01	C. Kutzer	

MEMO

From the QA Department

To: Department Supervisor
From: Lisa Reyes / Vicky Collom
Date:
RE: SOP Annual Review/ Newly Revised SOP

SOP for Metals Analysis by Graphite Furnace
SOP number MET-GFAA
Revision number 3
Date: 11/1/01

☐ It has been about a year since this SOP was last reviewed and it now needs to be reviewed again. Please review the SOP with your staff and complete the applicable section below.

☒ This SOP has been revised to include the changes summarized in Section 19.0. Please review this SOP with your staff and complete the section below.

☐ I have reviewed this SOP with the following personnel and it still reflects current practice.

Signature (supervisor):_____ Date:_____

We have read, understood, and agree to perform the most recent version of this SOP or test method.

Signature	Date	Signature	Date
[signature]	11/1/01		
[signature]	11-01-01		
[signature]	11/1/01		
[signature]	11/1/01		

☐ This SOP needs to be revised and updated to reflect current practices. This will be completed by _____.
(date)

Signature (supervisor):_____ Date:_____

Please indicate the outcome of your review and return this memo to me within 5 working days. Thank you for your help!!

STANDARD OPERATING PROCEDURE

TOTAL SULFUR FOR ION CHROMATOGRAPHY FOR INDIANA PINES SITE

MET-ICSPINES
Revision 0
September 23, 2004

Approved By:

_____	Supervisor	9/23/04 Date
_____	QA Manager	9/23/04 Date
_____	Laboratory Manager	9/23/04 Date

COLUMBIA ANALYTICAL SERVICES, INC.
1 Mustard Street, Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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1. SCOPE AND APPLICABILITY

This procedure is used to determine the concentration of oxidizable sulfur in a sample using peroxide digestion and ion chromatography. This SOP describes the sample preparation step for the analysis and refers to the determinative procedure used for ion chromatography. The procedure is applicable to most sample matrices including water, wastewater, soils, and miscellaneous solids. The PQL for soils is 200 mg/Kg. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

A portion of the sample is digested using a heated peroxide solution. The resulting digestate is filtered and analyzed for sulfate using ion chromatography. The sulfate result is converted to concentration of sulfur.

3. DEFINITIONS

3.1. Laboratory Control Sample (LCS): A laboratory blank that has been fortified with target analyte and used to determine that the analysis is in control.

3.2. Matrix Spike (MS) Analysis - In the matrix spike analysis, a predetermined quantity of target analyte is added to a sample matrix prior to sample preparation and analysis. The percent recovery is calculated. The MS is used to evaluate the effects of the sample matrix on the method used for the analysis

3.3. Duplicate Sample (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4. Method Blank / Preparation Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The blank is carried through the entire analytical procedure.

3.5. Batch – Up to 20 samples of the same matrix digested together on the same day.

4. HEALTH AND SAFETY WARNINGS

The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. The laboratory maintains a compilation of Material Safety Data Sheets in binders the conference room. Always wear safety glasses or a shield for eye protection, and protective clothing, and observe proper mixing when working with these reagents.

5. CAUTIONS

Boiling samples to dryness may cause combustion

6. INTERFERENCES

Samples impervious to peroxide digestion will yield results of low bias. Samples with high organic content may require additional digestions.

7. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8. EQUIPMENT AND SUPPLIES

8.1. 50ml Digestion Vessel for Hot Block

8.2. 250 mL glass beaker and ribbed watch glasses

8.3. Hotplate capable of maintaining a digestion temperature of 90-95°C.

8.4. Hot Block Digestor- Environmental Express

8.5. Filter Mate 2u filter paper and plunger for Environmental Express Digestion Vessel.

8.6. Dionex Ion Chromatograph Series 4000i, as described in GEN-300.0 SOP.

8.7. 10 N Sodium Hydroxide (NaOH): Dissolve 400g sodium hydroxide in distilled water, cool and dilute to 1 liter. Store at room temperature for up to 1 year.

8.8. 30% peroxide; purchased solution. Store at room temperature. Expires upon manufacturer's indications or in 1 year, whichever is sooner.

8.9. Laboratory D.I. water

8.10. Granular sodium sulfite, Na_2SO_3 anhydrous FW=126.04. 254390 mg/Kg (25.4%) sulfur. To be used for the LCS and for spiking the MS.

9. PROCEDURE

9.1. Sample Collection

9.1.1. Samples are to be collected in purchased, precleaned, certified sample containers – (plastic, glass, etc). Samples are to be cooled upon collection and shipment to lab.

9.1.2. The amount of sample collected should be 3 times the analytical aliquot, at a minimum.

9.2. Sample Handling and Preservation

9.2.1. Maintain samples at 0-6 °C upon receipt until analysis.

9.2.2. No specific holding time applies.

9.2.3. For further sample handling, storage, and custody procedures, see SMO-GEN.

9.3. Sample Preparation

9.3.1. Aqueous samples: Measure a 50 ml sample aliquot into a digestion vessel. Record the volume.

9.3.2. Soil samples: weigh out 0.5-5g of sample into a digestion vessel. Record the weight.

9.3.3. Add 2 drops of 10 N NaOH to each vessel, or until the sample is basic in nature.

9.3.4. Add appropriate standard to matrix spike and LCS aliquots.

9.3.5. Add 3 mL 30% peroxide to each vessel.

9.3.6. Bring each vessel to 50 ml with D.I. water.

9.3.7. Place digestion vessel in hotblock digester OR transfer contents of digestion vessel to a beaker and place on a hotplate.

9.3.8. Digest each sample until digestate is clear, or three times. Bring the volume of the digestate to ~ 5 - 10 mL each time taking care to not evaporate the samples to dryness. BOILING SAMPLE TO DRYNESS MAY CAUSE COMBUSTION.

9.3.9. Allow samples to cool. Bring soil and water samples to a final volume of 20.0 mL in the digestion vessel. Record the final volume. If particulates are present in the sample, filter using 2u FilterMate filter for Environmental Express digestion vessels. If one sample is filtered, the entire batch is to be filtered, including the MB and LCS.

9.3.10. Give the batch of samples and a copy of the digest sheet to Wetchem for analysis. Document custody transfer.

9.4. Sample Analysis

The extract is analyzed for sulfate by ion chromatography (IC) using SOP GEN-300. Refer to that SOP for specific analysis instructions.

9.5. Troubleshooting and Preventive Maintenance – Wipe down all hoods in the Metals Prep Lab once a week with DI water.

9.6. Data Acquisition, Calculations, and Data Reduction Requirements

9.6.1. The PeakNet software will multiply the solution result by any dilution made at the IC and by the final volume. Divide by the initial volume or weight.

9.6.2. The IC sulfate result will be multiplied by 0.3338 to obtain the concentration of the sulfur (S is 33.38% of SO_4 by atomic weight).

10. DATA AND RECORDS MANAGEMENT

10.1. **Responsibilities** – It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data 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 SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS v.6.11.a on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet (attached), digests the samples and turns the samples and digest sheet over to the IC analyst. The samples are analyzed for sulfate using Dionex PeakNet 5 Chromatography software and the results are transferred into the StarLIMS computer system for final calculation, validation, reporting, and invoicing.

10.3. **Data Review** - Data will be reviewed by the IC analyst and a qualified peer using a Data Review Checklist (attached to GEN-300) and validated by a supervisor.

11. QUALITY CONTROL AND QUALITY ASSURANCE

11.1. **Method Blank-**

11.1.1. Frequency - Prepare one method blank per batch of 20 samples.

11.1.2. Acceptance Criteria – The result of the method blank must be less than the reporting limit. If there is method blank contamination, samples which have results less than the reporting limit may be reported.

11.1.3. Corrective Action - If there is method blank contamination, attempt to find the source of the contamination, correct the problem, and re-digest the batch (with the exception of the samples accepted as above).

11.2. **LCS** –

11.2.1. Frequency – one per batch of 20 or fewer samples.

11.2.2. Acceptance criteria – The result of the LCS must be within 80-120% of the true value.

11.2.3. Corrective action – If the LCS is out of control limits, find and correct the problem and re-digest the batch.

11.3. **Matrix Spike** –

11.3.1. Frequency – one per batch of 20 or fewer samples of the same matrix.

11.3.2. Acceptance criteria – The result of the MS should be within 70-130% of the true value.

11.3.3. Corrective Action – If the MS is out of control limits, and the LCS is compliant, assume matrix interference and report. If the MS is out of control and the LCS is out of control, find the problem and redigest the batch.

11.4. IC QC Requirements are outlined in Section 12 of GEN-300.

12. REFERENCES

NELAC, 2002 Standard
CAS SOP for Ion Chromatography, GEN-300.

CAS - Rochester,NY: Total Sulfur for IC Digestion Log

Report Type: Routine // 6 // ASP // Pkg5

Analyst:_____ Date:_____

Prep Method: Total Sulfur for IC by Method 300

Digest: Initial // Redigest Of:_____

Spike Witness / Lot Approval: _____

Batch ID: _____

Batch Temp: _____

	Submission / Order #	pH	Initial Vol. / Wt. (ml / g)	Final Vol(ml)	Initial Color / Clarity	Final Color / Clarity	Analyte	Spike Added Vol(ml)
1							Total Sulfur/Sulfate	
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								
26								

Spiking Standards / Reagent Lot Numbers:

10 N Sodium Hydroxide (NaOH): _____

30 % Peroxide: _____

Sodium Sulfite (Na2SO4):_____

Color / Clarity Key:
Color: C = Colorless ; Y = Yellow ; B = Brown ; G = Grey
BL = Black
Clarity: CDY = Cloudy ; CLR = Clear ; OP = Opaque
Texture: F = Fine ; M = Medium ; C = Coarse ; NA = Non Aqueous

COMMENTS: _____

Metals Digestion Training Plan

Procedure:_____

SOP:_____ Revision:_____ Date:_____

Trainee:_____

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated familiarity with related SOPs
   -ADM-BATCHSEQ -ADM-PCAL -ADM-SIGFIG
   -ADM-DATAENTRY -ADM-SPSR -ADM-MDL
   -ADM-TRANDOC
   Trainer:____ Trainee:____ Date:____

3. Observe performance of SOP
   -standard and reagent prep and documentation – including pipet use and balance use and calibration, if applicable
   -digestion unit set-up
   -sample prep and reagent and spike addition
   -holding times
   -benchsheet/logbook use
   -analytical sequence, batch QC required
   -time and temperature needed to digest sample, if applicable
   -preventive maintenance and other troubleshooting
   -digestate filtering and dilution
   -digestate labelling and storage
   Trainer:____ Trainee:____ Date:____

4. I have read, understood and agree to perform the most recent version of the SOP:
   Signature:_____ Date:_____

5. Perform SOP with supervision
   - including all items in 4.
   Trainer:____ Trainee:____ Date:____

6. Independent performance of the SOP
   -all of the item listed in 4
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.
   Trainer:____ Trainee:____ Date:____

STANDARD OPERATING PROCEDURE

DETERMINATION OF SULFUR IN SOILS USING ION CHROMATOGRAGPHY AFTER ALKALINE DIGESTION FOR INDIANA PINES SITE

GEN-300Pines

Revision 0

September 24, 2004

Approved By:

Supervisor	Date: 9/24/04
QA Coordinator	Date: 9/24/04
Laboratory Manager	Date: 9/24/04

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

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Will Not Be Updated

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1 SCOPE AND APPLICABILITY

1.1 This SOP uses Method 300.0 for the analysis of sulfate by Ion Chromatography in soil samples prepared by alkaline digestion according to MET-ICS.

1.2 Range

Using the settings and calibration techniques outlined in this SOP, the upper range for sulfate is 10 ppm (solution concentration). Higher concentrations of sulfate may be determined using appropriate dilutions. Review current calibration for specific ranges.

1.3 The PQL for the current system is 0.20 mg/L

2 SUMMARY OF METHOD

Sample digested by alkaline digestion. The extract is filtered and injected into an ion chromatograph (Dionex Series 4000i). Sulfate is chromatographically separated and measured with a conductivity detector. Suppression is accomplished using an ion exchange membrane. It is assumed that all of the sulfur is converted to sulfate during the digestion. The sulfate results are converted by calculation to concentration of sulfur in the original soil sample.

3 DEFINITIONS

3.1 **Initial Calibration** - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

3.2 **Independent Calibration Verification (ICV)** - ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization. The ICV is analyzed immediately following the calibration standards.

3.3 **Relative Percent Difference (RPD)** – The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.4 Batch - Samples processed together as a unit, not to exceed 20 investigative samples.

3.5 **Method Detection Limit (MDL):** a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.6 **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

3.7 **QA/QC Samples**: Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis.

3.7.1 **Matrix Spike (MS)** - In the matrix spike analysis, predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for the analyte detected. In this method, spikes are very useful in determining proper retention times when a low concentration of an analyte is detected or expected to be adjacent to a large concentration of analyte. When a spike is used to verify retention time, calculation of recovery is not necessary.

3.7.2 **Duplicate Sample (DUP)** - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.7.3 **Continuing Calibration Verification Standard (CCV)** - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.7.4 **Instrument Blank (ICB/CCB)** - The instrument blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples (ie. not chemically preserved). The purpose of the ICB/CCB is to determine the levels of contamination associated with the instrumental analysis. The ICB is performed once, immediately after the ICV.

3.7.5 **Laboratory Control Standard (LCS)** - In the LCS or blank spike analysis, predetermined quantities of standard solutions of certain analytes are added to a blank prior to sample analysis. Percent recoveries are calculated for the analyte detected.

4 HEALTH AND SAFETY WARNINGS

- Take all appropriate safety precautions for handling reagents and samples when performing this procedure. This includes the use of personnel protective equipment, such as safety glasses, lab coat and the correct gloves.

- Handle chemicals, reagents and standards as described in the CAS safety policies, approved methods and in MSDSs where available.

- The use of pressurized gases is required for this procedure. Exercise care when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

- When releasing the cap on the suppressor reagent, wear a face shield and exercise caution. The container is pressurized and the reagent will emit a fine mist. Turn the cap slowly.

5 INTERFERENCES

5.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems. The most common examples of this are:

5.1.1 Sulfite will interfere with the sulfate peak.

5.1.2 Thiosulfate can interfere if the run time of the entire chromatogram is too short.

6 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

7 EQUIPMENT AND SUPPLIES

7.1 Analytical Balance, capable of accurately weighing to the nearest 0.0001 g.

7.2 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Dionex Ionpac AG4A-SC 4×50 mm (P/N 43175)

7.3 Anion separator column: Dionex AS14 4x250 (P/N 046124). Expires when separation between the anions of interest is no longer acceptable or upon manufacturer's indications, whichever occurs first.

7.4 Anion suppressor device: Dionex anion micro membrane suppressor (P/N 53946).

7.5 Detector-Conductivity Cell: approximately 1.25 µL internal volume.

7.6 Dionex PeakNet 5.1 Chromatography Workstation software or equivalent. Personal computer connected to network, capable of running the PeakNet software.

7.7 Calibrated MicroPipettor and tips.

7.8 Calibrated repipettor.

7.9 System configuration

An automated sampler	(Dionex P/N 39534)
An analytical gradient pump	(Dionex System 4000i)
A separator column	(Dionex AS14 4x250mm P/N 046124)
A conductivity detector	(Dionex P/N 40157)
A 50µL sample loop	
Pump rate of 2.0 mL/min	

7.10 **Standards Preparation General Information**

- Bring any cooled parent stocks to room temperature before use.
- All standards and reagents are to be tightly capped when not in immediate use. Protect standards and reagents from light whenever possible.

7.11 Reagent water: Distilled or deionized water, free of the anions of interest.

7.12 Stock Eluent solutions for AS14 column

7.12.1 0.5 M Sodium Carbonate Concentrate– Dissolve 26.49g Na2CO3 in 400 mLs DI. Bring to volume in a 500 mL volumetric flask. Expires one year. Store at room temperature.

7.12.2 0.5M Sodium Bicarbonate Concentrate – Dissolve 21.00 g of $NaHCO_3$ in 400 mL DI. Dilute to a final volume of 500 mLs with DI. Store at room temperature. Expires in one year.

7.13 Working Eluent Solution for AS 14 Column – 3.5 mM Sodium Carbonate / 1.0 mM Sodium Bicarbonate – Filter a sufficient volume of each of the 2 eluent reagents through 0.2 µm syringe filters into separate dispo cups. Pipette 7.0 mL of 0.5 M Na_2CO_3 and 2.0 mL of 0.5 M $NaHCO_3$ into a 2 Liter volumetric flask. Dilute to volume with DI. Degas for 5 minutes with ultra high purity Helium at a rate of 1-5 bubbles per second. Store at room temperature. Expires in 1 week.

7.14 Regeneration solution (micro membrane suppressor): Sulfuric acid 0.1N. Dilute 5.6 mL of conc. sulfuric acid (H_2SO_4) to 2L with reagent grade water. Degas for 5 minutes with ultra high purity Helium at a rate of 1-5 bubbles per second. This solution is stable for one week from date of preparation. Store at room temperature in plastic.

7.15 Stock standard solutions

7.15.1 Sodium Sulfate – ACS reagent grade dried at 103-105°C for 30 mins. Store dried material in a small glass beaker. Enclose the beaker in aluminum foil to protect from light. Store the covered beaker in a desiccator. Expires in one year.

7.15.2 Sulfate ($SO_4^{=}$) 1000 mg/L: Dissolve 1.479 g prepared (as above) sodium sulfate (Na_2SO_4) in reagent water and dilute to 1 L. Store at 0-6°C in amber glass for up to 1 year.

7.16 Intermediate Calibration Standards –

7.16.1 Routine Intermediate Stock – Store at 0-6°C in plastic. Expires in 6 months. Also used as LCS and MS Intermediate stock.

Analyte:	SO_4
Stock Conc (mg/L):	1000
mLs Stock:	20.0
Final Vol (mLs):	200.0
Int. Stock Conc (mg/L):	100.0

7.17 Calibration Standards - prepared in 100 mL volumetric flask as follows: record the pipette ID used in the reagent prep logbook. Make fresh weekly. Store at 0-6°C in glass or plastic.

Standard ID	mLs of Intermediate Stock	Final Volume, mLs	Working conc. SO_4 mg/L
Std # 9	10.0	100.0	10.0
Std # 8	8.0	100.0	8.0
Std # 7	5.0	100.0	5.0
Std # 6	2.0	100.0	2.0
Std # 5	1.0	100.0	1.0
Std # 4	0.5	100.0	0.50
Std # 3	0.2	100.0	0.20
Std # 2	0.1	100.0	0.10
Std # 1	0.0	100.0	0.00

7.18 Reference Standard Stocks:

7.18.1 Potassium Sulfate – ACS reagent grade dried at 103-105°C for 30 mins. Store dried material in a small glass beaker. Enclose the beaker in aluminum foil to protect from light. Store the covered beaker in a desiccator. Expires in one year.

7.18.2 Sulfate (SO_4) 3200 mg/L: Dissolve 5.80g dried (as above) K_2SO_4 in reagent water and dilute to 1 L. Store at 0-6 °C in amber glass for up to 1 year.

7.19 ICV/CCV Intermediate stock (12.8 mg/L) - Dilute 4.0 mL of 3200 mg/L reference stock to 1 Liter in a volumetric flask. Store at 0-6°C in plastic for up to 6 months.

7.20 ICV/CCV (6.4 mg/L) - prepare by diluting the CCV intermediate stock solution with equal parts water in small quantity (about 30 mLs DI and 30 mLs intermediate stock solution). The resulting concentrations are half of those of the intermediate solution. Prepare fresh when needed or at least once a week. Store at room temperature in plastic.

7.21 LCS (2.0 mg/L): Store at room temperature in glass or plastic for up to one week. Add 2.0 mLs of the intermediate stock solution (prepared same as the intermediate solution used for calibration standards) to DI in a 100 mL volumetric flask and bring to volume.

7.22 Matrix Spike Solution - Add 2.0 mL of the intermediate stock solution to 100 mL sample (or dilution of sample). Prepare fresh before use.

7.23 Consumable materials.

- 5 mL vials with filter caps. (Dionex P/N 038141)
- 0.2 µm syringe filters.

8 PROCEDURE

8.1 Calibration and Standardization-

8.1.1 Prepare calibration standards according to Section 7. Document preparation in standards log book. Load standards according to Autosampler Vial Loading Section. Start instrument and analyze according to sections below.

8.1.2 The initial calibration is made by linear regression. This method of quantitation uses the equation of a line ($y=mx+b$). The curve must not be forced through zero. System calibration must have correlation coefficient of 0.995 or better. Delete outlier standards. Standards must be within 10% of their true value. Method 300.0 requires a minimum of 3 standards and a blank. If the removal of outlier standards does not bring the curve into compliance, recalibrate.

8.1.3 Immediately after an acceptable calibration has been achieved, run the ICV, ICB, and an LCS. If these are compliant, continue with samples as described in the daily analytical sequence.

8.2 **Sample Collection** – Samples should be collected in purchased, certified clean glass or polyethylene bottles or jars.

8.3 Sample Handling and Preservation – Sulfate holding time is 28 days from collection. Samples stored at 0-6°C from receipt until analysis. Sample handling, storage, and custody procedures are in accordance with NELAC 2002 Standard.

8.4 Sample Preparation – Soil samples for Total Sulfur are digested according to MET-ICS. Further preparation of the extract is given below.

8.5 Sample Analysis –

8.5.1 **Prepare the Instrument** –

8.5.1.1 Be sure there is a current MDL and IDC for the system.

8.5.1.2 Check eluent and regenerant levels in containers. Fill to appropriate levels as necessary. Hand tighten caps of both jugs.

8.5.1.3 Remove plugs from the waste lines on the back of the instrument. Screw flow restrictor onto end of suppressor drain line (both lines are labeled).

8.5.1.4 Turn on Helium carrier gas (should be at approximately 17psi.) and compressed air (100 psi.) by turning the yellow handles to the up-down position and the small valves to IC#1. These are located along the column to the left of the computer.

8.5.1.5 Start the Dionex Gradient pump – on the bottom right half of the instrument there is a button with stop / start indicator. Press the button to light the start indicator.

8.5.1.6 Turn on the Conductivity Cell. In the middle of the instrument there is a CELL off/on indicator. Press the button to light the "on" indicator. Allow the system to warm up for about an hour.

8.5.2 Create a schedule in the PeakNet software -

8.5.2.1 While the system is warming up, determine whether an ICAL is to be run. The instruments must be calibrated if any of the following apply:

- when a new column is put in
- when system configuration changes warrant calibration
- every 6 months
- when QC samples indicate the old calibration is no longer acceptable.

8.5.2.2 Determine which samples are to be analyzed.

8.5.2.3 Remove any standards or reagents needed from the cooler and allow to warm to room temperature before use.

8.5.2.4 Create the schedule of the day's run in the software. This may be modified later as needed, but will help with initial organization.

8.5.2.5 If a calibration is not to be run – set up the schedule to analyze samples in the following analytical sequence: CCV, CCB, LCS, 10 samples, CCV, CCB, 10 samples, CCV, CCB, LCS, etc. with a CCV/CCB set after every 10 samples and an LCS after every 20 samples and DUP/MS where appropriate (at no particular position but one set for every 10 samples). Skip the initial calibration section. Prepare the samples and load the autosampler as described below.

8.5.2.6 If a calibration is to be run – set up the schedule to analyze the calibration standards, ICV, ICB, LCS, 10 samples, CCV, CCB, 10 samples, CCV, CCB, LCS, etc. with a CCV/CCB set after every 10 samples and an LCS after every 20 samples and DUP/MS where appropriate (at no particular position but one set for every 10 samples). Continue with initial calibration section.

8.5.3 **Prepare the extract for analysis**–

8.5.3.1 Draw the extract up into a 10 mL pipette. Place a 0.2 µm syringe filter on the end of the pipette and push some of the sample (only enough to make a dilution – 2 mLs is plenty) through the filter into a dispo cup.

8.5.3.2 Use the filtered extract to make an appropriate dilution.

8.5.4 Autosampler Vial Loading

8.5.4.1 Rinse all sample vials and caps to remove any debris present from the manufacture.

8.5.4.2 Once the sample or standard has been placed in the sample vial, place a vial cap in the vial and use the tool to press the cap down flush with the top of the vial.

8.5.4.3 Place the loaded vials into cassettes according to the schedule created and in compliance with the analytical sequence described below. Place the holder in the autosampler.

8.5.5 Start Instrumental Analysis

8.5.5.1 Open the run screen in the PeakNet software. Load the schedule. Select Start.

8.5.5.2 Push the "auto off-set" button on the IC unit to reset the conductivity baseline.

8.5.5.3 Press "Run" on the autosampler.

8.5.6 Evaluate sample analysis

8.5.6.1 Examine solution concentrations of target analytes in the samples. If the concentration is greater than the high calibration standard, reanalyze the sample at a dilution.

8.5.6.2 Check peak integrations.

8.5.6.2.1 Where possible, all integrations should be performed consistent with integration of the corresponding calibration standards.

8.5.6.2.2 Be sure the peaks on the chromatogram and the instrument calculated concentration make sense. Sometimes the software will attempt to integrate overrange peaks and will incorrectly assign them a concentration which would be acceptable for the dilution if it was a reasonable integration.

8.5.6.2.3 On occasion, the software integrates peaks incorrectly. The sample may be reanalyzed or the analyst may use the software to correct the integration. Any manual integration or manipulation of peaks must be consistent with the calibration standards and the QC samples.

8.5.6.3 Evaluate QC samples. All samples must be bracketed by acceptable CCVs and CCBs. See Section 10 for further discussion of QC and sample acceptance and corrective action.

8.5.7 Instrument Shut Down –

8.5.7.1 Take the daily readings. Then turn the auto offset & cell to off and the pump to stop.

8.5.7.2 Turn the gas and air off to each IC individually by turning the small valve handles perpendicular to the gas flow direction.

8.5.7.3 Vent the eluent first, leave the cap very loose, and then ASAP vent the suppressor. (Vent the suppressor by slowly opening both jugs. The

suppressor is acidic, so use care. Wear face shield and cover the jugs with a plastic bag for added protection).

8.5.7.4 Take the flow restrictor off of the suppressor drain line and plug both the eluent and suppressor drain lines.

8.5.7.5 After the last IC is shut off, turn both the gas and air yellow handles to the right.

8.6 Troubleshooting –

8.6.1 Rinsing the IC pump and valves. This should be done weekly, preferably Friday night or Saturday.

8.6.1.1 Disconnect the column from the valve. Plug the column with one of the solid plugs so that it doesn't dry out.

8.6.1.2 Attach the old column to the valve (the old column is in the IC "tool drawer" in the box on the left, behind the filters, B-cups, etc. Get the syringe then, too. It has to have the orange union fitting attached to its tip) Place the tube at the end of the column in the graduated cylinder.

8.6.1.3 Disconnect the eluent line, and plug it up, because it will continue to siphon all over you if you don't. Keep the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads.

8.6.1.4 Fill the carboy labeled "DI" about halfway with DI (rinse it once or twice first). Put the carboy back in the rack and feed the long tubing to the side of the IC. Attach the syringe to the fitting at the end of the tubing and pull the DI into the syringe to get the siphon going. When it is going, detach it from the syringe and attach it to the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads. Be sure to allow some of the water dribbling out of the DI carboy tubing to fill up any lost liquid in the brown-colored union fitting, so that you won't (hopefully) have to prime the pump.

8.6.1.5 Now you can turn on the pump. The DI should start flowing out the old column. Let it go for at least 15 minutes, after which time it can be turned off and you can go home.

8.6.1.6 As per Dionex Tech Support, this is to be done only every 6 months: While the DI is pumping through the pump & valves, lubricate the pump by opening up the pump drawer about 2 inches, exposing the pump motor housing. There is a little port in the front of the motor, with yellow grease in it. Attach the grease syringe (located in the cupboard below the IC) and squirt in 0.1 mL of grease (Dionex P/N 39440).

8.6.2 To re-configure back to operation mode:

8.6.2.1 Take off the DI carboy.

8.6.2.2 Attach the filled eluent carboy to the brown-colored union fitting after having starting the siphon, etc.

8.6.2.3 Allow the eluent to pump through the old column until you are sure that all DI has been displaced. Check with pH paper, or allow to pump >8-10 minutes.

8.6.2.4 Re-attach the valve to the guard column/analytical column.

8.6.3 Nightly: Release gas pressure in eluant/suppressor bottles and cap both waste ports. Fill in the daily log, recording Date, Column ID, Helium inlet pressure, System backpressure, Eluant pressure, Detector Background, and Reagent flow.

8.6.3.1 The incoming pressure of the Helium carrier is checked (should be approx. 17 psi.)

8.6.3.2 The system pressure is checked (usually around 1500 psi.).

8.6.3.3 The background of the detector should be around 22-24 µs.

8.6.3.4 The flow rate of the suppressor coming from the waste line should be 3-4 mL per minute.

8.6.4 Maintenance log – Document all preventive maintenance, as well as instrument repair, in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

8.7 Data Acquisition, Calculations, and Data Reduction Requirements

8.7.1 The results which are printed on the instrument report will be adjusted for any dilution made at the instrument. Further adjustment for initial weight and final volume will be made separately. The final multiplication by 0.3338 (sulfur is 33.38% of sulfate by molecular weight) will be done by StarLIMS.

8.7.2 Data will be reviewed by the analyst and a qualified peer using the Data Quality Checklist (attached) and validated by supervisor.

8.7.3 All sample data and QC data, including calibration verification must reference the name (date or filename) of the ICAL on the raw data report

8.8 Computer Hardware and Software

8.8.1 StarLIMS v.6.11.a
8.8.2 Personal Computer running Dionex PeakNet v5.1

9 DATA AND RECORDS MANAGEMENT

9.1 **Responsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data 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 SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

9.2 **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the IC analyst. The samples are analyzed for sulfate using PeakNet software. The results are printed and hand entered into StarLIMS. StarLIMS makes the final calculations and the results are printed for data review. When the results are approved, the StarLIMS is used for reporting, and invoicing.

9.3 Data Review - Data will be reviewed by the IC analyst and a qualified peer using a Data Review Checklist (attached) and validated by a supervisor.

10 QA/QC REQUIREMENTS

10.1 Laboratory Control Standards (LCS)

10.1.1 An LCS must be run daily and once every 20 samples.

10.1.2 The LCS must be within 10% of the true value.

10.1.3 If the LCS is outside the acceptance criteria stop the run, correct the problem and reanalyze the LCS. Exception: if the LCS recovery is high and sample results less than the reporting limit, analysis may continue and data may be reported.

10.2 Method Detection Limits (MDL)

MDLs should be performed every 6 months, when a new operator begins work or whenever there is a significant change in the background or instrument response. The result of the MDL must be less than the PQL. If it is not, correct the problem and do another MDL study or raise the PQL. See 40 CFR Part 136 Appendix B.

10.3 Initial and Continuing Calibration Verification (ICV/CCV)

10.3.1 An ICV is analyzed immediately after the standards. The ICV must be 90-110% of the true value or the curve may not be used.

10.3.2 A CCV is analyzed every 10 samples.

10.3.3 All CCVs must be within 10% of the true value. If the CCV is not in control, correct the problem, obtain a compliant CCV and reanalyze all samples bound by the non-compliant CCV. Recalibrate if necessary. Exception: if the CCV recovery is high and sample results are less than the reporting limit, analysis may continue and data may be reported.

10.4 Continuing Calibration Blanks (CCB)

10.4.1 A CCB must be analyzed every 10 samples immediately following the CCV.

10.4.2 All CCB's must be less than the PQL. If the CCB is above the PQL, correct the problem and obtain a compliant CCB following a compliant CCV. Reanalyze samples bound by non-compliant CCB. Recalibrate if necessary. Exception: If there is blank contamination and the sample results are less than the reporting limit, analysis may continue and data may be reported.

10.5 Matrix Spikes (MS)

10.5.1 A matrix spike must be analyzed once every 10 samples. Do not choose field blanks for the analysis of MS.

10.5.2 The matrix spike should be within the lab-generated limits of 69-120% for waters and 70-130 % for soils. If it is not, note the outlying recovery in the case narrative. If the MS is out and the LCS is in, matrix interference is assumed and the batch is acceptable. It is recommended that the MS be reanalyzed to confirm the outliers, however it is not required.

10.6 Duplicates (DUP)

10.6.1 A DUP must be analyzed every 20 samples. The DUP is regularly analyzed every 10 samples since the MS must be analyzed every 10 samples. Do not choose field blanks for analysis of DUP.

10.6.2 The acceptance criteria for a DUP is less than 20% RPD or ± the reporting limit if the sample is less than 5 times the reporting limit.

10.6.3 If a DUP is outside of the acceptance criteria, reanalyze to confirm and flag with an asterisk (estimated).

11 REFERENCES

- Method 300.0, *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA/600/R-93/100 Revised August 1993.
- Method 4110 B in *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.
- NELAC 2002 Standard
- 40CFR Part 136 Appendix B

Ion Chromatography Analysis Training Plan

Procedure:_____

SOP:_____ Revision:_____ Date:_____

Trainee:_____

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
   -column separation, retention time
   -supressor and eluent functions
   -method of detection
   -Correlation co-efficients and results based on calculated curves
   Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs

-ADM-BATCHSEQ	-ADM-PCAL	-ADM-SIGFIG
-ADM-DATAENTRY	-ADM-DIL	-ADM-SPSR
-ADM-MDL	-ADM-DREV	-ADM-TRANDOC

   Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
   -sample preparation (soil, water, other matrices)
   -standard and reagent prep and documentation – including pipet(s) used
   -IC start-up and warm-up procedures
   -software use, entering sample IDs in analytical sequence
   -sample dilution guidelines (1/10 or more unless F, OPO4; 1/50 or more for leachates; other nasties; use of historical data)
   -holding times
   -use and loading of vials (filter if necessary, no air in tubes)
   -use and loading of autosampler
   -sample analysis including:
      -calibration
      -software command of instrument
      -recognition of normal vs. abnormal peaks
         -linear range
         -manual integration
      -use of QC samples and QC criteria
   -IC instrument logbook use
   -data reduction, reporting, and review
   Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

   Signature:_____ Date:_____

6. Perform SOP with supervision
   - including all items in 4.
   Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
   -all of the item listed in 4
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.
   Trainer:____ Trainee:____ Date:____

Columbia Analytical Services, Inc.
An Employee-Owned Company

WET CHEMISTRY
DATA QUALITY CHECKLIST

Analysis:_____

Date: _____

Yes	No	NA			Yes	No	NA
☐	☐	☐	1.	**Holding Times** met method requirements?	1. ☐	☐	☐
☐	☐	☐	2.	**ICAL** met method requirements?	2. ☐	☐	☐
☐	☐	☐	3.	**ICV** acceptable?	3. ☐	☐	☐
☐	☐	☐	4.	**CCVs** acceptable? Analyzed per 10 samples?	4. ☐	☐	☐
☐	☐	☐	5.	**CCBs** acceptable? Analyzed per 10 samples?	5. ☐	☐	☐
☐	☐	☐	6.	**Method Blank** results <RL?	6. ☐	☐	☐
☐	☐	☐	7.	**LCS** recoveries within QC limits?	7. ☐	☐	☐
☐	☐	☐	8.	All reported sample **concentrations within LR**?	8. ☐	☐	☐
☐	☐	☐	9.	**MS** recoveries within QC limits?	9. ☐	☐	☐
☐	☐	☐	10.	**Duplicate** RPD within QC limits?	10. ☐	☐	☐
☐	☐	☐	11.	**Dilution factors** verified and calculated correctly?	11. ☐	☐	☐
☐	☐	☐	12.	**Bench Sheet** complete, initials, date, and time:	12. ☐	☐	☐
☐	☐	☐		•Are standards and reagents **traceable**?	☐	☐	☐
☐	☐	☐		•Is **unused space** on the sheet crossed out?	☐	☐	☐
☐	☐	☐		•**Pipette ID** referenced?	☐	☐	☐
☐	☐	☐	13.	**All applicable Log Books** filled in?			
			14.	**Manual data entry to LIMS correct? Date? Time?**	14. ☐	☐	☐

Analyst:_____ Peer Review:_____

Date:_____ Date:_____

COMMENTS:
****Comments must be provided for any items noted above as "No"**

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

for

The Determination of Method Detection Limits

SOP Code: ADM - MDL

Revision: 5

August 1, 2003

Approved by: Lawrence V Jacoby — Quality Assurance Director — 8/1/2003 — Date

Chief Quality Officer — 8/1/03 — Date

Steve Lucent — President — 8/1/2003 — Date

1317 South 13th Avenue
Kelso, Washington 98626

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

Standard Operating Procedure for The Determination of Method Detection Limits

1.0 PURPOSE

This standard operating procedure (SOP) documents the procedure for the determination of method detection limits (MDLs).

2.0 APPLICABILITY

The procedure described in this SOP is designed for applicability to a wide variety of sample types ranging from reagent (blank) water or wastewater containing the analyte to solids (such as soil) containing the analyte to the analyte in a gaseous matrix. The MDL for an analytical procedure will vary as a function of sample matrix. This SOP requires a complete, specific, and well-defined analytical procedure. It is essential that all sample-processing steps of the analytical procedure are included in the deter-mination of the MDL; that is, all the steps that a sample is processed through, from sample preparation to analytical completion, must be included in the MDL determination. The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample. This SOP for the determination of MDLs was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device or instrument-type independent.

3.0 DEFINITIONS

3.1 Method Detection Limit (MDL)

The MDL is the minimum concentration of a substance or analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

3.1.1 The Calculated MDL (MDL_C) is the MDL as calculated in Section 6.10 and will typically contain two or more significant figures.

3.1.2 The Reported MDL (MDL_R) is the MDL that is used for reporting purposes. MDLs for organic analytes will be reported with two significant figures.[1] MDLs for inorganic analytes will be reported with either one or two significant figures depending upon the number of significant figures in the analytes' MRL.[2]

3.2 Analytical Procedure

The written, step-by-step description of the operation by which samples are processed in order to obtain the concentration of an analyte in a sample.

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[1] Organic analyte MDLs: see Section 6.3.2 in Reference 9.2.
[2] Inorganic analyte MDLs: see Section 6.4.2 in Reference 9.2

3.3 Spike Level

The spike level is the known concentration of analyte that is added to a matrix for the determination of the MDL.

3.4 Interferences

Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of known or unknown species (interferent) that hinder an accurate analysis of the target analyte(s).

3.5 Matrix[3]

3.5.1 When the matrix analyzed is aqueous (includes ground water, surface water, waste water, drinking water, etc.), analyte-free reagent water is to be used. When the matrix analyzed is solid (includes soil, sand, tissue, or other solid materials), analyte-free soil, sand, tissue, or a suitable material is to be used. When the matrix analyzed is gaseous (i.e., air or emissions), an analyte-free, inert gas (such as zero-grade air or ultrapure helium or nitrogen) is to be used.

3.5.2 If the analysis is performed on a matrix for which there is not available an appropriate or similar, analyte-free matrix (such as, metals analysis on soil samples), the MDL analysis will be done as prescribed by the SOP for the analysis except the sample (weight) will be omitted; that is, the analysis will be done on all the reagents but without addition of any sample.

4.0 DISCUSSION

The MDL is a property of the analytical procedure, sample matrix, and measurement system (e.g., an instrument if one is used in the analytical procedure). The MDL is a statistic. It is an estimate that includes both the systematic and random errors that are an inherent part of the analytical procedure. The MDL for a given analyte will be unique for the sample's matrix and may be different than the MDLs shown in published methods. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

The relative uncertainty of an analytical measurement increases as the measured value approaches the MDL and at the MDL the uncertainty in the measured value may be 100% or greater.

[3] For a list of matrices, see Section 3.3 in Reference 9.3

Regarding Method Proficiency, in Chapter One of the Third Edition of SW-846 (as updated) it states:

> *Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit (MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.*

This SOP is based upon the procedure described in *40 CFR Part 136*, *Appendix B* (Reference 9.1).

5.0 RESPONSIBILITIES

It is the responsibility of the laboratory manager, working with the quality assurance program manager (QA PM) and department managers and supervisors, to schedule MDL determinations as they come due. It is the responsibility of the QA PM to track the status of MDLs. Completed MDL determinations are to be reviewed by the QA PM and approved by the laboratory manager and/or the QA PM before they are implemented. The QA PM is responsible for maintaining the MDL file described in Section 8.0.

6.0 PROCEDURE

6.1 General Requirements

6.1.1 MDLs are to be determined for each analyte and for each matrix. This SOP describes procedures for determining MDLs for the generic matrices aqueous, solid, and gaseous. MDLs for specific matrix types may be adapted from the procedures in this SOP. See Section 3.5.1.

6.1.2 All sample processing steps in the analysis procedure shall be included in the determination of the MDL. MDLs shall be generated for all preparatory and cleanup procedures routinely used on samples.

6.1.3 An MDL study is required for PCB Aroclors 1016 and 1260 only; i.e., it is not necessary to perform an MDL study for all the PCB Aroclors, unless required by specific clients or accreditation programs.

6.1.4 An MDL study is not required for any analyte for which spiking solutions or quality control samples are not available; e.g., temperature.

6.2 Frequency of MDL Determination

6.2.1 An MDL study shall be determined initially; i.e., when the procedure is first put into production. An MDL study may also be done as part a procedure's training requirements.

6.2.2 An MDL study shall be performed at the frequency specified in the applicable method or as specified by an accrediting authority. For example, some state accrediting programs require annual MDL studies.

6.2.3 If an MDL study is not performed annually, an MDL verification check shall be performed quarterly[4] on every instrument used to perform a particular analysis. The MDL verification check sample is spiked at approximately two times the current MDL. The MDL verification check sample shall be acceptable if it produces a response that is at least three times above the instrument's noise level. If the MDL verification check fails, additional MDL verification checks shall be performed at a higher level to set a higher MDL, or a new MDL study shall be performed.

6.2.4 A new MDL determination is to be performed "…each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation occurs that affects the sensitivity of the analysis."[5]

6.3 Estimation of the MDL

Use one of the following guides to help estimate the MDL.

6.3.1 The concentration value that corresponds to an instrument signal-to-noise ratio in the range of 2.5 to 5.

6.3.2 The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

6.3.3 That region of the calibration curve where there is a significant change in sensitivity, i.e., a break in the slope of the calibration curve.

6.3.4 Instrumental limitations.

---

[4] The quarterly MDL verification checking procedure is based on the procedure in Reference 9.7, Section D.1.4, Clarification Box D-12.

[5] See Reference 9.6, Section D.1.2.c) and Reference 9.7, Section D.1.4.c).

6.4 Aqueous Blank MDLs

6.4.1 Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at or above the MDL of each analyte of interest.

6.4.2 Prepare a minimum of 7 (preferably 8 to 12) analyte-spiked reagent water samples at a concentration that is 3 to 5 times the estimated MDL from Section 6.3.

6.4.3 Analyze the analyte-spiked reagent water samples prepared in Section 6.4.2 by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure with the final results reported in the same units as used for water samples.
Proceed to Section 6.10.

6.5 Aqueous Sample MDLs

6.5.1 Analyze the aqueous sample by processing it through the **entire** analytical procedure.

6.5.2 Calculate the analyte concentration.

6.5.2.1 If the measured concentration of the analyte is in the recommended range of 3 to 5 times the estimated MDL from Section 6.3, proceed to Section 6.5.3.

6.5.2.2 If the measured concentration of the analyte is less than the recommended 3 to 5 times the estimated MDL, add a known amount of analyte to bring the concentration of analyte between 3 to 5 times the estimated MDL and proceed to Section 6.5.3.

6.5.2.3 If the measured concentration of the analyte is greater than 5 times the estimated MDL, either obtain another sample with a lower concentration of analyte in the same matrix, or the sample may be used as is for determining the MDL if the analyte concentration does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical procedure changes as the analyte concentration increases from the MDL; hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations. Proceed to Section 6.5.3.

6.5.3 Prepare and analyze a minimum of 7 (preferably 8 to 12) aliquots of the aqueous sample by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure

with the final results reported in the same units as used for water samples. Proceed to Section 6.10.

6.6 Solid Blank MDLs

6.6.1 Prepare a solid material (e.g., soil, sand, tissue, Na_2SO_4, Teflon chips, or other appropriate material) that is free of analyte.

6.6.2 Prepare a minimum of 7 (preferably 8 to 12) analyte-spiked solid samples at a concentration that is 3 to 5 times the estimated MDL from Section 6.3. The same weight of analyte-spiked solid is substituted for the sample weight in the analytical procedure.

6.6.3 Analyze the analyte-spiked solid samples prepared in Section 6.6.2 by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure with the final results reported in the same units as used for solid samples. Proceed to Section 6.10.

6.7 Solid Sample MDLs

6.7.1 Analyze the solid sample by processing it through the **entire** analytical procedure.

6.7.2 Calculate the analyte concentration.

6.7.2.1 If the measured concentration of the analyte is in the recommended range of 3 to 5 times the estimated MDL from Section 6.3, proceed to Section 6.7.3.

6.7.2.2 If the measured concentration of the analyte is less than the recommended 3 to 5 times the estimated MDL, add a known amount of analyte to bring the concentration of analyte between 3 to 5 times the estimated MDL and proceed to Section 6.7.3.

6.7.2.3 If the measured concentration of the analyte is greater than 5 times the estimated MDL, either obtain another sample with a lower concentration of analyte in the same matrix, or the sample may be used as is for determining the MDL if the analyte concentration does not exceed 10 times the MDL of the analyte in soil. The variance of the analytical procedure changes as the analyte concentration increases from the MDL; hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations. Proceed to Section 6.7.3.

6.7.3 Prepare and analyze a minimum of 7 (preferably 8 to 12) aliquots of the soil sample by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure with the final results reported in the same units as used for solid samples.
Proceed to Section 6.10.

6.8 Gaseous Blank MDLs

6.8.1 Using an appropriate sample container (e.g., Tedlar® bag or SUMMA® passivated canister) and appropriate analyte-free inert gas (such as zero-grade air or ultrapure nitrogen), prepare a minimum of 7 (preferably 8 to 12) analyte-spiked inert gas samples at a concentration that is 3 to 5 times the estimated MDL from Section 6.3.

6.8.2 Analyze the analyte-spiked inert gas samples prepared in Section 6.8.1 by processing them through the **entire** analytical procedure. Make all computations according to the directions in the analytical procedure with the final results reported in the same units as used for air samples. Proceed to Section 6.10.

6.9 Rejection of Replicate Sample Results

6.9.1 A replicate sample result may only be rejected if there is an assignable cause for not using that result. Assignable causes include, but are not limited to, replicate sample preparation error, instrument malfunction, bad injection or purge, and internal standard(s) missing or response uncharacteristically high or low. The cause for rejecting the replicate sample result must be documented in the MDL data package.

6.9.2 For multi-analyte analyses, if a replicate sample result is rejected for an assignable cause, results for all the analytes from that sample are to be rejected; that is, "picking and choosing" analyte results from a sample is not permitted.

6.10 Calculation of MDL_C

6.10.1 Determine the standard deviation, *s*, of the replicate sample results.

$$s = \sqrt{\frac{\sum_{n=1}^{i} (x_i - \bar{x})^2}{n - 1}}$$

where $\bar{x} = \frac{\sum_{n=1}^{i} x_i}{n}$

6.10.2 Multiply the standard deviation obtained in Section 6.10.1 times the appropriate one-sided 99% Student's t-statistic, which is found in the following table.

$MDL_C = s_x$ {appropriate Student's t-statistic}

No. of Samples (n)	Student's t-statistic	Degrees of Freedom (n - 1)
7	3.143	6
8	2.998	7
9	2.896	8
10	2.821	9
11	2.764	10
12	2.718	11
13	2.681	12
14	2.650	13
15	2.624	14
16	2.602	15
17	2.583	16
18	2.567	17
19	2.552	18
20	2.539	19
21	2.528	20

6.11 Determination of MDL_R

The Reported MDL (MDL_R) is the calculated MDL rounded **up** to the appropriate number of significant figures. See Section 3.1.2.

6.12 Evaluation of the Quality of the MDL Study

The quality of the MDL is evaluated using the following criteria.

6.12.1 Spike Level The spike level is **too low** if the MDL_C is greater than the spike level. The spike level is **too high** if the spike level is greater than ten times the MDL_C.

6.12.2 Percent Relative Standard Deviation (%RSD) The %RSD should be some value close to 20, where the %RSD is equal to the standard deviation (s) divided by the average of the spike recoveries times 100. [%RSD = ($s \div \bar{x}$) 100]

6.12.3 Percent Spike Recovery The spike recovery should be approximately what is to be expected for that analyte from the analytical procedure; i.e., a 40% spike recovery for an analyte is too low if the method normally recovers 80% or more for that analyte.

6.12.4 MDL Quality The criteria in Section 6.12.1 must be true. At least one of the criteria in Sections 6.12.2 and 6.12.3 should also be true. If the MDL_C does not meet these criteria, then the study should be repeated, adjusting the spike level appropriately.

6.13 Instruments

If more than one instrument is used for the same analytical procedure, the replicate samples should be analyzed on each instrument to ensure there is no instrument bias. Under some specific customer contracts and for some programs (such as the Navy's Installation Restoration program), instrument-specific MDLs are required. There are two options for complying with this requirement:

1. Analyze the replicate samples on each instrument used for the analytical procedure and calculate the MDL_C for each instrument. The MDL_R will be the largest of the several MDL_C's; or

2. Analyze the replicate samples on each instrument used for the analytical procedure and calculate a single MDL_C using all the values from each instrument. A minimum of five values is needed from each instrument. For example, if two instruments are used, there would be a minimum of two times five or ten values to be used to calculate the MDL_C. Make sure to use the appropriate Student's t-statistic that corresponds to the number of values used to calculate the standard deviation. Note: This option may not be acceptable under some specific customer contracts or for some programs, such as the DOD quality systems for environmental laboratories.[6]

6.14 Review and Approval

Completed MDL determinations are to be reviewed by the supervisor of the analysis. The QA PM will review and approve the MDL determination before it is implemented.

[6] See Reference 9.7, Section D.1.4.

6.15 Department of Defense (DoD) Requirements[6]

6.15.1 An MDL verification check shall always be performed immediately following an MDL study. DoD requires that the MDL check sample be spiked at approximately 2 times the current reported MDL.

6.15.2 If an annual MDL study is not performed, MDL verification checks shall be performed quarterly. If the quarterly MDL verification check fails, additional MDL verification checks shall be performed at a higher level to set a higher MDL, or the MDL study shall be reconducted.

6.15.3 For DoD, the MDL verification check sample shall be acceptable if it produces a response that lies at least 3 times above the instrument's noise level.

7.0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

7.1 Replicate Samples

No fewer then **7** replicate samples can be used; **8** to **12** replicate samples is preferred.

7.2 Analysis of the Replicate Samples

The replicate samples do not have to all be analyzed in the same analytical batch on the same day. In fact, it is preferred to spread out the replicate samples among several analytical batches analyzed on several days (to increase the contribution of the day-to-day variability). Furthermore, it is recommended that at least one MDL spike be routinely analyzed monthly and data accumulated and calculated at a later time.

7.3 MDL Quality

The MDL determination must meet the criteria in Section 6.12. If the MDLs from more than one instrument are combined as in Section 6.13, the combined MDL must meet the criteria in Section 6.12.

7.4 Matrices

MDLs shall be generated for all applicable matrices. See Section 6.1.1.

7.5 Preparatory and Clean-up Procedures

MDLs shall be generated for all preparatory and clean-up procedures routinely used on samples. See Section 6.1.2.

8.0 RECORDS

The data for the MDL determination is summarized in a table similar to the one shown in Figure 1. An Excel spread sheet similar to Figure 1 is available for this purpose. This summary and the reference to the location of the raw data are to be filed in a readily available file of MDLs. This file is to be located both in the department performing the analytical procedure and in a centralized location for MDLs from the entire laboratory. Also shown in Figure 1 are two examples illustrating how MDL data is to be summarized.

9.0 REFERENCES

9.1 *40 CFR Part 136, Appendix B*, Definition and Procedure for the Determination of the Method Detection Limit--Revision 1.11.

9.2 *SOP for Significant Figures*, ADM-SIGFIG.

9.3 *SOP for Sample Batches*, ADM-BATCH.

9.4 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, Third Edition, September 1986 and as amended by Updates I, II, IIA, IIB, III, and IIIA.

9.5 *Standard Methods for the Examination of Water and Wastewater*, APHA/AWWA/WEF, 19th Edition, 1995, Method 1030E; 20th Edition, 1998, Method 1030C.

9.6 National Environmental Laboratory Accreditation Conference (NELAC), Quality Systems Standard, Appendix D, Section D.1.2.

9.7 Department of Defense *Quality Systems Manual for Environmental Laboratories*, Final Version 2, June 2002, Appendix D, Section D.1.4.

10.0 CHANGES FROM PREVIOUS REVISION

- Section 3.1.1 Section 6.10 cross reference corrected
- Section 3.3 Corrected Section number
- Section 3.4 Corrected Section number
- Section 3.5 Corrected Section number
- Section 3.5.1 Changed matrices to generic matrices aqueous, solid and gaseous
- ★ Section 6.1 Section completely revised
- ★ Section 6.2 New section – causing subsequent sections to be renumbered and section cross-references to be revised
- Sections 6.3 through 6.15 Sections renumbered and internal cross references updated
- Section 6.4 "Water" changed to "Aqueous" to be consistent with Section 3.5.1
- Section 6.5 "Water" changed to "Aqueous" to be consistent with Section 3.5.1
- Section 6.7 "Soil" changed to "Solid" to be consistent with Section 3.5.1
- ★ Section 6.12.1 MDL_R changed to MDL_C
- ★ Section 6.12.4 MDL_R changed to MDL_C
- Section 6.13 "Navy's Installation and Restoration program" changed to "DOD quality systems for environmental laboratories" at end of paragraph 2.
- Section 7.4 Cross reference changed to Section 6.1.1
- Reference 9.7 Updated

Figure 1

MDL Determination Summary

Analytical Method: 8270C Instrument: SVM GC/MS No. 03
Extraction/Digestion Method: 3520C
Matrix: Water / ~~Soil~~ / ~~Air~~ Units: ug/L (ppb)
Analyst(s): I. M. Good Approved by: _____ Date: _____

Date Analyzed			1/2/03	1/2/03	1/9/03	1/9/03	2/4/03	2/4/03	2/4/03	2/9/03	2/9/03	3/1/03								
Instrument Identification			03	03	03	03	03	03	03	03	03	03								
Analyte	Low Std	Spike Level	1	2	3	4	5	6	7	8	9	10	11	12	Mean	Std Dev	%RSD	MDL_C	**MDL_R**	NOTES
NPTH[1]	20	5.0	4.1	4.8	5.2	5.9	4.9	5.1	5.0	4.5	4.8	5.6			5.0	0.51	10	1.45	**1.5**[3]	
PCP[2]	50	10	6.1	4.8	5.2	4.5	5.8	4.7	4.1	5.1	6.0	4.0			5.0	0.75	15	2.12	**2.2**[3]	

[1] Naphthalene [2] Pentachlorophenol [3] Since these are organic analytes, the MDL is rounded up to two significant figures, per Section 3.1.2.

STANDARD OPERATING PROCEDURE

SAMPLE RECEIVING

SMO-GEN

Revision 2
December 8, 2004

Approved By: _____ _____
Supervisor Date

_____ _____
QA Coordinator Date

_____ _____
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed
and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

1 SCOPE AND APPLICATION

This Sample Management SOP provides a key foundation to the SMO department. It explains the process of receiving samples and the steps that lead to the distribution of samples throughout the lab. By implementing an organized and thorough approach to the initial stages of the process, we can maintain an efficient and well-documented account of the samples status and condition.

2 METHOD SUMMARY

The process of receiving and distributing samples is outlined in this SOP. Upon receipt, a CR/PF is completed for each cooler. The sample information is logged into the LIMS database and then broken-down and distributed within the lab.

3 DEFINITIONS

SMO	Sample Management Office
PM	Project Manager
CR/PF	Cooler Receipt & Preservation Form
QA/QC	Quality Assurance / Quality Control
LIMS	Laboratory Information Management System
COC	Chain of Custody
BREAKDOWN	The act of removing samples form coolers, labeling the samples, checking preservations, and distributing them to the correct destinations.
LOG-IN	Entering the information from the COC, CRPF, and the specifics of the job into the LIMS
MATRIX	The physical form of a sample. (water, oil, soil, solid, air)
NELAC	National Environmental Laboratory Accreditation Conference

4 INTERFERENCES

To avoid errors during log-in, detailed information shall be obtained from clients to complete chain of custody documentation.

5 SAFETY

5.1 The characteristics of incoming samples are often unknown. Treat all samples as potentially hazardous. SMO has first contact with samples and must be especially cautious.

5.2 All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.3 Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

5.4 Hydrochloric and Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

5.5 Refer to the Safety Manual for further discussion of general safety procedures and information.

6 SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

Sample preservation and storage are discussed as part of the procedure later in this SOP.

7 APPARATUS AND EQUIPMENT

- Infrared or digital thermometer – calibrated and maintained as per ADM-DALYCK.

8 PREVENTIVE MAINTENANCE

Not Applicable

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 The following reagents are purchased commercially, stored at room temperature and expire upon manufacturer's indications or 3 years from receipt if no other indication is given:

Sulfuric Acid; Instranalyzed grade
Nitric Acid; Instranalyzed grade
Hydrochloric Acid; Instranalyzed grade
Sodium Hydroxide; Lab grade

9.2 Consumable materials:
PH indicator Paper
Potassium-Iodide Starch Paper for detection of residual chlorine

10 RESPONSIBILITIES

It is the responsibility of the analyst to receive samples according to this SOP and to complete all documentation required.

11 PROCEDURE

11.1 SAMPLE ACCEPTANCE POLICY

11.1.1 The laboratory's sample acceptance policy outlines the circumstances under which samples shall be accepted or rejected. This information is made available to the sampler by an instruction sheet that accompanies each bottle set sent to the client (attached).

11.1.2 The samples received need to conform to the following acceptance criteria as per NELAC:

- Proper, full, and complete documentation (COCs), which shall include sample identification, the location, date and time of collection, collector's name, preservation type, sample type and any special remarks concerning the sample;
- Proper sample labeling to include unique identification and a labeling system for the samples with requirements concerning the durability of the labels (water resistant) and the use of indelible ink;
- Use of appropriate sample containers;
- Adherence to specified holding times;
- Adequate sample volume. Sufficient sample volume must be available to perform the necessary tests; and
- Procedures to be used when samples show signs of damage, contamination, and inadequate preservation.

The above criteria are addressed in the rest of this section. In the event of an unacceptable sample, the Project Manager is notified and they will contact the client or recommend a proper course of action. Any data from samples which do not meet the acceptance policy must be written up in the case narrative in the report.

11.2 PROCEDURES FOR SAMPLE RECEIPT

11.2.1 The CAS Cooler Receipt and Preservation Form (CR/PF) (attached) is used for the next steps to document the condition of the samples and coolers as per the Acceptance Policy.

11.2.2 Upon receipt, the coolers are examined for presence and condition of custody seals, locks, shipping bills, etc. The shipping labels are removed and placed on scrap paper and added to the receiving paper work.

11.2.3 The coolers are opened and examined for any existing hazards before subsequent processing.

CAUTION: *If samples exhibit any strong odors, or samples have been damaged, move cooler to the hood and continue processing per client.*

11.2.4 Chain of Custody (COC) forms (attached) and any other documents are located, removed and signed with date & time as received. Visually scan the COC for short holding time samples.

11.2.5 The temperature of the cooler is measured following the guidelines in this SOP. The acceptance criteria for samples is 0-6°C. If a cooler exhibits a temperature greater than 6°C, or exhibits any other anomalies (deviations from the Acceptance Policy), the anomalies are noted on the CR/PF and the CR/PF is placed on top of the COC packet.

11.2.5.1 Samples which are hand delivered immediately after collection (delivered within 4 hours of sampling) may not have had time to cool. The samples are considered acceptable by NELAC if there is evidence that the chilling process has begun. Document the presence of ice on the CR/PF with a note about the 4-hour rule.

11.2.6 Once the coolers are initially examined and observations and temperature are recorded, all of the COCs with corresponding CR/PF forms and shipping labels are submitted for review to the appropriate Project Manager. (The receiving paper work is comprised of at least 3 pages; the COC, a CR/PF, and a shipping label).

11.2.7 Rush requests and samples with short holding times are always given top priority for initial processing. CAS follows EPA guidelines for preservation and holding time as outlined in our QA/QC manual Table 7-1. A list of short holding time parameters are attached to this SOP. An additional list of holding times may be found in SMO-BPS. If short holding time samples need to be distributed immediately (before log-in and labeling), distribute the samples with the attached form for Internal Tracking. Write all short holding time samples on the white board in Wetchem.

11.2.8 In the down time between receiving and actual breakdown of samples, the coolers are stored in the SMO walk-in cooler, which also maintains a temperature of 0-6°C.

11.3 LOG-IN/LIMS

11.3.1 At log-in, the Project Manager enters the entire job into the LIMS system. The job is given a submission number, which consists of the lab location, year, and a unique sequential number. (R20-1508)

11.3.2 Each sample is given a unique order number during log-in. This number is unique to a given location or sample site. A single sample site may consist of many bottles according to the analyses requested. The individual bottles within an order number are uniquely identified with the use of a bar code placed on the bottles during sample breakdown. See SMO-ICOC.

11.3.3 COC's are returned to SMO after the Project Manager has approved all anomalies (See ADM-PCR) and entered the job into the LIMS database. At this point, the jobs are approved for breakdown.

11.4 SAMPLE BREAKDOWN

11.4.1 Sample containers are removed and organized according to chain of custody identification and analysis.

11.4.2 The following verifications are made as to the agreement of chain of custody information as it applies to samples and containers received:

- Sample identification, time, date
- Number of containers received
- Matrix
- Correct bottles for analysis requested.
- Correct sample volume for analysis
- Correct preservatives for analysis – according to the labels. The actual preservation will be tested as below.

Any discrepancies are reported to the Project Manager. Tests may be added or deleted so that LIMS matches the actual samples received. See the discrepancies section of this SOP (i.e. jobs can not have tests scheduled when the sample containers do not exist.)

11.4.3 Labels are printed from the LIMS database and placed on the sample containers.

11.4.4 Barcodes are generated which are unique to each container for the purpose of sample tracking. VOA bags receive one barcode and each vial within the bag must be labeled with a different number (if not already done so when preparing the bottle set)

11.4.5 Preservations are checked on the appropriate samples and recorded on the job paperwork, the preservation check log, and preservative lot numbers are recorded on the front page of the paper work (the Analytical Request).

11.4.6 To check the preservation, place a small piece of pH test paper in a dispo-cup and pour a small aliquot of the sample into a dispo-cup. Observe the color of the paper and compare to the colors on the paper dispenser to determine the pH. The preservation of samples should be as below:

HCl, HNO_3, H_2SO_4 pH < 2
NaOH pH > 12
PCB 608 pH 5-9

If the sample was not sufficiently preserved, notify the Project Manager to determine whether more preservative should be added.

11.4.7 To check the chlorine residual, place a small piece of starch paper in a dispo-cup and pour a small aliquot of the sample into a dispo-cup (this may be done on the same aliquot used to test pH). If the paper turns blue there is chlorine residual present in the sample. Note the discrepancy on the CR/PC and notify the Project Manager. The Project Manager may contact the client to determine if ascorbic acid should be added to eliminate the chlorine residual.

11.4.8 The CR/PC form is finished by the person who broke down the job.

11.4.9 All of the jobs are reviewed for completeness at the end of the day (or the following morning), and the walk-in cooler temperatures are logged into a temperature logbook.

11.5 SAMPLE DISTRIBUTION

11.5.1 After a job is labeled, the samples are distributed to the appropriate department. The samples are scanned into the appropriate storage areas as listed below.

11.5.2 CAS-Rochester currently maintains 3 walk-in coolers to refrigerate samples. Extractables share a cooler with Metals, VOAs have a cooler, and WetChem shares the cooler with SMO. Metals are maintained at room temperature and are placed on a dedicated cart in the metals department. Mercury and TCLP samples are placed in the Metals/Extractables cooler. SMO is responsible for documenting the location of the Wetchem samples in the Wetchem/SMO cooler.

11.6 SAMPLE SECURITY AND STORAGE:

11.6.1 Bar-coding is used as a means of sample tracking. Custody is maintained according to SMO-ICOC.

11.6.2 The sample coolers are secured with locks, which can be accessed by technical laboratory personnel, project managers, administrative support personnel and all senior staff members. All of the sample storage facilities are located in our building which is a secured area. Storage areas are kept clean and dry to avoid any damage or deterioration of samples while in storage.

11.6.3 Samples are held in refrigerators (if applicable) until analysis is completed and reported to the Client. Routine samples are typically held for 30 days after mailing of report and CLP samples are stored for 90 days after report has been mailed.

11.6.4 Refrigeration is maintained at a temperature of 0-6° Celsius.

11.7 DISCREPANCIES

11.7.1 Any discrepancies or concerns such as non-matching identifications, missing samples, and tests not scheduled correctly are to be verbally communicated to the Project Manager. Any action taken is recorded on the COC and/or cooler receipt form, "as per" Project Manager. The Project Manager will make any contact to the client when they deem it necessary. If a Chain of Custody is not received, the Project Manager is informed and a CAS COC is filled out.

11.7.2 In the event of broken samples, a note is entered on the Chain of Custody and/or the CR/PF accompanying the samples. Information pertaining to the sample is forwarded to the Project Manager for follow up purposes. Cleanup procedures are as follows:

- Liquids: Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box. The liquid is disposed of in the SMO sink or under a hood if strong odors are evident. Any packing material is disposed of appropriately.

- Soils: The same documentation as liquids applies. Broken glass is disposed of in the Glass Disposal Box and the soil is disposed of into the garbage.

11.8 RECEIVING SAMPLE COOLERS ON WEEKENDS OR AFTER HOURS

11.8.1 The date received is the date on which the Laboratory Personnel takes possession of the samples. The client shall sign the COC as relinquished and the CAS employee shall sign in the adjacent box as received. If an employee outside of the SMO department receives the samples, the coolers or samples

are stored in a locked walk-in cooler and all paperwork is left on the lab bench in SMO for login the next working day.

11.8.2 If the samples are received by SMO staff but the samples cannot be processed through the complete log-in procedure on the date received, the receiving procedure is performed as outlined in 11.1 and 11.2. Then SMO needs to check for short holding time samples. Short holding time tests are posted in breakdown. Most of the tests have holding times of 48 hours which means samples received on Saturday need to be run before Monday. Any cooler integrity issues shall be handled on the next business day, but the samples need to be tested so that holding times are maintained. To maintain an organized system, notes are indicated on the COC and on the white board in Wetchem as to which samples have been sent for analysis. Use the attached form for Internal Tracking of Short holding time samples.

11.9 SAMPLE SHIPPING TO SUBCONTRACT LABS

11.9.1 The sample is logged in and the test code for subcontracted analysis is assigned.

11.9.2 For CAS Network Labs: Subcontracted samples are shipped to the network lab with a copy of the Internal Service Request form (ISR) and copy of the COC. The tests being subcontracted must be highlighted and the number of containers adjusted or a new COC is completed.

11.9.3 For other labs: A purchase order (PO) is filled out for work going to another contract laboratory. TAT, deliverables, etc. should be clearly specified. A new Chain of Custody form is filled out with the pertinent information so the samples can be analyzed in a fashion that meets the client's needs.

11.9.4 Samples are prepared for shipping by packing in bubble wrap, and ice. Temperature blanks, and the chain of custody are placed in shipping coolers. Custody seals are signed and dated and placed on the front of the cooler. The cooler is then sealed with packaging tape and shipped overnight through the courier system (confirm with Project Manager for am or pm delivery requirements).

11.10 THERMOMETER MEASUREMENTS

11.10.1 Unless unavailable, measure the cooler/sample temperature of an incoming cooler with the Infrared (IR) thermometer. Turn on the thermometer and point it at the temp blank or a sample (preferably clear glass or amber glass). Wipe the container with a dry paper towel. Hold the thermometer approximately 3-6 inches from the container and at least 3 inches above the counter. Temperature is rounded to the nearest whole number and recorded to the nearest whole

number on the cooler receipt form and COC. This method is preferred to the digital thermometer method.

11.10.2 If the IR thermometer is not available, a digital thermometer may be used. Place the thermometer in the temperature blank or plunge it into the packing material or place it as deep into the cooler as is practical with the lid closed. Allow to equilibrate 5 minutes. After measurement, the temperature is recorded to the nearest whole number in the appropriate space on the cooler receipt form and COC.

12 QA/QC REQUIREMENTS

12.1 Not Applicable

13 DATA REDUCTION AND REPORTING

13.1 All samples, custody documents and discrepancy forms must be clearly completed with permanent ink and filed with the project folder.

14 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1 Not applicable.

15 REFERENCES

15.1 *Test Methods for Solid and Hazardous Waste Physical and Chemical Analyses*, USEPA SW846, December 1996.

15.2 NYSDEC *Analytical Services Protocol*, October 1995.

15.3 NELAC Standard, Chapter 5, July 2002.

16 TRAINING OUTLINE

- Read this SOP.
- Follow policies in ADM-TRANDOC.
- Observe performance of this SOP. Follow Breakdown Training Plan Form.
- Perform this SOP with guidance.
- Perform this SOP independently and have a trained analyst check the trainee's work. If work is acceptable, complete Training Plan Form and file with QA.

17 INSTRUMENT-SPECIFIC ADDENDUM

Not Applicable

18 ATTACHMENTS

18.1 Sampling Instructions

18.2 Short Holding Time Parameters List

18.3 Cooler Receipt and Preservation Form

18.4 COC: Chain of Custody

18.5 Internal Tracking Form for Short Holding Time Samples.

19 CHANGES FROM PREVIOUS REVISION

- 3 – Added Definition of Log-In
- 5 – Modified Safety for consistency with other SOPs
- 9 – Added pH paper and KI-Starch paper to supplies
- 11.2.4 Added need to check COC for shorties
- 11.2.5 Eliminated that discrepancies are highlighted in yellow on COC
- 11.2.7 Added procedure if shorties need done before log-in
- 11.3.2 Added reference to SMO-ICOC
- 11.3.3 Added reference to ADM-PCR
- 11.4.2 Moved preservative requirements out of this section and into (new) 11.4.6+.7
- 11.4.6 +.7 Added detail of how to check preservatives
- 11.5 Simplified wording – eliminated the holding cart. Added that SMO responsible for documenting the location of samples in cooler
- 11.6 Eliminated wording about paper chains and phasing in barcoding
- 11.8.2 Changed white board from SMO to WC
- 11.9.4 Changed from UPS to "courier"
- 11.10.1 Changed the use of the IR gun distance from 7-12 inches to 3-6 inches. Added need to wipe container with a dry paper towel when using IR gun.
- 15 Changed NELAC reference from 1999 to 2002.

SAMPLING INSTRUCTIONS

1. Please Use Caution! Some bottles contain Preservatives such as Acids and Bases that are CORROSIVE! These bottles are marked with colored stickers to inform the sampler but gloves should be worn at all times during sampling for your own protection. (preservative information is on the flip side for emergencies)

2. Please overfill VOA vials and stoppered bottles to eliminate headspace that interferes in the analysis of the samples – but do not overfill too much or the preservative will be flushed out.

3. Please use all of the containers that we provide for a sampling location. This will ensure that the proper containers and volumes are returned for the tests that were requested.

4. Vials labeled TRIP BLANK or TB are included in each cooler containing vials used for testing volatile organics. These vials are a control to determine if the cooler was exposed to contamination while in route or during sampling. Please indicate on the Chain of Custody if you wish to have these vials tested.

Returning Coolers Checklist – Please Read!

Incomplete information will result in a phone call and hence delayed processing of your samples.

1. ***Labeling*** all bottles or soil jars is essential. We look for a **location ID**, a **date**, a **time, initials, preservation, and sample type** on all bottles to verify a location against the Chain of Custody. (Remember that ice water can smudge or remove your makings. a permanent marker on a dry bottle works best)

2. The ***Chain of Custody*** should include: the **client information and sampler's signature** in the top left box, the **location ID**'s of the sample with the **analysis and preservation** indicated in the center section, **turn-around-time and reporting** information in the bottom center section, and **sign-off** (signature/date/time) to the courier on the bottom left section.

3. ***Custody stickers*** are very important for CLP or ASP package work and are encouraged for all coolers. The sticker should be placed over the lid and body of the cooler and taped securely. These stickers provide an added level of security, and if they are broken when the coolers arrive at CAS, we will contact you.

4. ***Packaging coolers*** well is a key to avoid resampling. Beware of glass and make sure they are in the bubble bags that we provide. Also a snug fit is suggested. Extra paper or cardboard (especially with amber liters) is encouraged. **Note** that when the ice melts, the bottles can move inside of the cooler. **Any Leaking Coolers in shipment will be considered HAZARDOUS** by the courier (UPS). Please seal the cooler with packing tape and/or place samples and ice in a plastic bag in the cooler. A leaking cooler will likely result in a delay at UPS and missed holding times at the LAB.

5. ***Receiving Temperature at CAS*** is a key element to the validity of your results to withstand scrutiny in a court of law. Our Data is only considered valid if the samples have a temperature of 6 degrees Celsius or less. A temperature blank is include in all coolers and should be returned in ice with the other samples. Ice should be bagged **or** put the ice and samples in a large plastic bag and tie it off to reduce leakage. Submersion is the best way to cool the samples but watch out for labels falling off or smudging.

6. ***Your supplies*** (like coolers or icepacks) will gladly be returned if we have complete return-address information! Please document **your return-address on the cooler** or ice packs in the form of a sticker, or permanent marker so we can return your supplies.

7. ***Ship samples*** using overnight service or deliver within 24 hours of sampling time. If shipping for **Saturday**, Check mark the Saturday-delivery Box and you must affix several "Saturday" stickers to the cooler.

SHORT HOLDING TIMES

BREAK DOWN:	HOLDING TIME	WHEN
pH	ASAP	Run daily
Conductivity	48hr from sample date	Run daily
Color	48hr from sample date	Run as needed
Turbidity	48hr from sample date	Run as needed
Sett. Solids	48hr from sample date	Run Same day

WET CHEM:

BOD	Wed./Friday	48hr from sample date
NO3	ASAP (IC)	48hr from sample date
NO2	ASAP (lachat)	48hr from sample date
Residual Chlorine	ASAP	
Odor	ASAP	
Dissolved Oxygen	ASAP	
Coliform test	ASAP (Bev)	
Orthophosphate	ASAP	48hr from sample date
Chrome Hex	ASAP	24hr from sample date
Surfactants	ASAP	48hr from sample date
Ferrous Iron	ASAP	24hr from sample date
TSS,TDS,TS,TVS	(ck sample date 7 days)	
Sulfite	ASAP	
Sulfides	(ck sample date 7 days)	

Cooler Receipt And Preservation Check Form

Project/Client_____Submission Number_____.

Cooler received on_____ by:_____**COURIER:** CAS UPS FEDEX CD&L CLIENT

1.	Were custody seals on outside of cooler?			YES	NO	
2.	Were custody papers properly filled out (ink, signed, etc.)?			YES	NO	
3.	Did all bottles arrive in good condition (unbroken)?			YES	NO	
4.	Did any VOA vials have significant air bubbles?			YES	NO	N/A
5.	Were **Ice** or **Ice packs** present?			YES	NO	
6.	Where did the bottles originate?			CAS/ROC, CLIENT		
7.	Temperature of cooler(s) upon receipt:	_____	_____	_____	_____	_____
	Is the temperature within 0° - 6° C?:	Yes	Yes	Yes	Yes	Yes
	If No, Explain Below	No	No	No	No	No

Date/Time Temperatures Taken: _____

Thermometer ID: 161 or IR GUN Reading From: Temp Blank or Sample Bottle

If out of Temperature, Client Approval to Run Samples_____

Cooler Breakdown: Date :_____by:_____

1.	Were all bottle labels complete (*i.e.* analysis, preservation, etc.)?	YES	NO	
2.	Did all bottle labels and tags agree with custody papers?	YES	NO	
3.	Were correct containers used for the tests indicated?	YES	NO	
4.	Air Samples: Cassettes / Tubes Intact	Canisters Pressurized	Tedlar® Bags Inflated	N/A

Explain any discrepancies: _____

		YES	NO	Sample I.D.	Reagent	Vol. Added
pH	Reagent					
12	NaOH					
2	HNO_3					
2	H_2SO_4					
Residual Chlorine (+/-)	for TCN & Phenol					
5-9**	P/PCBs (608 only)					

YES = All samples OK NO = Samples were preserved at lab as listed PC OK to adjust pH_____

**If pH adjustment is required, use NaOH and/or H_2SO_4

VOC Vial pH Verification (Tested after Analysis) Following Samples Exhibited pH > 2				

Other Comments:

Columbia Analytical Services, Inc.
An Employee - Owned Company
www.caslab.com

CHAIN OF CUSTODY/LABORATORY ANALYSIS REQUEST FORM

One Mustard St., Suite 250 • Rochester, NY 14609-0859 • (585) 288-5380 • 800-695-7222 x11 • FAX (585) 288-8475 PAGE _____ OF _____

SR #

CAS Contact

Project Name	Project Number
Project Manager	Report CC
Company/Address	
Phone #	FAX#
Sampler's Signature	Sampler's Printed Name

ANALYSIS REQUESTED *(Include Method Number and Container Preservative)*

PRESERVATIVE

NUMBER OF CONTAINERS

- GC/MS VOA's ☐ 8260 ☐ 624 ☐ CLP
- GC/MS SVOA's ☐ 8270 ☐ 625 ☐ CLP
- GC VOA's ☐ 8021 ☐ 601/602
- PESTICIDES ☐ 8081 ☐ 608 ☐ CLP
- PCB's ☐ 8082 ☐ 608 ☐ CLP
- METALS, TOTAL (List in comments below)
- METALS, DISSOLVED (List in comments below)

Preservative Key
0. NONE
1. HCL
2. HNO_3
3. H_2SO_4
4. NaOH
5. Zn. Acetate
6. MeOH
7. $NaHSO_4$
8. Other _____

CLIENT SAMPLE ID	FOR OFFICE USE ONLY LAB ID	SAMPLING DATE	SAMPLING TIME	MATRIX	REMARKS/ ALTERNATE DESCRIPTION

SPECIAL INSTRUCTIONS/COMMENTS
Metals

See QAPP ☐

TURNAROUND REQUIREMENTS
_____ **RUSH** (SURCHARGES APPLY)
_____ **24 hr** _____ **48 hr** _____ **5 day**
_____ **STANDARD**
REQUESTED FAX DATE
_____
REQUESTED REPORT DATE
_____

REPORT REQUIREMENTS
_____ I. Results Only
_____ II. Results + QC Summaries (LCS, DUP, MS/MSD as required)
_____ III. Results + QC and Calibration Summaries
_____ IV. Data Validation Report with Raw Data
_____ V. Speicalized Forms / Custom Report
Edata _____ Yes _____ No

INVOICE INFORMATION
PO#
BILL TO:
SUBMISSION #:

SAMPLE RECEIPT: CONDITION/COOLER TEMP: _____ CUSTODY SEALS: Y N

RELINQUISHED BY	RECEIVED BY	RELINQUISHED BY	RECEIVED BY	RELINQUISHED BY	RECEIVED BY
Signature	Signature	Signature	Signature	Signature	Signature
Printed Name	Printed Name	Printed Name	Printed Name	Printed Name	Printed Name
Firm	Firm	Firm	Firm	Firm	Firm
Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time

SCOC-1102-08

Distribution: White - Return to Originator; Yellow - Lab Copy; Pink - Retained by Client

INTERNAL TRACKING FOR SHORT HOLDING TIME SAMPLES

DATE : _____

TIME : _____

CLIENT : _____

SUBMISSION # : _____

SAMPLE ID	TEST	RELINQUISH SMO Initial	RECEIVED WC Initial	Barcoded	SAMPLE RETURNED Initial / Date / Time

ATTACHMENT A-2

GENERAL ENGINEERING LABORATORIES, LLC
STANDARD OPERATING PROCEDURES

GL-RAD-A-013, Rev. 10	**The Determination of Gamma Isotopes**
GL-RAD-A-045, Rev. 1	**The Isotopic Determination of Plutonium, Uranium, Americium, Curium, and Thorium**
GL-SR-E-001, Rev. 17	**Sample Receipt, Login and Storage**

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF GAMMA ISOTOPES

(GL-RAD-A-013 REVISION 10)

APPLICABLE TO METHODS:
EPA 600/4-80-032 Method 901.1 (Modified)
DOE EML HASL-300 (Modified)

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1.0 THE DETERMINATION OF GAMMA ISOTOPES

2.0 METHOD OBJECTIVE, PURPOSE, CODE AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for Gamma Isotopes in water, soil, urine and miscellaneous matrices.

2.2 Water samples are counted in Marinelli beakers. Soil samples are sealed in aluminum cans, which are counted immediately if Ra-226 is not desired. If Ra-226 is desired, the sealed can is set aside to allow secular equilibrium between Rn-222 and Bi-214. Quantification is done by the abundance of the 609 KeV Bi-214 line.

2.3 This method has been modified from the source method EPA 600/4-80-032 "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," August 1980, Method 901.1, and the Department of Energy (DOE) EML Procedures Manual source method for Gamma PHA in soils and sediments, HASL-300. For all matrices, similar principles of radiochemical concentration and counting are used.

2.4 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

3.0 METHOD APPLICABILITY

3.1 Minimum Detectable Activity (MDA): The MDA is based upon sample volume, instrument background, instrument efficiency, count time and other statistical factors, as well as specific isotopic values such as abundance and half-life.

3.2 Method Precision: Typical relative percent difference (RPD) is less that 20%.

3.3 Method Bias (Accuracy): The method accuracy requirement for gamma, measured by running a laboratory control sample (LCS) with each batch, is 25% of the true value.

3.4 Analysts go through a partnered training program with an already certified analyst for gamma spectroscopy. The analyst receives training on reviewing of standard analytical requirement such as RPD, method bias and technical review of gamma spectra. The analyst can then become qualified to perform the analysis by passing an unknown sample analysis and correctly identifying the isotope(s). Technical training records are maintained electronically by the Quality Systems staff.

4.0 DEFINITIONS

4.1 Clean Line: An energy line of an isotope with no known energy lines of other isotopes within 2 KeV. (This excludes daughters that use the same line for quantification.)

4.2 Interfered Line: An energy line of an isotope with one or more energy lines of one or more different isotopes within 2 KeV.

4.3 Single and Double Escape Interference Lines: When high energy gamma lines above 1022 KeV have a large emission rate, it is possible to see single and double escape peaks caused by escape of the 511 KeV annihilation photon(s) from the detector.

4.4 Summation Interference: When high gamma emission rates are seen, sample summation can occur. Prominent in geometries close to detection and in low energy range (i.e., 10,000 gps at 88 KeV, 15,000 gps at 210 KeV), a summation interference can be seen at 88+88=176 KeV, 210+210=420 KeV, 210+88=298KeV.

4.5 False Positive: An isotope that has failed one or more of several tests including half-life, abundance, and energy tolerance (± 2 KeV)

4.6 Abundance Test: The test where the software verifies the presence of 75% of the total abundance of a nuclide in the system library is present. The presence of greater than 75% of the total abundance will cause a nuclide to be identified. The abundance criteria may be reduced to less that 75% for nuclides with several lower abundant photons.

4.7 Energy Tolerance: The test where the software checks the energy line in the spectrum to see if it is within the energy tolerance setting. (The standard setting is 2 KeV.) If it is within this setting then the line is associated with that nuclide. The energy line can be associated with more than one nuclide.

4.8 Half-Life Test: The test to determine if the half-life of the isotope is long enough not to have decayed away. The half-life of the sample is the time from sample date to analysis date plus 1/2 the count time. A limit of no more than eight half-life is the standard setting.

4.9 Key Line: The line chosen by the builder of the library to be the prominent line of the isotope. This line is used in the MDA table for purposes of calculating activity, error and MDA. For non-identified isotopes the key line energy is used as the basis of determining the region used to calculate the activity, error, and the MDA. Usually this line is the most abundant line on a line that is relatively free from interference.

4.10 Abundance (Photon Intensity): The value, usually expressed in percent, given to a photon of specific energy which is emitted during the decay of a radionuclide. The abundance represents the probability of emission of a specific energy photon when a radionuclide is decaying (gamma/disintegration).

4.11 Counting Uncertainty: The error of the reported result due to the counting statistics of the instrument used for qualification.

4.12 Back Scatter: The detection of a count that occurs when an event interacts with counting materials, changes direction, and scatters back to the detector.

5.0 METHOD VARIATIONS

Modifications to the procedure are limited to GEL's use of additional isotopes for the daily calibration check and the inclusion of a more stringent calibration and resolution periodicity.

6.0 SAFETY PRECAUTIONS AND WARNINGS

6.1 Keep hands free from moving parts of canning device and Gamma shields.

6.2 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

6.3 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

6.4 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for Handling Biological Materials.

6.5 If there is any question regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

7.0 INTERFERENCES

7.1 Some Gamma isotopes emit gamma lines that may overlap with other isotopes. If the energies of the two isotopes are within 2 KeV, the peaks may not be resolvable and will give a positive bias to the result. This problem is minimized by careful review of the peak search.

7.2 Soil samples may vary in density from the standard used for calibration. This may bias the results due to self-absorption of lower energy (<100 K).

8.0 APPARATUS, MATERIALS, REAGENTS, EQUIPMENT, AND INSTRUMENTATION

8.1 Ancillary Equipment

8.1.1 100 cc aluminum cans with lids for soil and miscellaneous samples
8.1.2 Gelman Sciences PETRI dish for soil, filters and miscellaneous samples
8.1.3 2 L and 500 mL Marinelli beakers for water samples
8.1.4 Air displacement pipettes.
8.1.5 Can annealing tool
8.1.6 Graduated cylinder

8.2 Reagents, Chemicals and Standards

8.2.1 NIST traceable mixed gamma standard in 100cc aluminum can
8.2.2 NIST traceable 2.0 liter mixed gamma standard in 2 L Marinelli beaker
8.2.3 NIST traceable mixed gamma standard in 0.5 L Marinelli
8.2.4 NIST traceable mixed gamma standard in Gelman Sciences PETRI dish
8.2.5 Standard soil blank
8.2.6 NIST traceable mixed gamma standard of 13-47mm glass fiber filter composites in Gelman Sciences PETRI dish.
8.2.7 NIST traceable aqueous Mixed Gamma Standard: Contains Am-241, Co-60, and Cs-137 as a minimum.
8.2.8 NIST traceable mixed gamma standard of 1-47mm glass fiber
8.2.9 NIST traceable mixed gamma standard frontloaded in BG-300 Impregnated Charcoal Sample Cartridge.
8.2.10 Nitric Acid, reagent grade. (16M)
8.2.11 Hydrofluoric acid, 48%.
8.2.12 Hydrochloric acid, reagent grade. (12M)
8.2.13 Boric acid, 5%. Dissolve 50 grams of H_3BO_3 per liter of water

8.3 Instrumentation

8.3.1 High purity germanium detector, with associated electronics and data reduction software
8.3.2 Top loader balance

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 For soil samples, 500g of sample should be collected, preferably in a plastic container to avoid breakage.

9.2 For water samples, 2 liters of sample should be collected in a plastic container and preserved to pH2 with Nitric acid.

10.0 SAMPLE PREPARATION

10.1 Soil sample preparation.

10.1.1 Prepare the sample for gamma counting in accordance with SOP GL-RAD-A-021 “Soil sample preparation for the determination of radionuclides”.

10.1.2 Fill the appropriate container with sample prepared from step 10.1.1 using the following steps as a guideline:

10.1.2.1 If Ra-226 analysis is required, the sample is placed in a 100cc can for in-growth.

NOTE: It is recommended that in-growth be allowed 7 days to quantify Ra-226. Longer intervals can be used at the request of the client. However, shorter in-growth periods may decrease the accuracy of the data. If there is insufficient mass of sample to fill the 100cc can, contact the team or group leader.

10.1.2.2 All homogenized samples shall be placed in the 100cc can. Determine the net weight of the sample. If the net weight is less than 55 grams or greater than 190 grams, contact the team or group leader to determine the appropriate counting container. Record sample weight and date on sample container.

10.1.2.3 If there is insufficient sample to fill the 100cc can, place sample in the 10cc petri dish, cap and seal. Record sample weight and date on sample container.

10.1.2.4 If there is insufficient sample to fill the 10cc petri dish, perform the following digestion process:

10.1.2.4.1 Weigh out an appropriate aliquot into a labeled teflon beaker. Record this weight on the sample container.

10.1.2.4.2 Add 10 mL of concentrated nitric acid to each sample.

10.1.2.4.3 Place samples on medium heat (~300 °F) and cover each sample with a teflon lid. Reflux all samples for 30 minutes.

10.1.2.4.4 Remove teflon lids and add 5 mL concentrated hydrochloric acid and 10 mL hydrofluoric acid to each sample. Cover samples and reflux for 120 minutes.

10.1.2.4.5 Remove teflon lids and allow samples to evaporate to dryness.

10.1.2.4.6 Add 5 mL of concentrated nitric acid and evaporate to dryness.

10.1.2.4.7 Repeat Step 10.1.2.4.6.

10.1.2.4.8 Add 5 mL of concentrated nitric acid to the dry samples. Add 1 ml of 5% boric acid. Place the samples back on the hotplate long enough so that the dried sample dissolves into solution.

10.1.2.4.9 Transfer solution to a 500 mL marinelli beaker and dilute to 500 mL. Record the original sample mass and diluted volume on sample container. Record the original sample mass on batch que sheet.

10.2 Water sample preparation

10.2.1 Mix and measure an appropriate volume into a 2 L or 500 mL Marinelli beaker and record the volume on the batch Que Sheet. If applicable, record the standard identification code, volume and expiration date on the batch Que sheet.

10.3 Urine Sample Preparation

10.3.1 Place a 24-hour urine container (or other suitable container) on a balance and tare the balance.

10.3.2 Transfer the entire volume of the sample received to the tared container and record the volume of sample received.

10.3.3 Add 8 M HNO_3 acid to the original sample container (typically 25 – 50 mL). Shake in the container and then heat in a microwave for approximately 30 seconds to remove sample residue from the sides of the sample container.

10.3.4 Add the nitric acid rinse to the 24-hour urine container and record the volume of the original sample plus acid.

10.3.5 Cap and shake the 24-hour urine container to homogenize the sample. Transfer an aliquot (typically 500 mL) of this solution to a Marinelli Beaker.

10.3.6 Record the amount of the original sample, excluding the nitric acid added, on the gamma spec que sheet.

Example: 800 mL is received and 50 mL of 8 M HNO_3 is added from the rinse of the sample container. 500 mL is transferred to the Marinelli Beaker. The recorded volume on the que sheet should be (500 mL/850 mL) x 800 mL = 470.6 mL.

10.4 Preparation of miscellaneous matrices

10.4.1 Prepare the sample in accordance with SOP GL-RAD-A-026 "Preparation of Special Matrices for the Determination of Radionuclides."

10.4.2 Once the appropriate section of GL-RAD-A-026 has been performed, prepare the sample for gamma counting by referring to section 10.1.2 above.

11.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL STANDARDS

11.1 A blank is performed with each batch. DI Water should be used to prepare the blank.

11.2 A duplicate should be run with each sample batch. Refer to the batch pull sheet to determine the designated batch duplicate sample.

11.3 A matrix spike sample is prepared by adding a known volume of standard directly to the designated sample. Refer to the batch pull sheet to determine the designated batch matrix spike sample.

11.4 A laboratory control sample is prepared by adding a known volume of standard directly to a Marinelli beaker with DI water.

12.0 INSTRUMENT CALIBRATION AND PERFORMANCE

12.1 Refer to "Gamma Spectroscopy System Operating Procedure" (GL-RAD-I-001) for calibration periodicity and instructions.

12.2 Refer to "Counting Room Instrument Maintenance and Performance Checks" (GL-RAD-I-010) for instructions concerning instrument maintenance.

13.0 ANALYSIS AND INSTRUMENT OPERATION

13.1 Place the sample on the detector and count the sample an appropriate amount of time in the gamma shield. See "Gamma Spectroscopy System Operating Procedure" (GL-RAD-I-001) for specific instructions on operating the gamma spectrometers.

14.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

14.1 Refer to "Gamma Spectroscopy System Operating Procedure" (GL-RAD-I-001) for instructions concerning the Gamma Spectrometer.

14.2 Refer to "Counting Room Instrument Maintenance and Performance Checks" " (GL-RAD-I-001) for instructions concerning instrument maintenance.

15.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

15.1 Data Recording

Record the following information on the Gamma Que Sheet: preparation date, analyst's initials, spike isotope, spike code, spike volume, LCS isotope, LCS code, LCS volume, nominal concentration LCS, and nominal concentration MS. For each sample record the detector number, sample mass, sample date and time.

15.2 The instrument will report sample pCi/unit according to the following equation:

$$\text{Sample pCi/unit} = \frac{A * d}{2.22 * E * V * B * Ct * ABS}$$

Where:

A = net peak area (counts)
ABS = relative absorption factor
B = abundance (gammas/disintegration)
E = counting Efficiency (counts/gamma)
V = sample volume (grams or liters)
Ct = sample count time (minutes)
d = decay factor = $\frac{1}{e^{-\lambda t}}$

15.3 Counting uncertainty is calculated according to the following equation:

$$\text{pCi/unit} = Ac * 1.96\sqrt{\left(\frac{ef - er}{E}\right)^2 + \left(\frac{pk - er}{pk}\right)^2 + \left(\frac{ab - er}{A}\right)^2 + \left(\frac{sy}{100}\right)^2 + (\text{Decay})}$$

Where:

Ac = Activity from 15.2

$$\text{Decay} = \left(\frac{T_{1/2err}}{T_{1/2}}\right)^2 * \left[\frac{\lambda Er}{1 - e^{-\lambda Er}} - \lambda\left(T_s + Er\right) - 1\right]$$

15.4 The method MDA in pCi/g or pCi/L are calculated according to the following equations:

$$\text{MDA (pCi/unit)} = \frac{d * \left(2.71 + 4.66\sqrt{cpm_b * ct}\right)}{2.22 * E * V * B * ct}$$

Where:

A = net peak area (counts)
ABS = relative absorption factor
B = abundance (gammas/disintegration)
E = counting Efficiency (counts/gamma)
V = sample volume (grams or liters)
ct = sample count time (minutes)
d = decay factor = $d = \frac{1}{e^{-\lambda t}}$

15.5 The absorption factor is calculated by the following equations:

$$I_1 = \frac{\ln((SScpm - Scpm)/ECcpm)}{(((SScpm - Scpm)/ECcpm) - 1)}$$

$$I_0 = \frac{\ln((SSTcpm - STcpm)/ECcpm)}{(((SSTcpm - Scpm)/ECcpm) - 1)}$$

$$ABS = \frac{I_1}{I_0}$$

Where:

SScpm = sample plus the source cpm at the region of interest
Scpm = sample cpm at the region of interest
ECcpm = source cpm on the empty can at the region of interest
ln = natural logarithm
SStcpm = standard plus the source cpm at the region of interest
Stcpm = standard cpm at the region of interest

15.6 The VAX operating system will report the following information with each completed sample:

15.6.1 The nuclide identification report

15.6.2 The minimum detectable activity report

15.6.3 The peak search report.

15.7 The following criteria are used to accept a reported gamma isotope from the NID report:

15.7.1 The peak FWHM should be less than 3 KeV.

15.7.2 The activity of a non-target isotope will not be reported unless the result is greater than the minimum detectable activity and the result is greater than the three sigma uncertainty..

15.7.3 The energy tolerance should be between 2 and 3 KeV.

15.7.4 The sensitivity setting should be between 0.1 and 3. The default setting is 3.

15.7.5 Start channel on peak search should be approximately 50 and end channel should be 4096.

15.7.6 The confidence level setting should be 5.

15.7.7 These settings should not be changed without approval from a group leader.

15.8 The following guidelines are used to accept unidentified lines on the peak search after environmental background subtraction:

15.8.1 The line matches the natural fingerprint of the Uranium-238 or Thorium-232 decay chains (i.e. 63, 75, 93, 239, 295, 352, 511, 609, 1120, etc.).

15.8.2 The line matches as a summation peak from two other lines in the spectrum.

15.8.3 The line has a net area of less than 20.

15.8.4 The line matches as a escape peak from an identified nuclide which emits photons greater than 1022 KeV.

16.0 QUALITY CONTROL REQUIREMENTS

16.1 Analyst and Method Verification

Refer to "Analyst and Analytical Methods Validation Procedures" (G-RAD-D-003) for instructions concerning the validation of analysts and analytical methods.

16.2 Method Specific Quality Control Requirements

16.2.1 A method blank will accompany each batch of 20 or less samples. The reported value should be less than or equal to the CRDL for all target isotopes. Matrix spikes are prepared by spiking a portion of the QC sample with Cs-137 (as a minimum).

16.2.2 For water samples only, a matrix spike (MS) should be run with every batch of 20 samples. The recovery of the spike should fall between 75 and 125%. The recovery is calculated as follows:

$$\%\text{REC} = \frac{\text{spike(pCi/g)} - \text{sample(pCi/g)}}{\text{spikedamount(pCi/g)}} * 100$$

or:

$$\%\text{REC} = \frac{\text{spike(pCi/L)} - \text{sample(pCi/L)}}{\text{spikedamount(pCi/L)}} * 100$$

NOTE: Performing a matrix spike on a soil sample would result in direct contamination of the sample, therefore, only water samples require an MS.

16.2.3 A sample duplicate should be run with every batch of 20 or less samples. The relative percent difference (RPD) between the sample and the duplicate should be ≤o 20%. The RPD is calculated as follows.

$$RPD = \frac{\text{high sample (pCi/g)} - \text{low sample (pCi/g)}}{\text{Average (pCi/g)}}$$

or:

$$RPD = \frac{\text{high sample (pCi/L)} - \text{low sample (pCi/L)}}{\text{Average (pCi/L)}}$$

16.2.4 A laboratory control spike (LCS) should be run with every batch of 20 samples or less. The recovery of the spike should fall between 75 and 125%. The LCS should contain Cs-137 as a minimum. Some clients may request a mixed gamma standard. For soils, a mixed gamma expired calibration source may be used as an LCS. For liquids and filters, spike a blank sample with Cs-137 as a minimum.

16.2.5 The recovery is calculated as follows:

$$\text{LCS} = \frac{\text{observed\_pCi/g}}{\text{known\_pCi/g}} * 100$$

or:

$$\text{LCS} = \frac{\text{observed\_pCi/L}}{\text{known\_pCi/L}} * 100$$

16.3 Actions required if the Quality Control Requirements Are Not Met

If any of the above criteria cannot be satisfied, the analyst should inform the group leader and initiate a non-conformance report as outlined in "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

17.1 The data is transmitted from the laboratory personnel to the reporting personnel as outlined in “Data Review and Validation Procedures” (GL-RAD-D-003):

17.1.1 Visually check the que sheet, spreadsheet, raw data and data report to make sure the information has been transcribed correctly.

17.1.2 Review the raw data to see if there are any hits not on the requested list. If there are, report to the client by adding the information into LIMS.

A true identification or a “hit” is any isotope greater than 10 pCi/L or 5 pCi/g on the identified nuclide list. The error must also be less than 40% of the result and not have interference by another isotope or have a very short half-life.

17.1.3 Check to see that the required detection limit (RDL) is met if required.

17.1.4 Check hits to see if they are true hits and not an interference or a false positive.

Identifications are classified into two categories: false positives (interference), and true identification (hit). The false positives are rejected by checking the abundance test results for the isotope and by checking last results for the half-life. The result is considered interference and rejected by checking to see if there are any clean lines in sample spectrum for the isotope. If none exist, then the identification is rejected. If the key line has a possible interference and secondary lines do not confirm the activity calculation, the identification is rejected. Isotopes that pass these criteria are accepted as true identifications. The above tests and criteria are standard and will be followed unless directed otherwise by contract, specification or instructions.

17.1.5 Complete the batch checklist.

18.0 RECORDS MANAGEMENT

18.1 Each analysis that is performed on the instrument is documented in the run log according to "Run Logs" (GL-LB-E-009).

18.2 All raw data printouts, calculation spreadsheets and batch checklists are filed with the sample data for archival and review.

19.0 LABORATORY WASTE HANDLING AND WASTE DISPOSAL

19.1 After analysis, return sample containers to storage as outlined in "Verifying the maintenance of sample integrity" (GL-LB-E-012).

19.2 Radioactive waste is disposed of as outlined in the Laboratory Waste Management Plan (GL-LB-G-001).

20.0 REFERENCES

20.1 USEPA. Prescribed Procedures for Measurement of Radioactivity in Drinking Water. Method 901.1, August 1980.

20.2 Canberra Nuclear Genie System Spectroscopy, Applications and Display User's Guide. Vol. I and II, May 1991.

20.3 EML procedures manual. HASL-300-Ed.25, 1982.

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STANDARD OPERATING PROCEDURE

FOR

THE ISOTOPIC DETERMINATION OF PLUTONIUM, URANIUM, AMERICIUM, CURIUM, AND THORIUM

Applicable to:
EML HASL-300 E-U-04 (Modified)
EML HASL-300

(GL-RAD-A-045-REVISION 1)

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

SAMPLE RECEIPT, LOGIN AND STORAGE

(GL-SR-E-001 REVISION 17)

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1.0 STANDARD OPERATING PROCEDURE FOR SAMPLE RECEIPT, LOGIN AND STORAGE

2.0 PURPOSE

To describe the routine operational procedures for the receipt, login and storage of samples received by General Engineering Laboratories, LLC (GEL).

3.0 DISCUSSION

3.1 Sample custody is a pre-planned mechanism for tracking a sample from the collection of the sample in the field through the release of the finished analytical data to the client. At the collection site, the sample containers are filled with sample and the Chain of Custody form is initiated. The sample collector fills out the form, which includes the name of the client, the requested analysis parameters, sample location, the date and time of collection, sampling technique, preservatives used, and any comments or remarks that may be useful in the analytical work or data interpretation that will follow. Proper sample receipt, login and storage assure accurate chain of custody.

3.2 Custody is defined as:

3.2.1 Being in your physical possession, or
3.2.2 Being in your view, after being in your possession, or
3.2.3 Being locked up after being in your possession, or
3.2.4 Being in a designated secure area

3.3 Upon arrival at the laboratory, sampling personnel, delivery service and carriers relinquish the samples to the sample management group. Each sample container receives a unique sample identifier that is assigned electronically by LIMS (Laboratory Information Management System). LIMS tracks the status and location of each sample container, and serves as the database for analytical results.

4.0 DEFINITIONS

4.1 ALPHALIMS: Laboratory Information Management System.

4.2 Chain of Custody (COC): A written record of sample transfer and possession.

4.3 Custody Seal: Security seals that are attached to sample containers and/or bottles that are used to detect unauthorized tampering.

4.4 Holding Time: The period of time between sample collection and preparation or analysis.

4.5 Labeled Package: A package containing radioactive material labeled with a Radioactive White-I, Radioactive Yellow-II or Radioactive Yellow-III label as specified in US Department of Transportation Regulations, 49 CFR 172.403 and 172.436-440.

4.6 Matrix: The physical appearance or make-up of a sample (groundwater, drinking water, wastewater, soil, sludge, etc.) as determined by the client or Project Manager.

4.7 Material Safety Data Sheet (MSDS): A document that may accompany samples of known chemical characteristics. (See our "Safety, Health and Chemical Hygiene Plan" for more information on MSDSs.)

4.8 Preservative: Additives that are introduced to a sample at the time of collection to help retard chemical and biological changes that may occur.

4.9 Turn Around Time (TAT): A numeric designation to the degree of attention a sample should receive. This designation is used to convey the client's requested data delivery dates to the laboratory.

4.10 Sample Delivery Group (SDG): One or more samples (typically not to exceed 20 samples) from a specific client that are reported by the laboratory at the same time.

4.11 Sample Receipt Review (SRR): A form used to document a sample's arrival and the condition of its arrival at the laboratory.

4.12 Sample: Any item that has been submitted for analysis to GEL.

5.0 SAFETY, HEALTH AND ENVIRONMENTAL HAZARDS

5.1 All samples must be handled with care during the login process. Wear protective gear such as gloves, aprons, safety glasses and laboratory coats when handling all samples. Some samples may be accompanied by MSDSs that contain vital information on potential hazards. The sample description and client labels may also give this information.

NOTE: Gloves and protective eyewear must be worn when handling samples. Lab coats should be worn when handling any samples but are only required to be worn when handling radioactive or hazardous samples. (Refer to the "Safety, Health and Chemical Hygiene Plan.")

5.2 If there is a spill of a known hazard (based on historical results, MSDSs, and/or sample description), immediately contact the Group Leader, Laboratory Waste Manager, or Radiation Safety Officer as appropriate.

5.3 All sample management personnel are required to read and understand GEL's "Safety, Health and Chemical Hygiene Plan," which is found on GEL's Intranet.

6.0 PROCEDURES

6.1 Sample Package Receipt

6.1.1 All sample packages submitted to GEL are received by sample management personnel. Samples are received from a number of carriers including GEL field staff, GEL couriers, individual clients, and public and private shipping companies.

6.1.2 Upon arrival, all sample packages will be inspected for integrity. Note any unusual physical damage, signs of leakage, or evidence that custody seals have been tampered with. If the package appears to be leaking or has any unusual odor, place it under the fume hood and notify the Group Leader, Laboratory Waste Manager, Radiation Safety Officer, or Project Manager as appropriate before continuing.

6.1.3 All sample packages will also be screened for external contact radiation exposure. This screening is performed to determine the possible presence of radionuclides that may require special handling. If a radioactive "labeled" package is received, or any package exceeds 0.5 mrem/hr on contact, the RSO group should be notified, and the package is segregated in the GEL sample receiving area where the RSO or designee will unpack the package following the procedures described in GL-RAD-S-007 for "Receiving of Radioactive Samples."

6.1.4 Bioassay and Low Level Mercury (LLHG) sample packages are initially received and segregated in the GEL login area. Following package screening, they are then transported to the bioassay or LLHG login area for inspection, login and storage. Bioassay and LLHG receiving staff perform the same sample inspection, login and storage procedures using the Sample Receipt Review (SRR) in Appendix 2 or 3 as applicable, except as noted in Section 6.1.7.

6.1.5 Packages indicating <0.5 mrem/hr should be further segregated to identify samples intended to be received under the authority of GEL's Radioactive Material License. In addition to "Labeled" radioactive material, radioactive material is any material that meets the following criteria:

6.1.5.1 Any Material received that was shipped as DOT Hazard Class 7 Limited Quantity- Excepted Package.

6.1.5.2 Any material shipped and received that is marked as radioactive (i.e. conventional trefoil, yellow and magenta tape, etc.), or has otherwise been declared radioactive by the consignor in the accompanying documents. This material may be intended for receipt under the authority of a radioactive materials license although it was shipped under DOT exemption for radioactive material.

6.1.6 All discrepancies noted during receipt and inspection shall be recorded using a Sample Receipt Review (SRR) form in Appendix 2.

6.1.6.1 As required client specific Sample Receipt Review forms may be created by the Project Management Group. These checklists are created because additional sample management comments and checks are required in order to meet quality objectives established for these project samples.

6.1.7 Open all shipping containers (excluding bioassay & LLHG samples) under the high volume exhaust duct located in Sample Receiving. (NOTE: It is only necessary to open Bioassay & LHG samples under a fume hood when the integrity of the containers is suspected/determined to be compromised.)

6.1.7.1 All samples received (excluding bioassay) must be screened for radioactivity using a Geiger-Muller pancake probe. Results for the highest reading samples are to be noted on the SRR form. The Radiation Safety Group shall be notified when readings for any individual non-radioactive sample exceed 2x area background.

6.1.8 The COC should accompany all samples received by the Sample Management Group. The COC documentation includes sample identification (e.g., MW-1; Lagoon 17; #1234567), sampling date and time, sample collector, and requested parameters to be tested. If this documentation is not present, the Sample Management Group upon receipt shall initiate the COC. Identify this initiation by printing "INITIATED ON RECEIPT" on the COC form.

6.1.9 Compare the sample labels to the Chain of Custody; compare sample descriptions, collection dates, collection times, number of containers and any other available information. Note any discrepancies of the COC and the Sample Receipt Review form (SRR), and inform the Project Manager. Sign and date (including time) the COC in the appropriate box.

6.1.10 Analytical procedure may require preservation of the sample to ensure that changes in the samples chemistry or biology do not occur. The two predominant preservation techniques used are changing the pH of the sample and cooling the sample to about 4°C. It is important to check and document the holding time, preservation and temperature of the samples upon arrival to the laboratory. The correct methods of sample storage, chemical preservation, and maximum holding times are shown in Appendix 1. Those samples determined to be non-conforming shall be documented and the Project Manager notified.

Verify and document pH preservation using the following procedure:

6.1.10.1 Open the container.

6.1.10.2 Pour an aliquot of the original sample into a secondary container. Immerse a pH strip into the secondary container to take the measurement.

6.1.10.3 Observe the pH as indicated on the pH strip, and discard pH strip and secondary container.

NOTE: Never reuse a pH strip or one that has been contaminated.

6.1.10.4 Document results of the preservation verification on the appropriate line of the Sample Receipt Review form. (See Appendix 2 for example of a Sample Receipt Review form.)

NOTE: If the pH of the sample is determined to be non-conforming, place the sample on hold and notify the Project Manager. The Project Manager will call the client for further direction. If direction is given to adjust the preservation, continue processing the sample, and preserve the sample with the appropriate preservative (Appendix 1) recording the lot # of preservative used on the SRR. After adding the appropriate preservative to the sample, wait 2 minutes and perform steps 6.1.10.1 - 6.1.10.4 again. The preserved sample should now be placed on the preservation adjustment hold shelf located in the main cooler. This ensures that the 16-hour holding time for metals samples and the 24-hour holding time for radiochemistry samples is met following preservation or adjustment. Document this on the SRR: "SAMPLE PRESERVED UPON ARRIVAL."

6.1.10.6 Following is a list of tests that require pH verification upon arrival:

TEST	pH
Ammonia	<2
COD	<2
Cyanide	>12

Hardness	<2
Hydrazine	<2
Metals	<2
Nitrate/Nitrite	<2
Phenols	<2
Phosphates, Total	<2
Radiochemistry (all except Tritium, C-14, Rn-222, I-129, I-131)	<2
Sulfide	>9
TKN	<2
TOC/TIC/DOC	<2

NOTE: The pH of all aqueous sample fractions, preserved and unpreserved, shall be checked during sample login for the following DOE Albuquerque (DOE-AL) installations: (Exceptions to the pH check are Rn-222, tritium, iodine, VOC, TOX, oil and grease, and urine samples.)

- Los Alamos National Laboratories
- Mound Plant
- Pantex Plant
- Sandia National Laboratories, Albuquerque
- Sandia National Laboratories, Livermore

6.1.10.7 Sample receipt temperature is verified and documented upon using the following procedure:

6.1.10.7.1 Open the sample cooler.

6.1.10.7.2 Remove the Temperature Validation Container (TVC) if provided.

6.1.10.7.3 Open the TVC and immerse a thermometer with a valid calibration into the TVC.

6.1.10.7.4 Allow the thermometer reading to equilibrate, and read the thermometer result while it is still immersed in the TVC.

6.1.10.7.5 Alternately the receipt temperature can be measured with an infrared temperature (IR) gun with a valid calibration by selecting the TVC or another sample within the shipment.

6.1.10.7.6 Record the observed reading on the Sample Receipt Review form (Appendix 2), as well as on the COC if a space is provided: i.e. “TEMP. 4° UPON ARRIVAL.”

6.1.10.7.7 Temperature verification results of 4° ± 2°C, are considered conforming for those samples listed in Appendix 1 for 4°.

6.1.10.7.8 If the initial temperature verification results are determined to be non-conforming, select another sample container from the shipment for temperature verification and re-perform steps.

6.1.10.7.9 Record the verification temperature on the SRR as well as on the COC if a space is provided. Label the temperature as a verification temperature (i.e., VT=7°C).

6.1.10.7.10 If another container is not available within the shipment to verify the temperature, the secondary temperature verification is not performed and duly noted.

6.1.10.8 Project Managers may specify via client specific SRRs that aqueous organic analysis sample containers (excluding volatile 40-mL vials) be checked for the presence of chlorine residual at the time of sample receipt. If chlorine residual is present, document as such on the SRR and inform the Project Manager. The Project Manager may specify that samples with chlorine residual require the addition of $Na_2S_2O_3$.

6.1.11 Deliver the completed COC and SRR to the appropriate Project manager.

6.1.12 The Project Manager or Project Manager Assistant "logs" the data from the COC and SRR into ALPHALIMS. Once samples are logged into the system, unique bar code labels are generated for each sample container.

6.1.13 The bar code labels are ready to be affixed to the appropriate containers.

6.1.14 Sample bar code labels are color-coded as follows:

6.1.14.1 Yellow and magenta for radioactive samples.

6.1.14.2 Solid white for Federal Division non-radioactive samples

6.1.14.3 White and green for Industrial Division samples.

6.1.15 Compare the sample description on the printed GEL bar code label to the client sample bottle label before attaching labels to containers. You should not cover the client's label or any other information provided by the client or sample collector.

6.1.16 If the sample is a solid submitted for volatiles analysis and a single container is provided, a designation is generated on the barcode label indicating, "Volatiles must aliquot sample first." It is then stored in the appropriate volatile cooler until removed for volatiles testing. Once the volatiles lab takes its required aliquot the container will be marked with the analyst's initials and the date completed. The sample container will

then be placed in the appropriate walk in cooler and released for other laboratory analyses. Note exception in Section 6.2.2.1.

6.2 Sample Storage and Security

6.2.1 Once the samples have been properly labeled, the samples are placed in the appropriate storage areas. The storage areas are located within the laboratory area of the building. Access to the laboratory is limited to those with security clearance identification badges. Entrance into the laboratory is electronically monitored. All visitors to the building must sign in at the reception area where they will receive "Visitor" identification badges. Visitors must be escorted while they are in the laboratory.

The samples are scanned into the electronic tracking system. Containers are loaded into the system by container type and size (i.e., 1000 mL – nalgene), preservative (i.e., H_2S0_4), and storage area of destination.

6.2.2 Samples are placed in numerical order in the appropriate storage locations throughout the facility.

6.2.2.1 Samples requiring analysis of volatile organics shall be segregated from other samples by placing them in either the radioactive or non-radioactive coolers, which are located in the Volatiles area and maintained at 4° ± 2°C.

NOTE: Samples requiring volatile analyses known to contain high concentrations of organic solvents or hydrocarbons should not be stored in the volatiles coolers. Place these samples in either the general use walk-in cooler.

6.2.2.2 Samples requiring radiochemical analyses only (except radon) are stored, in numerical order, in ambient storage. Radioactive and Non Radioactive sample are segregated in these storage areas.

6.2.2.3 Samples required cold preservation (other than volatile organics samples) are stored, in numerical order, in general use walk-in coolers, which are maintained at 4° ± 2°C. Radioactive and non-radioactive samples are segregated in these storage areas.

6.2.3 The Sample Management Group monitors cooler temperature twice daily, every working day. Calibrated thermometers are located in each walk-in cooler and readings are taken once in the morning and once in the afternoon, no less than two hours apart. Contact the Group Leader if temperatures fall outside of acceptance ranges. Document all non-conformances and corrective actions in the temperature logs.

7.0 RECORDS MANAGEMENT

7.1 The Sample Receipt Review form is attached to the Chain of Custody and forwarded to the Project Manager.

7.2 Cooler temperature logs are reviewed each month by Quality Systems. At the end of the year, completed logs are forwarded to Quality Systems for archiving.

8.0 REFERENCES

8.1 Example Standard Operating Procedures for Contract Laboratory Program (CLP), National Enforcement Investigations Center (NEIC), Contract Evidence Audit Team (CEAT-TechLaw), EPA Contract 68-01-6838, 1986.

APPENDIX 1: STORAGE AND PRESERVATION

SAMPLE STORAGE AND PRESERVATION REQUIREMENTS

Parameter	Container[1]	Preservation	Holding Time[2]
Inorganics			
Acidity	P,G	4 Of C	14 days
Alkalinity	P,G	4 O C	14 days
Demand (BOD)	P,G	4 O C	48 hours
Bromide	P,G	None	28 days
Chemical Oxygen Demand (COD)	P,G	4 O C, H_2SO_4 to pH<2	28 days
Chlorine by Bomb	P,G	None	None
Chloride	P,G	None	28 days
Color	P,G	4 O C	48 hours
Conductivity	P,G	4 O C	28 days
Corrosivity by pH	**P**	**None**	**Immediate**
Corrosivity to Steel	P	None	None
Cyanide amenable to chlorination	P,G	4 O C, NaOH to pH>12, 0.6g ascorbic acid [3]	14 days [4]
Cyanide, total	P,G	4 O C, NaOH to ph>12, 0.6g ascorbic acid [3]	14 days [4]
Dissolved Oxygen	**G (bottle and tap)**	**None**	**Immediate**
Fixed and Volatile Solids	P,G	4 O C	7 days
Flashpoint	P,G	None	None
Fluoride	P	None	28 days
Hardness	P,G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
Heating Value	P	None	None
Hydrazine	**G**	**HC1 to pH<2**	**Immediate**
Percent (%) Moisture	P	4 O C	None
Ammonia Nitrogen	P,G	4 O C, H_2SO_4 to pH<2	28 days
Nitrate	P,G	4 O C	48 hours
Nitrite	P,G	4 O C	48 hours
Nitrate/Nitrite	P,G	4 O C, H_2SO_4 to pH<2	28 days
Total Kjeldahl and Organic Nitrogen	P,G	4 O C, H_2SO_4 to pH<2	28 days
Odor	**G**	**4 O C, Zero headspace**	**Immediate**
Oil and Grease	G	4 O C, HC1 or H_2SO_4 to pH<2	28 days
Orthophosphate	**P,G**	**Filter immediately, 4 O C**	**48 hours**
Total Phenols	G	4 O C, H_2SO_4 to pH<2	28 days
pH	**P,G**	**None**	**Immediate**
Total Phosphorus	P,G	4 O C, H_2SO_4 to pH<2	28 days
Residual Chlorine	**P,G**	**None**	**Immediate**
Salinity	P	None	28 days
Specific Gravity	P	4 O C	7 days
Sulfate	P,G	4 O C	28 days
Sulfide	P,G	4 O C, add ZNAce and NaOH to pH>9	7 days
Sulfite	**P,G**	**None**	**Immediate**
Sulfur by Bomb	G	None	None
Surfactants	P,G	4 O C	48 hours
Settleable Solid	P,G	4 O C	48 hours
Total Dissolved Solid	P,G	4 O C	7 days
Total Solid	P,G	4 O C	7 days
Total Suspended Solid	P,G	4 O C	7 days
Volatile Solid	P,G	4 O C	7 days
Total Organic Carbon	P,G	4 O C,HCl or H_2SO_4 to pH<2	28 days
Total Organic Halides	G	4 O C, H_2SO_4 to pH<2	28 days
Total Petroleum Hydrocarbons	G	4 O C, H_2SO_4 to pH<2	28 days
Turbidity	P,G	4 O C	48 hours
Metals (except chromium VI and mercury)	P	4 O C,HNO_3 to pH<2	6 months
Chromium VI - Aqueous	P	4 O C	24 hours

Chromium VI - Solids	P	$4^{O}C$	7 days for extraction
Mercury - Wastewater and Drinking water	P,G	$4^{O}C$,HNO_3 to pH<2	28 days
Mercury - Others	G	$4^{O}C$,HNO_3 to pH<2	28 days
Bacteriology			
Coliform, fecal	P,G	4, 0.008% $Na_2S_2O_3$ [3]	6 hours
Standard Plate Count	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	24 hours
Coliform, total - Wastewater	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	6 hours
Coliform, total - Groundwater	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	24 hours
Organics			
Base/Neutral and Acid Extractables - Water	Amber G, teflon-lined cap	$4^{O}C$ 0.008% sodium thiosulfate solution	7 days for extraction 40 days after extraction for analysis
Base/Neutral and Acid Extractables - Solid and Waste	G, teflon-lined cap	$4^{O}C$	14 days for extraction 40 days after extraction for analysis
Base/Neutral and Acid Extractables - Concentrated Waste	G, teflon-lined cap	None	7 days for extraction 40 days after extraction for analysis
BTEX - Solid and sludge	G, teflon-lined septum	$4^{O}C$	14 days
BTEX - Water	G, teflon-lined septum	$4^{O}C$, 0.008% $Na_2S_2O_3$, zero headspace	14 days
TPH-GRO	G, teflon-lined cap	$4^{O}C$, HCl to pH s, zero headspace	14 days
TPH-DRO	G, teflon-lined cap	$4^{O}C$	14 days
Volatiles - Groundwater	G, teflon-lined cap	$4^{O}C$, HCl to pH s, zero headspace	14 days
Chlorinated Herbicides - Water	Amber G, teflon-lined cap	$4^{O}C$ 0.008% sodium thiosulfate solution	7 days for extraction 40 days after extraction for analysis
Chlorinated Herbicides - Solid and Waste	G, teflon-lined cap	$4^{O}C$	14 days for extraction 40 days after extraction
Volatiles - Drinking Water	G, teflon-lined cap	$4^{O}C$, 0.008% $Na_2S_2O_3$[3], zero headspace	14 days
Volatiles (excluding 2 chloroethylvinylether) - Wastewater	Encore Sampler	$4^{O}C$, zero head-space, HC1 to pH 2	14 days
Volatiles - Wastewater	G, teflon-lined cap	$4^{O}C$, 0.008% $Na_2S_2O_3$[3], zero headspace	7 days
Volatiles - Solid and Sludge -	Encore Sampler	$4^{O}C$	14 days
Volatiles - Concentrated Waste	G, teflon-lined septum	None	14 days
Industrial Solvents	G, teflon-lined septum	$4^{O}C$	None
Organochlorine Pesticides and PCBs	Amber G, teflon-lined cap	$4^{O}C$ 0.008% sodium thiosulfate solution	7 days for extraction 40 days after extraction for analysis
PCBs in Oil	G, teflon-lined cap	None	7 days for extraction 40 days after extraction for analysis
Dioxin	G, teflon-lined cap	$4^{O}C$	7 days for extraction 40 days after extraction for analysis
Total Petroleum Hydrocarbon	G, teflon-lined septum	$4^{O}C$	14 days
Coliform, total - Drinking water	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	30 hours
Radiochemistry			
Carbon-14 - Water and Soil	P	$4^{O}C$	6 months
Gamma Isotopes - Water	P	HNO_3 to pH-2	6 months
Gamma Isotopes - Soil	P	None	6 months
Gross Alpha and Beta - Water	P	HNO_3 to pH-2	6 months

Gross Alpha and Beta - Soil	P	None	6 months
Iodine-129 - Water and Soil	P	None	6 months
Iodine -131 - Water	P	None	6 months
Neptunium - Water	P	HNO_3 to pH-2	6 months
Neptunium - Soil, Vegetation, and Air Filters	P	None	6 months
Plutonium - Water	P	HNO_3 to pH-2	6 months
Plutonium - Soil, Vegetation, and Air Filters	P	None	6 months
Thorium - Water	P	HNO_3 to pH-2	6 months
Thorium - Soil, Vegetation, and Air Filters	P	None	6 months
Uranium - Water	P	HNO_3 to pH-2	6 months
Uranium - Soil, Vegetation, and Air Filters	P	None	6 months
Americium - Water	P	HNO_3 to pH-2	6 months
Americium - Soil, Vegetation, and Air Filters	P	None	6 months
Curium - Water	P	HNO_3 to pH-2	6 months
Curium - Soil, Vegetation, and Air Filters	P	None	6 months
Lead-210 - Water	P	HNO_3 to pH-2	6 months
Nickel-59 - Water and Soil	P	None	6 months
Nickel-63 - Water and Soil	P	None	6 months
Phosphorus-32 -Water	P	HNO_3 to pH-2	6 months
Phosphorus-32 -Soil	P	None	6 months
Polonium -Water	P	HNO_3 to pH-2	6 months
Polonium -Soil	P	None	6 months
Promethium-147 -Water	P	HNO_3 to pH-2	6 months
Promethium-147 -Soil	P	None	6 months
Radium-223 - Water	P	None	6 months
Radium-224 - Water	P	None	6 months
Radium-226 - Water	P	HNO_3 to pH-2	6 months
Radium-228 - Water	P	HNO_3 to pH-2	6 months
Radon-222 - Water	40ml volatile bottle	4^OC, Zero headspace	7 days
Radon-222 - Soil	P	4^OC	6 months
Strontium-89/90 -Water	P	HNO_3 to pH-2	6 months
Strontium-89/90 -Soil	P	None	6 months
Technetium-99 -Water	P	HNO_3 to pH-2	6 months
Technetium-99 -Soil	P	None	6 months
Total Alpha Radium -Water	P	HNO_3 to pH-2	6 months
Total Alpha Radium -Soil	P	None	6 months
Total Uranium -Water	P	HNO_3 to pH-2	6 months
Tritium - Water, Soil, Vegetation, and Air Filters	P	4^OC	6 months
Iron 55 -Water	P	HNO_3 to pH-2	6 months
Iron 55 -Soil	P	None	6 months
Total Uranium -Soil	P	None	6 months

[1] P = Polyethylene; G = Glass
[2] Samples should be analyzed as soon as possible after collection. The holding times listed are maximum times that samples may be held before analysis and be considered valid.
[3] Used only in the presence of residual chlorine.
[4] Maximum holding time is 24 hours when sulfide is present. All samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If present, remove by adding cadmium nitrate powder until a negative spot test is obtained. Filter sample and add NaOH to pH12.

APPENDIX 2: SAMPLE RECEIPT REVIEW SHEET

SAMPLE RECEIPT & REVIEW FORM

PM use only

Client:	**SDG/ARCOC/Work Order:**
Date Received:	**PM(A) Review (ensure non-conforming items are resolved prior to signing):**
Received By:	

	Sample Receipt Criteria	Conforming	NA	Non-Conforming	Comments/Qualifiers (Required for Non-Conforming Items)
1	Shipping containers received intact and sealed?				Circle Applicable: seals broken damaged container leaking container other (describe)
2	Samples requiring cold preservation within (4 +/- 2 C)? Record preservation method.				Circle Temp device serial # ice bags blue ice dry ice none other(describe)
3	Chain of custody documents included with shipment?				
4	Sample containers intact and sealed?				Circle Applicable: seals broken damaged container leaking container other (describe)
5	Samples requiring chemical preservation at proper pH?				Sample ID's, containers affected and observed pH:
6	VOA vials free of headspace (defined as < 6mm bubble)?				Sample ID's and containers affected:
7	Samples received within holding time?				Id's and tests affected:
8	Sample ID's on COC match ID's on bottles?				Sample ID's and containers affected:
9	Date & time on COC match date & time on bottles?				Sample ID's affected:
10	Number of containers received match number indicated on COC?				Sample ID's affected:
11	COC form is properly signed in relinquished/received sections?				
12	Air Bill ,Tracking #'s, & Additional Comments				

Radiological Information	Non-RAD	RAD	RADI	RSO RAD Receipt #
What is the radiological classification of the samples?				Comments:
Radioactivity Screening Results (maximum observed CPM)				*If > x2 area background is observed on a non-radioactive sample, contact the RSO to investigate.

PM (or PMA) review of Receiving Rad classification: _____ Initials _____ Date

APPENDIX 3

BIOASSAY SAMPLE RECEIPT REVIEW

CLIENT_____

GEL COOLER _____ CLIENT COOLER_____ OTHER_____

SAMPLE REVIEW CRITERIA	YES	NO	COMMENTS/QUALIFIERS
Were shipping containers received intact and sealed?			
Were chain of custody documents included?			
Were chain of custody documents completed correctly?			
Were all sample containers properly labeled?			
Were all sample containers received?			
Were samples received within holding time?			
Were the sample containers 500 mL or less?			
For KHCO - Did the sample ID and the customer number match the			
Chain of custody?			

Signature:_____ Date:_____

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF PLUTONIUM, URANIUM, AMERICIUM, CURIUM, AND THORIUM

2.0 METHOD OBJECTIVE AND APPLICABILITY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for isotopic plutonium, uranium, americium, and thorium in variety of matrices.

2.2 A sample is aliquoted and if necessary digested. Actinide elements are scavenged by co-precipitation with iron hydroxide. The precipitate is dissolved and separation of elements is accomplished through ion exchange resins and solid phase extraction. The elements are then prepared for the measurement of radioactive isotopes by co-precipitation with Neodymium fluoride. The Neodymium fluoride precipitate is trapped on a filter, mounted on a stainless steel disk and placed in a partially evacuated chamber for measurement of isotopic alpha emission.

2.3 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

3.0 METHOD APPLICABLITY

3.1 Method Detection Limit: Typical minimum detectable activity (MDA) for samples analyzed for plutonium, uranium, and thorium is 1 pCi/L or 1 pCi/g.

3.2 Method Precision: Typical relative percent difference (RPD) is 20%.

3.3 Method Bias (Accuracy): Acceptable criteria for method accuracy, measured by running with each batch a laboratory control sample, is ±25% of true value.

3.4 Analysts are trained and certified to run this analysis after the analyst has completed a batch with acceptable duplicate and laboratory control sample, as well as completed an unknown sample within ±25% of true value. Analyst training records are kept on hand in the Human Resources department.

4.0 DEFINITIONS

4.1 National Institute of Standards and Technology (NIST). For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

4.2 Type II water: Deionized (DI) water.

4.3 ALPHA LIMS: Laboratory Information Management System. The database system used to store and report data.

5.0 METHOD VARIATIONS

Some variation may be necessary due to special matrices encountered in the laboratory. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

6.0 SAFETY PRECAUTIONS AND WARNINGS

6.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health & Chemical Hygiene Plan, GL-LB-N-001.

6.2 Personnel handling Radioactive Materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

6.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for Handling Biological Materials.

6.4 If there is any question regarding the safety of any laboratory practice, **stop immediately,** and consult senior qualified personnel such as a Group or Team Leader.

7.0 INTERFERENCES

7.1 Internal tracer standards may have ingrown daughters that may interfere with the analysis. For example, Th-228 will be present in aged U-232 standard. This problem is overcome by using a self-cleaning U-232 tracer that utilizes barium sulfate to remove the Th-228.

7.2 Uranium and Thorium may not be run together if U-236 is used as a tracer due to the decay of U-236 to Th-232. The U-236 tracer does not currently utilize a barium sulfate clean-up to remove Th-232.

7.3 Short-lived radioactive progeny may ingrow on prepared filters. For example, the Ra-224 alpha peak will be present if the Th-228 parent is present. Counting samples as soon as possible after separation chemistry is completed minimizes this interference.

7.4 When present, Th-228 alpha energies interfere with the proper quantification of Pu-238. Steps are taken to ensure that the final plutonium counting sources are free from thorium interference.

7.5 Pu-236 decays to U-232 therefore Pu-236 may not be used as a tracer for this method.

8.0 APPARATUS, MATERIALS, REAGENTS, EQUIPMENT, AND INSTRUMENTATION

8.1 Ancillary Equipment

8.1.1 Ion exchange columns
8.1.2 Polypropylene centrifuge tube (50 mL)
8.1.3 Sample drying apparatus
8.1.4 Sample homogenizing apparatus
8.1.5 AG1X8 anion exchange resin, 100 – 200 mesh
8.1.6 Eichrom Technologies TRU Resin, 100 – 200 mesh
8.1.7 Silicon surface barrier detectors with associated electronics, vacuum chambers, and data reduction capabilities
8.1.8 Vacuum pump and filtration apparatus (25 mm)
8.1.9 Gelman 25 mm filters with 0.1 µ pore size
8.1.10 Gelman polypropylene 25 mm support filter
8.1.11 Stainless steel disks, 29 mm
8.1.12 Stainless steel tweezers
8.1.13 Hotplate

8.2 Reagents, Chemicals, and Standards

8.2.1 Ammonium hydroxide concentrated (14 N).
8.2.2 Neodymium (500 mg/L)
8.2.3 Carbon Colorant. Place two 47mm cellulose nitrate filters in a beaker and add 5mL concentrated H_2SO_4. Cover and heat on a hot plate until fumes of H_2SO_4 appear. Cool. Slurry the residue in DI water and dilute to 1L with DI water.
8.2.4 Sulfuric acid concentrated (18N)

8.2.5 Hydrochloric acid concentrated (12 M).

8.2.6 Iron Carrier (10mg/mL). Dissolve 62.7 g of $Fe(NO_3)_3 \bullet 6H_20$ or 72.3 g $Fe(NO_3)_3 \bullet 9H_20$ in 800 mL DI water and dilute to 1 L with DI water.

8.2.7 Hydrochloric acid (9 M). Dilute 750 mL of concentrated hydrochloric acid to 1 L with DI water.

8.2.8 Hydrochloric acid (6 M). Dilute 500 mL of concentrated hydrochloric acid to 1 L with DI water.

8.2.9 Hydrochloric acid (4 M). Dilute 333 mL of concentrated hydrochloric acid to 1 L with DI water.

8.2.10 Hydrochloric acid (2 M). Dilute 167 mL of concentrated hydrochloric acid to 1 L with DI water.

8.2.11 Hydrochloric acid (0.1 M). Dilute 8.3 mL of concentrated hydrochloric acid to 1 L with DI water.

8.2.12 Hydrogen peroxide (30%).

8.2.13 Hydrazine dihydrochloride (25%). Dissolve 25 g of hydrazine dihydrochloride in 75 mL of DI water.

8.2.14 Hydrofluoric acid concentrated (49%).

8.2.15 Ethyl alcohol (80%). Dilute 400 mL ethanol to 500 mL with DI water.

8.2.16 NIST traceable standards: Pu-242, Pu-238, Pu-239, Th-229, Th-230, Th-232, U-232, U-236, U-238, Am-243, Am-241, Cm-244

8.2.17 Nitric acid concentrated (16 M).

8.2.18 6 M Hydrochloric acid / 0.52 M Hydrofluoric acid. Dilute 500 mL concentrated hydrochloric acid and 16.8 mL concentrated hydrofluoric acid to 1 L with DI water.

8.2.19 9 M Hydrochloric acid / 0.05 M Ammonium iodide. Dissolve 7.24 g of ammonium iodide in 750 mL concentrated hydrochloric acid and dilute to 1 L with DI water. PREPARE DAILY.

8.2.20 9 M Hydrochloric acid / 0.04% Hydrogen peroxide. Add 8 drops of 30% H_2O_2 to 1 L 9M hydrochloric acid. PREPARE DAILY.

8.2.21 1 M Hydrochloric acid / 0.05 M Oxalic acid. Dissolve 6.3 g Oxalic acid in 83.5 mL Hydrochloric acid and dilute to 1 L with DI water.

8.2.22 Titanium (III) Chloride. 20% reagent

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples should be preserved to approximately pH 2 with nitric acid and collected in a plastic bottle.

9.2 Before beginning an analysis the analyst should check the sample pH with a pH strip. If necessary, adjust the pH with nitric acid to a pH 1 – 2. If the sample was pH adjusted let the sample sit overnight before continuing the batch.

9.3 If the sample has exceeded the hold time the analyst should contact the Group Leader or Team Leader before continuing with the batch.

9.4 Soil samples require no preservation and may be shipped in any suitable container.

10.0 SAMPLE PREPARATION

10.1 Soil Sample Preparation

10.1.1 If not already done, prepare the sample by performing GL-RAD-A-021 "Preparation of Soils for the Determination of Radionuclides".

10.1.2 It is recommended that the samples be ashed in a muffle furnace by performing GL-RAD-A-021B "Soil Sample Ashing for the Determination of Radionuclides".

10.1.3 For plutonium, uranium, and thorium analysis, take an appropriate aliquot and digest as specified in GL-RAD-A-015 "Digestion for Soils and Sand".

10.1.4 Proceed to step 10.2.5.

10.2 Aqueous Sample Preparation

10.2.1 Add an appropriate aliquot of sample to a labeled beaker. Add a certified dpm of appropriate tracers to each sample.

NOTE: Other sample matrices, such as vegetation, air filters, tissue etc. are run as outlined in GL-RAD-A-026 "Preparation of Special Matrices for the Determination of Radionuclides".

10.2.2 Add 1 mL of iron carrier.

10.2.3 Bring to a slight boil and add concentrated NH_4OH until turbidity persists, or pH > 9. Heat to boiling for 10 minutes and then allow to settle and cool.

10.2.4 Decant excess supernate and discard. Collect the remaining precipitate by centrifugation in a 50 mL centrifuge tube and discard the supernate.

NOTE: Exercise care in this step because finely divided material that contains the actinides may also be present in addition to the large iron hydroxide flocks.

10.2.5 Dissolve the precipitate from 10.2.4 or the residue from 10.1.4 in 10 mL of 9 M HCl / 0.04% H_2O_2.

NOTE: Samples may be dissolved with 10 to 15 mL of 9M HCl and then add 1 drop of 30% H_2O_2 as an alternative to dissolving with 9M HCl/0.04% H_2O_2.

NOTE: The load solution needs to be 10 mL due to limitations of the americium portion of this procedure. If the load solution needs to be increased then refer to GL-RAD-A-011 for the determination of americium, plutonium, and uranium.

10.2.6 Slurry AG 1X8 anion resin (Cl^- form 100 – 200 mesh) in a squirt bottle with DI water. Transfer the resin to a small column to obtain a settled resin bed of 2.5 mL.

10.2.7 Condition the column with 10 mL 9 M HCl. Catch in a drip pan for disposal.

10.2.8 Pass the sample solution for step 10.2.5 through the column and catch the effluent in a labeled, disposable 50 mL centrifuge tube for americium and thorium analysis.

10.2.9 Rinse the column with 5 mL of 9 M HCl and catch in centrifuge tube for americium and thorium analysis. Proceed to step 10.2.15 for americium and thorium analysis.

10.2.10 Rinse the column with 15 mL of 9 M HCl and catch in a drip pan for disposal.

10.2.11 Elute plutonium with 15 mL 9 M HCl / 0.05 M NH_4I catching in a clean, labeled, disposable centrifuge tube. Proceed to step 10.2.21 for plutonium micro-precipitation source preparation for alpha spectroscopy.

10.2.12 Rinse the column with 15 mL of 6 M HCl / 0.52 M HF and catch in a drip pan for disposal.

10.2.13 Rinse the column with 5 mL of 6 M HCl and catch in a drip pan for disposal.

10.2.14 Elute uranium from the column by adding 15mL of 0.1M HCl, catching the uranium elute in a labeled, disposable 50mL centrifuge tube.

10.2.14.1 Transfer sample to a clean beaker with DI water and evaporate to dryness over low heat.

10.2.14.2 Dissolve sample with 4mL of 2M HCl. Transfer to a clean centrifuge tube with DI water.

10.2.14.3 Proceed to step 10.2.23 for uranium microprecipitation source preparation for alpha spectroscopy.

10.2.15 Precondition a 2 mL TRU column with 5 mL of 9 M HCl.

10.2.16 Pass the sample solution from step 10.2.9 through the column catching in a drip pan for disposal.

10.2.17 Rinse the column with 5 mL of 9 M HCl catching in a drip pan for disposal.

10.2.18 Elute Americium and Curium with 20 mL of 4 M HCl catching in a clean, labeled, disposable centrifuge tube. Proceed to step 10.2.24 for americium and curium micro-precipitation source preparation for alpha spectroscopy.

NOTE: If Americium and Curium are not required then catch this rinse in a drip pan for disposal.

10.2.19 Elute Thorium with 20 mL of 1 M HCl / 0.05 M Oxalic acid catching in a clean, labeled, disposable centrifuge tube.

10.2.20 Add 0.1 mL Neodymium (500 mg/L) to the solution and swirl to mix. Add 2 mL concentrated Hydrofluoric acid and swirl. Allow the solution to sit for 30 minutes then proceed to Step 10.2.28 for source preparation.

10.2.21 Transfer the plutonium solution from step 10.2.11 to a clean beaker. Add 4 drops of iron carrier (10 mg/mL) and 10 mL of concentrated nitric acid. Evaporate the solution to dryness on medium to low heat. Dissolve the residue with 4 mL of 2 M HCl. Use DI water to transfer the solution to a centrifuge tube.

10.2.22 Add 0.1 mL of Neodymium (500 mg/L) and swirl. Add 3 to 4 drops of 25% Hydrazine dihydrochloride and swirl to mix. Let the solution sit for 10 minutes, then add 2 mL of 49% Hydrofluoric acid. Swirl to mix. Allow to sit for 30 minutes, then proceed to step 10.2.28 for source preparation.

10.2.23 To the uranium solution from step 10.2.14, add 1 mL of titanium trichloride solution and allow the sample to sit for 30 seconds. Add 0.1 mL of Neodymium (500 mg/L) and swirl to mix. Add 2 mL of concentrated hydrofluoric acid to precipitate fluorides. Allow the solution to sit for 30 minutes, then proceed to step 10.2.28 for source preparation.

10.2.24 Transfer the Am/Cm elution from step 10.2.18 to a clean beaker. Add 4 drops of iron carrier and gently cook dry.

10.2.25 Add 10 mL of concentrated Nitric acid and 2 mL of 30% Hydrogen peroxide, cover and reflux until evolution of gas bubbles ceases. Remove the cover and gently cook dry.

10.2.26 Dissolve the residue in 4 mL of 2 M HCl with gentle heating. If residue does not dissolve repeat Step 10.2.25. Cool and transfer to a clean disposable centrifuge tube using 1 to 2 mL of DI water to rinse the beaker.

10.2.27 Add 0.1 mL Neodymium (500 mg/L) to the solution and swirl to mix. Add 2.0 mL concentrated Hydrofluoric acid and swirl. Allow the solution to sit for 30 minutes then proceed to Step 10.2.28 for source preparation.

10.2.28 Place a 25mm 0.1µm filter on the filter support screen. Wet the filter with 80% ethyl alcohol. Center the filter on the filter support screen and apply vacuum.

10.2.29 Place the filter funnel on the filter stem. Tighten firmly, being careful not to wrinkle the filter.

10.2.30 Rinse the funnel with 80% ethyl alcohol.

10.2.31 Add 1 mL of the carbon colorant.

10.2.32 Filter the fluoride precipitated solution through the filter paper. Rinse the centrifuge tube with ≈ 5 mL DI water and pass through filter.

10.2.33 Rinse the centrifuge tube with ≈ 5 mL 80% ethyl alcohol and pass through filter.

10.2.34 Rinse the funnel with 80% ethyl alcohol.

Caution – Directing a stream of liquid onto the filter will disturb the distribution of the precipitate on the filter and render the sample unsuitable for alpha spectrometry resolution.

10.2.35 Without turning off the vacuum, remove the funnel.

10.2.36 Turn off vacuum and remove filter. Mount filter on a labeled 29mm flat planchet. Ensure that the filter is centered and as flat as possible on the planchet.

NOTE: Care should be taken not to touch the active area of the filter with tweezers.

10.2.37 Place the mounted filter under a heat lamp for 5 minutes prior to alpha spectrometry measurement.

10.2.38 Count under vacuum on the alpha spectrometer long enough to reach requested MDA. Consult the operating manual for instruction on operating the alpha spectrometer.

11.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL STANDARDS

Refer to “Preparation of Radioactive Standards” (GL-RAD-M-001).

12.0 INSTRUMENT CALIBRATION AND PERFORMANCE

For direction on calibration and instrument performance see “The Alpha Spectroscopy System” (GL-RAD-I-009).

13.0 ANALYSIS AND INSTRUMENT OPERATION

For analysis and instrument operation see "The Alpha Spectroscopy System" (GL-RAD-I-009).

14.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

For maintenance of system see "Counting Room Instrumentation Maintenance and Performance Checks" (GL-RAD-I-010).

15.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

15.1 The instrument will report sample pCi/unit according to the following equation:

$$\text{pCi / unit} = \frac{S_{cpm} - B_{cpm}}{2.22 * E * V * A * decay * R}$$

15.2 Counting uncertainty is propagated according to the following equation:

$$\text{pCi / unit} = Ac * 1.96\sqrt{\left(\frac{ef\_er}{E}\right)^2 + \left(\frac{pk\_er}{pk}\right)^2 + \left(\frac{ab\_er}{A}\right)^2 + \left(\frac{sy}{100}\right)^2 + (dk)^2}$$

15.3 The minimum detectable activity (MDA) is calculated according to the following equation:

$$MDA(\text{pCi / unit}) = \frac{2.71 + 4.65 * \sqrt{B_{cpm} * T_c}}{(2.22 * E * V * R * A * decay * T_c)}$$

Where:

$$decay = e\left(\frac{-1n(2)T_d}{T_{1/2}}\right)$$

$$R = \frac{T_{cpm} - B_{cpm}}{T_{dpm} * E}$$

$$dk = \frac{T_{1/2}err}{T_{1/2}} * \left(\frac{\lambda Tr}{1 - e^{-\lambda Tr}} - \lambda\left(T_c + T_r\right) - 1\right)$$

And where:

S_{cpm}	=	Sample counts per minute
B_{cpm}	=	Background counts per minute
E	=	Counting efficiency (decimal form)
V	=	Volume in liters, g, cfm, etc.
A	=	Isotopic abundance (decimal form)
ef_er	=	1 sigma efficiency error (decimal form)
pk_er	=	1 sigma peak error
ab_er	=	1 sigma isotopic abundance error (decimal form)
sy	=	1 sigma systematic error
pk	=	peak area
Tc	=	Sample count time in minutes
Td	=	Time interval for radioactive decay

Tr	=	Elapsed real time in minutes
T_{cpm}	=	Tracer counts per minute
T_{dpm}	=	Tracer known disintegrations per minute
Ac	=	Sample calculated activity
T1/2	=	Isotopic half life
T1/2err	=	Isotopic half life error
λ	=	Isotopic decay constant
E	=	exponential function
R	=	Tracer Recovery
ln	=	natural log function

15.4 Record the following information on the alpha que sheet: preparation date, analyst initials, spike isotope, spike code, spike volume, LCS isotope, LCS code, LCS volume. For each sample record the detector number, sample mass, sample date, and sample time.

16.0 QUALITY CONTROL REQUIREMENTS

16.1 Analyst and Method Verification

16.1.1 Refer to "Analytical Methods Validation for Radiochemistry" (GL-RAD-D-002) for instructions concerning the validation of analysts and analytical methods.

16.2 Method Specific Quality Control Requirements

16.2.1 A method blank will accompany each batch of 20 or less samples. The reported value should be less than or equal to the CRDL for all target isotopes.

16.2.2 A matrix spike (MS) should be run with every batch of 20 samples. The recovery of the spike should fall between 75 and 125%. The recovery is calculated as follows:

$$\%Rec = \frac{spike(pCi/unit) - sample(pCi/unit)}{spiked amount(pCi/unit)} * 100$$

16.2.3 A sample duplicate should be run with every batch of 20 or less samples. The relative percent difference (RPD) between the sample and the duplicate should be less than or equal to 20%. The RPD is calculated as follows.

$$RPD = \frac{high sample(pCi/unit) - low sample(pCi/unit)}{Average\ (pCi/unit)} * 100$$

16.2.4 A laboratory control spike (LCS) should be run with every batch of 20 samples or less. The recovery of the spike should fall between 75 and 125%. The recovery is calculated as follows:

$$LCS = \frac{observed\_pCi/unit}{known\_pCi/unit} * 100$$

16.3 Actions required if the Quality Control Requirements are not met

16.3.1 If any of the above criteria cannot be satisfied, the analyst should inform the Group Leader and initiate a non-conformance report as outlined in "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

Refer to "Data Review, Validation and Data Package Assembly" (GL-RAD-D-003) for instructions concerning the data review process, approval, and transmittal.

18.0 RECORDS MANAGEMENT

18.1 All raw data, calculation spreadsheets and batch checklists are filed with the sample data and maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

18.2 Each analysis that is performed on the instrument is documented in the run log according to "Run Logs" (GL-LB-E-009).

18.3 All raw data printouts, calculation spreadsheets and batch checklists are filed with the sample data for archival and review.

19.0 LABORATORY WASTE HANDLING AND WASTE DISPOSAL

Radioactive samples and material shall be handled and disposed of as outlined in the Laboratory Waste Management Plan (GL-LB-G-001).

20.0 REFERENCES

20.1 EPA Environmental Monitoring and Support Laboratory. Las Vegas. Radiochemical Analytical Procedures for Analysis of Environmental Samples. March 1979.

20.2 EML Procedures Manual HASL-300, 1982.

20.3 DOE Methods Manual for Evaluating Environmental and Waste Management Samples, 1997 Edition, RP800, "Sequential Separation of Americium and Plutonium by Extraction Chromatography".

20.4 Analytical Chemistry. Rapid Determination of Th-230 in Mill Tailings by alpha spectroscopy. UNC Geotech, Grand Junction Projects Office. Steve Donivan, Mark Hollenbach, and Mary Costello. Vol. 59, No. 21, 1987.

20.5 Los Alamos Health and Environmental Chemistry: Analytical Techniques. LA-10300-M Vol. 1, September 1987.

APPENDIX 1

PLUTONIUM, URANIUM, AMERICIUM, CURIUM, and THORIUM

Use a 2.5 cm^3 column with 1X8 anion resin (Cl^- form 100-200 mesh)

COLUMN WORK

____ 10mL 9M HCl (Conditioning)

____ Load solution: 10mL 9M HCl / 0.04% H_20_2 (Catch in C-Tube for Am/Cm)

____ 5mL 9M HCl (Catch in C-Tube for Am/Cm/Th then proceed to Appendix 2 for Am/Cm/Th procedure)

____ 15mL 9M HCl (Rinse)

____ **Elute** Pu: 15mL 9M HCl / 0.05M NH_4I (Catch in C-Tube then proceed to Plutonium Cook-down)

____ 15mL 6M HCl / 0.52M HF (Rinse)

____ 5mL 6M HCl (Rinse)

____ **Elute** U: 15mL 0.1M HCl (Catch in C-Tube)

____ Transfer to a clean beaker and evaporate to dryness

____ Dissolve with 4mL of 2M HCl and transfer to centrifuge tube with DI water.

____ Proceed to Appendix 3 for Uranium Precipitation

PLUTONIUM COOK-DOWN

____ Transfer to a clean beaker. Add 4-6 drops of Fe carrier, 10 mL of [HNO_3], and evaporate the solution to dryness on medium heat.

____ Dissolve with 4 mL of 2 M HCl and transfer to centrifuge tube with DI water.

____ Proceed to Appendix 3 for Plutonium Precipitation

APPENDIX 2

AMERICIUM / CURIUM / THORIUM CONTINUATION

Use a 2.5 cm^3 column with TRU Resin, 100 – 200 mesh

AMERICIUM / CURIUM / THORIUM

____ 5mL 9M HCl (Conditioning)

____ Load Solution from Appendix 1 (Catch in drip pan)

____ 5mL 9M HCl (Rinse)

____ **Elute** Am/Cm: 20mL 4M HCl (Catch in C-Tube)

____ Transfer to a clean beaker. Add 4-6 drops of Fe carrier, and gently cook dry

____ 10mL [HNO_3] and 2mL 30% H_2O_2, reflux, then gently cook dry

____ Dissolve with 4mL of 2M HCl and transfer to centrifuge tube with DI water

____ Proceed to Appendix 3 for Am/Cm precipitation

____ **Elute** Th: 20mL 1M HCl / 0.05M Oxalic acid (Catch in C-Tube)

____ Proceed to Appendix 3 for Th precipitation

APPENDIX 3

AMERICIUM / CURIUM PRECIPITATION

____ 0.1mL 500mg/L Neodymium and swirl
____ 2mL 49% HF and swirl
____ Wait 30 minutes
____ Filter

PLUTONIUM PRECIPITATION

____ 0.1 mL 500mg/L Neodymium and swirl
____ 3 – 4 drops 25% Hydrazine dihydrochloride and swirl
____ Wait 10 minutes
____ 2mL 49% HF and swirl
____ Wait 30 minutes
____ Filter

URANIUM PRECIPITATION

____ 0.1 mL 500mg/L Neodymium and swirl
____ 1 mL Titanium chloride and swirl
____ Wait 30 seconds
____ 2mL 49% HF and swirl
____ Wait 30 minutes
____ Filter

THORIUM PRECIPITATION

____ 0.1mL 500mg/L Neodymium and swirl
____ 2mL 49% HF and swirl
____ Wait 30 minutes
____ Filter

ATTACHMENT B

ENSR DATA VALIDATION PROTOCOLS

Full: _____ ENSR Data Pkg#: _____

Limited: _____ Site Name: _____

Project Number: _____

REVIEW OF DIOXIN/FURAN DATA PACKAGE

The following guidelines for evaluating dioxins and/or furans were created to delineate required validation actions. This document will assist the reviewer in using professional judgment to make more informed decisions and in better serving the needs of the data users. Quality control validation criteria were derived from United States Environmental Protection Agency (USEPA) publications: *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846* (Final Update III, December 1996), specifically SW-846 Method 8290 *Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)*. Validation actions were derived from *USEPA Analytical Operations/Data Quality Center (AOC), National Functional Guidelines For Chlorinated Dioxin/Furan Data Review,* (Final August 2002).

The hardcopied (laboratory name) _____ data package has been reviewed and the quality assurance and performance data summarized.

The data review for dioxins/furans included the following samples:

Lab Project No. _____ Sampling Date(s) _____

No. of Samples _____ Shipping Date(s) _____

Sample Matrix _____ Date(s) Rec'd by Lab _____

Equipment Blank IDs: _____

_____

Field Blank IDs: _____

_____

Field Duplicate IDs: _____

_____

The general criteria used to determine the performance were based on an examination of the following:

___ Data Completeness
___ Holding Times
___ GC/MS Performance Checks
___ Calibrations
___ Blanks
___ Matrix Spike/Matrix Spike Duplicate
___ Laboratory Control Sample
___ Field Duplicates
___ Internal Standard Recoveries
___ Compound Identification
___ Compound Quantification
___ Percent Solids

Overall Comments: _____

_____

_____

_____

_____

Reviewer: _____ Date: _____

NATIONAL FUNCTIONAL GUIDELINES DIOXIN/FURAN DATA QUALIFIER DEFINITIONS

U - The analyte was analyzed for but not detected.

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”.

NJ - 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. However, the reported detection limit is approximated and may be inaccurate or imprecise.

R - The sample results are unusable. The analyte may or may not be present in the sample.

All criteria were met: ____
Criteria were not met, and/or see below: _____

I. DATA COMPLETENESS

A. Data Package:

Missing Information	Date Lab Contacted	Date Received

B. Other Discrepancies:

II. HOLDING TIMES

The objective of this parameter is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of extraction, and subsequently from the time of extraction to the time of analysis.

Complete table for all samples and circle the extraction and/or analysis date for samples not within criteria.

Sample ID	Date Sampled	Date Extracted	Date Analyzed	Action

Cooler Temperature(s): _____

Preservation Criteria:

Waters - If residual chlorine is present, treat the sample with sodium thiosulfate and if pH >9, adjust the pH to between 7-9 with sulfuric acid. Cooler temperatures must be at 2-4°C ± 2°. Samples must be stored in the dark

Soils - Cooler temperatures must be 2-4°C ± 2°. Samples must be stored in the dark.

Tissue - Samples must be stored at -20° C. Samples must be stored in the dark.

Holding Time Criteria for Waters, Soils, and Tissues:

Extract within 30 days of sample collection and analyze within 45 days of extraction

Actions:

If the samples were not properly preserved, qualify as estimated (J and UJ) all positive and non-detect results.

If holding times are exceeded, qualify as estimated (J and UJ) all positive and non-detect results.

If holding times are grossly exceeded, (>60 days for extraction and >90 days for analysis), qualify as estimates positive results (J) and reject (R) the non-detect results.

III. GC/MS TUNING & PERFORMANCE CHECK

GC/MS instrument performance checks are performed to ensure proper mass resolution, identification, and sensitivity.

A. MS Resolution – Perfluorokerosene (PFK) Molecular Leak:

1. Was the PFK molecular leak performed at the proper frequency? Yes No

Criteria: Beginning and end of each 12-hour period of operation

2. If calculated resolution results **are** available, was the resolution greater than or equal to 10,000 (10% valley) at m/z 304.9824 (PFK) or any reference signal close to m/z 303.9016 (TCDF)?
Yes No Unavailable

3. For each descriptor listed in Table 6 were reference peaks selected that cover the mass range of the descriptor? Yes No

4. If calculated results **are** available for each descriptor, was the resolution greater than or equal to 10,000 (10% valley) and the deviation between the exact m/z and the theoretical m/z (in Table 6) for each exact m/z less than 5 ppm? Yes No Unavailable

5. If calculated results for resolution and deviation from exact m/z **are not** available for each descriptor, visually inspect the shape of the peak profiles for symmetry and baseline. Were the peak shapes symmetrical and were the baselines adequate? Yes No

Actions:

If the mass spectrometer resolution is <10,000, all of the associated data should be rejected (R) If no for any of the other above questions, use professional judgment in the qualification of the data. Explain actions and list affected samples below.

_____
_____
_____

B. GC Column Performance Check – Window Defining Mixture (WDM)

1. Was the GC column performance check (*i.e*. WDM) performed at the proper frequency?
Yes No

Criteria: Beginning of each 12-hour period during which samples are analyzed and prior to initial calibration.

2. Are the 1st and last isomers in each homologue series present in the WDM? Yes No

Actions:

If no to either 1 or 2, but the calibration standards met specifications, then the individual 2,3,7,8-substituted congener results may be usable without qualification. Total homologue results, however, should be qualified as estimated (J and UJ) since one or more CDDs/CDFs may not have been detected. If the calibration standards indicate a significant problem with the descriptor switching times, all the associated results should be qualified as rejected (R).

III. GC/MS PERFORMANCE CHECKS (continued)

3. Was the chromatographic separation between 2,3,7,8-TCDD and the peaks representing other unlabeled TCDD isomers resolved with a valley of ≤ 25%? Yes No

List performance checks which did not meet this resolution criteria and the associated samples below.

Check Standard ID	Valley %	Associated Samples

Actions:

If the GC resolution does not meet the criteria, qualify as estimated (J and UJ) the positive results and non-detect results for tetras, pentas, and hexas (dioxins and furans). The hepta isomers are not believed to be affected. OCDD and OCDF are not affected as there is only one isomer in each group. Non-detects are not affected.

4. Were the absolute retention times for the switching of SIM ions from one homologous series to the next higher homologous series greater than 10 seconds apart? Yes No

Note: Be sure to check for adequate separation between 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF since these elute within 15 seconds of each other.

Action:

If the switching times are less than 10 seconds apart, this may result in false negative or low biased results for some of the congeners or totals. Use professional judgment and qualify as estimated (J and UJ) all positive and non-detect results with retention time shifts greater than 10 seconds of the corresponding homologue.

IV. CALIBRATIONS

A. Initial Calibration

1. Were the five concentration calibration solutions listed in Table 5 of the method utilized in the initial calibration of the instrument (particularly the lowest calibration standard)?

Yes No

Action: If no, use professional judgment in the qualification of the data.

2. Were SIM data acquired for each of the ions listed in Table 6 of the method? Yes No

Action:

If no, ask lab for an explanation. If an incorrect ion was used, reject (R) all associated data for the affected analyte.

3. Retention Times (RTs)

a. For 2,3,7,8-substituted congeners which have an isotopically labeled internal or recovery standard, the RT of the 2 ions must be within -1 to +3 seconds of the isotopically labeled standard.

b. For 2,3,7,8-substituted congeners which do not have an isotopically labeled internal or recovery standard, the RT of the 2 ions must fall within 0.005 RT units of the Relative RT (RRT) measured in the calibration standard. (Note: Identification of OCDF is based on its RT relative to $^{13}C_{12}$-OCDD).

Action:

If the above criteria are not met, qualify all associated results as rejected (R).

4. The ion abundance ratios for all compounds in all standards must be evaluated. List the ion abundance ratios which are outside the acceptance criteria.

Criteria: Table 8 of the method lists the ion abundance ratio acceptance criteria.

Standard ID	Ion Ratio	Analyte	Samples Affected

Actions:

If the ion abundance ratio is not met for a 2,3,7,8-substituted congener (see Table below for limits), qualify as rejected (R) all associated sample results for compounds with failed ion ratios in the initial calibration. At the reviewer's discretion, a more in-depth review to minimize the amount of data rejected may be accomplished by the following:

- If the ion abundance ratio is outside the limits for an analyte in the HRCC-1 solution, then low-end results for that analyte (below the HRCC-2 standard) should be qualified as rejected (R).
- If the ion abundance ratio is outside the limits for an analyte in the HRCC-5 solution, then high-end results for that analyte (above the HRCC-4 standard) should be qualified as rejected (R).

IV. CALIBRATIONS (continued)

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	±15 %QC Limits
4[1]	M/(M+2)	0.77	0.65-0.89
5	(M+2)/M+4)	1.55	1.32-1.78
6	(M+2)/M+4)	1.24	1.05-1.43
6[2]	M/(M+2)	0.51	0.43-0.59
7	(M+2)/M+4)	1.04	0.88-1.20
7[3]	M/(M+2)	0.44	0.37-0.51
8	(M+2)/M+4)	0.89	0.76-1.02

[1]-Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).
[2]-Used for $^{13}C_{12}$-HxCDF only
[3]-Used for $^{13}C_{12}$-HpCDF only

5. Were the signal/noise ratios for all peaks greater than or equal to 10? Yes No

Action:

If no, and if the signal/noise ratio is <10 for any 2,3,7,8-substituted congeners (unlabeled), the instrument sensitivity may be impacted. In this case, all non-detect results in samples associated with this initial calibration should be rejected (R) and the positive results should be estimated (J).

If the signal/noise ratio for a labeled internal standard or recovery standard are <10, sensitivity of the instrument may have been impacted or the standard was not properly spiked. Use professional judgment to determine effect on data quality.

6. List the percent relative standard deviations (%RSDs) that were outside the QC acceptance criteria of ≤ 20% for all 2,3,7,8-substituted congeners (unlabeled) and ≤ 30% for internal standards (labeled).
7.

DATE	LAB FILE ID#	%RSD	ANALYTE	SAMPLES AFFECTED

Actions:

If the %RSD is >20 for a 2,3,7,8-substituted congener (unlabeled), qualify as estimated (J and UJ) the positive and non-detect results for the affected analyte in samples associated with this initial calibration. If the RSD is ≥ 20%for an unlabeled congener, examine the possibility of directing the RSD to within 20% by discarding either the HRCC-1 or HRCC-5 standard response factors. If discarding either of those two points brings the RSD within 20%, qualify as estimated (J and UJ) the positive and non-detect results associated with the offending portion of the initial calibration (low or high). If non-linearity impacted a majority of data, all positive and non-detect results should be qualified as estimated (J and UJ). Use professional judgment to qualify the data in cases where the internal standard %RSD is ≥ 30%.

IV. CALIBRATIONS (continued)

B. Continuing Calibration

1. Was the calibration verification standard analyzed at the proper frequency (*i.e.* HRCC-3)? Yes No

Criteria: Beginning of each 12-hour period of operation and at the end of the 12-hour shift.

Action: If no, use professional judgment in the qualification of the data.

8. Were SIM data acquired for each of the ions listed in Table 6 of the method? Yes No

Action:

If no, ask lab for an explanation. If an incorrect ion was used, qualify as rejected (R) all associated data for the affected analyte.

3. Retention Times

a. For 2,3,7,8-substituted congeners which have an isotopically labeled internal or recovery standard, the RT of the 2 ions must be within -1 to +3 seconds of the isotopically labeled standard.

a. For 2,3,7,8-substituted congeners which do not have an isotopically labeled internal or recovery standard, the RT of the 2 ions must fall within 0.005 RT units of the RRT measured in the calibration standard. Note: The identification of OCDF is based on its RT relative to $^{13}C_{12}$-OCDD.

Actions:

If the retention times for any 2,3,7,8-substituted congeners (unlabeled) in the continuing calibration standard are not within the retention time windows, use professional judgment and qualify as estimated (J and UJ) all positive and non-detect results for the affected analyte in samples associated with this continuing calibration.

If the recovery standard retention times drift by more than ±15 seconds from the initial HRCC-3 analysis and the continuing calibration standard, use professional judgment to qualify all associated sample results. All positive and non-detect results should be rejected (R) unless based on a review of the selected ion current profile (SICP), there appears to be no affect on the results.

4. Do the 2 SIM ions maximize simultaneously (±2 seconds) for each analyte? Yes No

Actions:

Use professional judgment if the required retention times are not met for the 2 SIM ions.

IV. CALIBRATIONS (continued)

5. The ion abundance ratios for all compounds in all standards must be evaluated. List the ion abundance ratios which are outside the acceptance criteria.

Criteria: Table 8 of the method lists the ion abundance ratio acceptance criteria.

Standard ID	Ion Ratio	Affected Compound	Associated Samples

Actions:

If the ion abundance ratio is not met for a 2,3,7,8-substituted congener (see Table below for limits), qualify as estimated (J and UJ) all associated positive and non-detect sample results for compounds with failed ion ratios in the continuing calibration.

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	±15 %QC Limits
4[1]	M/(M+2)	0.77	0.65-0.89
5	(M+2)/M+4)	1.55	1.32-1.78
6	(M+2)/M+4)	1.24	1.05-1.43
6[2]	M/(M+2)	0.51	0.43-0.59
7	(M+2)/M+4)	1.04	0.88-1.20
7[3]	M/(M+2)	0.44	0.37-0.51
8	(M+2)/M+4)	0.89	0.76-1.02

[1]-Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).
[2]-Used for $^{13}C_{12}$-HxCDF only
[3]-Used for $^{13}C_{12}$-HpCDF only

6. Were the signal/noise ratios for all peaks greater than or equal to 10? Yes No

Action:

If no, and if the signal/noise ratio is <10 for any 2,3,7,8-substituted congeners (unlabeled), the instrument sensitivity may be impacted. In this case, all non-detect results in samples associated with this continuing calibration should be rejected (R) and the positive results should be estimated (J).

If the signal/noise ratio for a labeled internal standard or recovery standard are <10, sensitivity of the instrument may have been impacted or the standard was not properly spiked. Use professional judgment to determine effect on data quality.

IV. CALIBRATIONS (continued)

7. List the percent difference (%Ds) that were outside the QC acceptance criteria of ≤ 20% for all 2,3,7,8-substituted congeners (unlabeled) and ≤ 30% for internal standards (ending calibration standard QC acceptance criteria of ≤ 25% for all 2,3,7,8-substituted congeners (unlabeled) and ≤ 35% for internal standards).

DATE	LAB FILE ID#	%D	ANALYTE	SAMPLES AFFECTED

Note: for ending calibration standard only: If %D > 25% (for any unlabeled compounds) and/or %D > 35% (for labeled compounds), verify that the laboratory used the mean response factor (RF) from the beginning and ending continuing calibration standards in sample calculations instead of the mean RF from the initial calibration.

Actions:

Qualify positive results and non-detects as estimated (J and UJ) if the continuing calibration acceptance criterion is exceeded.

V. BLANKS

The assessment of the blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples, including field, equipment and laboratory blanks. If problems with any blanks exist, all data associated with the case must 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.

List the contamination in the blanks below. Medium and low level blanks must be treated separately.

1. Laboratory Blanks

Date Analyzed	Lab ID	Level/ Matrix	Compound	Concentration/ Unit

2. Field and Equipment Blanks

Date Analyzed	Lab ID	Level/ Matrix	Compound	Concentration/ Unit

V. BLANKS (continued)

3. Blank Actions

Action levels should be based upon the highest concentration of contaminant determined in any blank. The action level for samples which have been concentrated or diluted should be multiplied by the concentration/dilution factor. No positive sample result should be reported unless the concentration of the compound in the sample exceeds the action level of 10x the amount in the blank for OCDD and OCDF, or 5x the amount for any other compound. Use professional judgment to apply the following actions:

Evaluation of all samples using method, field, and equipment blanks:

1. For all analytes except OCDD and OCDF: If the concentration in the sample is <5x the concentration in the blank, the associated sample result should be qualified as non-detect (U).

2. For OCDD and OCDF: If the concentration in the sample is <10x the concentration in the blank, the associated sample result should be qualified as non-detect (U).

3. If the concentration in the sample is >10x the concentration in the blank (for OCDD and OCDF) and >5x the concentration in the blank (for other analytes), qualification of the data is not required.

Review Project Quality Assurance Project Plan (QAPP) for project-specific information.

Contamination Source/Level	Analyte	Concentration Units	Action Level/Units	Sample Quantitation Limit	Affected Samples

V. BLANKS (continued)

1. Was a method blank extracted with each batch of 20 samples/matrix? Yes No

2. Was the method blank analyzed between the calibration standard and the first sample? Yes No

If no, use professional judgment and explain actions below. If contamination is suspected, use professional judgment to qualify as estimated (J) all positive results associated with the suspected contaminant.

_____
_____
_____
_____

VI. MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD)

This data is generated to determine long-term precision and accuracy of the analytical method for various matrices. This data alone cannot be used to evaluate the precision and accuracy of individual samples.

1. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Recoveries and Precision

Level / Matrix: _____ Sample ID: _____

List the percent recoveries (%R) and relative percent differences (RPDs) of spiked analytes which do not meet criteria. Refer to the QAPP for QC acceptance limits. If limits are not listed, apply professional judgment criteria of 40-135%R and 25%RPD.

MS or MSD	Compound	%R or RPD	QC Limits	Action

Actions:

	%R is > Upper QC Limit	%R is ≥ 10% but < Lower QC Limit	%R is < 10%	RPD Outside QC Criteria
Positive results	J	J	J	J
Non-detect results	Accept	UJ	R	UJ

Notes: (1) Qualifications should be applied to the affected compound in the unspiked sample only.

(2) If the majority of spike compound %Rs or RPDs are outside the QC acceptance criteria, use professional judgment to J, UJ, and/or R all compounds in the unspiked sample.

(3) No action is necessary if the concentration in the unspiked sample exceeds 4x the concentration of the spike added.

A separate worksheet should be used for each MS/MSD pair.

VIB. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

2. MS/MSD - Unspiked Compounds

Level / Matrix: _____ Sample ID: _____

List the concentrations of the unspiked compounds and determine the %RSDs of these compounds in the unspiked sample, matrix spike, and matrix spike duplicate.

Compound	Concentration			%RSD	Action
	Sample	MS	MSD		

Criteria:

% RSD $\leq$ 50.

Actions:

If the %RSD > 50, qualify the positive or non-detect result in the unspiked sample as estimated (J and UJ).

If the %RSD is not calculable (NC) due to a non-detect value in the sample, MS, and/or MSD, use professional judgment to qualify sample data.

VII. LABORATORY CONTROL SAMPLES

This data is generated to determine accuracy of the analytical method for various matrices.

1. Laboratory Control Sample (LCS) Recoveries

List the percent recoveries (%R) of spiked analytes which do not meet criteria. Refer to the QAPP for QC acceptance limits. If limits are not listed, use professional judgment criteria of 40-135%R.

LCS ID	Compound	%R	QC Limits	Action

Actions:

	%R is > Upper QC Limit	%R is ≥ 10% but < Lower QC Limit	%R is < 10%
Positive results	J	J	J
Non-detect results	Accept	UJ	R

Note: (1) If the LCS exhibits many %Rs which are outside the QC acceptance criteria and this appears to be an isolated, explainable incident affecting the LCS only, use professional judgment in the qualification of sample data.

(2) If the majority of spike compound %Rs are outside the QC acceptance criteria, and there is no reasonable explaination for all the exceedances, use professional judgment to J, UJ, and/or R all compounds in the associated samples.

2. LCS Frequency

1. Was an LCS extracted with each batch of 20 samples/matrix? Yes No

If no, use professional judgment and explain actions below.

_____
_____
_____
_____

VIII. FIELD DUPLICATES

Sample IDs. _____ _____ Matrix: _____

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and lab precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field duplicate samples.

Criteria:
Soils RPD ≤ 50, Aqueous RPD ≤ 30, if both the sample and duplicate results are ≥ 5x sample quantitation limit (SQL). The RPD criterion is doubled, if both the sample and duplicate results are < 5x SQL.

Compound	Sample Quantitation Limit	Sample Concentration	Duplicate Sample Concentration	% RPD	Action

Actions:

- If the concentrations in the sample and field duplicate are positive and the RPD criterion is exceeded, qualify the positive results as estimated (J).
- If a dioxin/furan in a field duplicate pair is detected at ≥ 5x SQL in one sample and non-detect in the other sample qualify the positive and non-detect results as estimated (J and UJ).
- If a dioxin/furan in a field duplicate pair is non-detect in one sample but detected at < 5x SQL in the other, use professional judgment to qualify sample results.
- If one dioxin/furan is non-detect in a field duplicate pair and in the other sample is ≥ 5x SQL; and the SQLs for the sample and duplicate are significantly different, use professional judgment to qualify sample data.

IX. INTERNAL STANDARD RECOVERIES

Isotopically labeled internal standards (IS) (for PCDDs and PCDFs) are added to each sample, LCS, and method blank prior to extraction. These labeled ISs serve as a measure of the extraction efficiency of each sample, LCS, and blank. These compounds are also used for the quantitation of the PCDD and PCDF isomers.

1. Were samples spiked with all internal standards as specified in Table 2 of the method? Yes No

2. List the internal standards and the associated samples that fell outside the QC acceptance criteria of 40-135 %R.

Sample ID	Internal Standard	%R	Action

Actions:

If the IS %Rs fall outside the QC acceptance limits, qualify positive and non-detects results (including EMPCs and EDLs) as follows:

	%R is > 135%R	%R is ≥ 10% but < 40%R	%R is < 10%
Positive results	J	J	J
Non-detect results	Accept	UJ	R

Note: (1) Actions are only applicable to the results associated with the failed internal standard.

(2) If the IS recoveries are low, but the clean-up standard recovery is not, then the recovery problems may be associated with the extraction procedures or related to a particularly difficult matrix.

(3) If the IS recoveries are low, but the clean-up standard recovery is not, then the recovery problems may be associated with the extraction procedures or related to a particularly difficult matrix.

X. COMPOUND IDENTIFICATION

1. Were SIM data acquired for each of the ions listed in Table 2 of the method? Yes No

Action: If no, ask lab for an explanation. If an incorrect ion was used, reject (R) all associated data for the affected analyte.

2. Retention Times (RTs)

a. For 2,3,7,8-substituted congeners which have an isotopically labeled internal or recovery standard, the RT of the 2 ions must be within -1 to +3 seconds of the isotopically labeled standard.

b. For 2,3,7,8-substituted congeners which do not have an isotopically labeled internal or recovery standard, the RT of the 2 ions must fall within 0.005 RT units of the RRT measured in the calibration standard. Note: The identification of OCDF is based on its RT relative to $^{13}C_{12}$-OCDD.

c. For non-2,3,7,8-substituted compounds, the RT must be within the homologous RT windows established by analyzing the GC column performance check (*i.e.* WDM).

Actions:

If the retention times for any 2,3,7,8-substituted congeners (labeled and unlabeled) are not within the established retention time windows, the results cannot be positively identified as dioxins/furans and qualify the results as rejected (R).

3. Do the 2 SIM ions maximize simultaneously (±2 seconds) for each analyte? Yes No

Actions:

If the required retention times are not met for the 2 SIM ions, qualify the results as rejected (R).

4. The ion ratios for all compounds in all standards must be evaluated. List the ion ratios which are outside the acceptance criteria.

Criteria: Table 8 of the method lists the ion abundance ratio acceptance criteria.

Standard ID	Ion Ratio	Affected Compound	Associated Samples

X. COMPOUND IDENTIFICATION (continued)

Actions:

National Function Guidelines states that "If ion abundance criteria are not satisfied, then the data should be rejected (R)". However it also states that "professional judgment should always be used in determining the proper identification of analytes". Use the following professional judgment to qualify the data since the method allows for analytes that do not meet ion abundance ratios to be reported as EMPCs:

If the ion abundance ratio is >15% (see Table below) for a 2,3,7,8-substituted congener (unlabeled), but all other identification criteria (signal/noise and retention times) qualify as estimated (J) the positive result in the sample. Confirm that the value is reported as an EMPC by the laboratory. The presence of EMPC should be noted in the validation report narrative

If the ion abundance ratio is outside the limits for an internal standard or recovery standard, the stability of the mass spectra is in question since the analyte cannot be positively identified in the standard. Qualify positive results as estimated (J) and reject (R) the non-detect results.

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	±15 %QC Limits
4[1]	M/(M+2)	0.77	0.65-0.89
5	(M+2)/M+4)	1.55	1.32-1.78
6	(M+2)/M+4)	1.24	1.05-1.43
6[2]	M/(M+2)	0.51	0.43-0.59
7	(M+2)/M+4)	1.04	0.88-1.20
7[3]	M/(M+2)	0.44	0.37-0.51
8	(M+2)/M+4)	0.89	0.76-1.02

[1]-Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).
[2]-Used for $^{13}Cl_{12}$-HxCDF only
[3]-Used for $^{13}Cl_{12}$-HpCDF only

5. Were the signal/noise ratios for all peaks greater than or equal to 2.5 for 2,3,7,8 substituted congeners and >10 for internal standards? Yes No

Actions:

If the signal/noise ratio is <2.5 for 2,3,7,8-substituted congeners (unlabeled) or <10 for internal standards, positive results should be considered to estimated (J).

6. For peaks that were identified as furans, does a signal/noise ratio ≥ 2.5 at the same time in the corresponding polychlorinated diphenyl ether (PCDPE) channel exist and is the retention time relative to the furan isomer within ±2 seconds? Yes No

Actions:

If PCDPE interferences exist, qualify the positive furan result as estimated (J).

If the laboratory did not monitor for PCDPEs, qualify all positive furan data as estimated (J).

X. COMPOUND IDENTIFICATION (continued)

7. Second Column Confirmation

a. Was the sample extract re-analyzed on a 30 m DB-225, fused silica capillary column for 2,3,7,8-TCDF? Yes No
b. Did the second column meet calibration specifications? Yes No
c. Did the laboratory report the concentration of 2,3,7,8-TCDF from the secondary column Yes No

Actions:

National Function Guidelines states that "If ion abundance criteria are not satisfied, then the data should be rejected (R)". However, use the following professional judgment:

If no, the result for 2,3,7,8-TCDF should be reported from the secondary column; the primary column should only be used for confirmation purposes. If 2,3,7,8-TCDF was not confirmed and reported from a DB-5 column, use professional judgment and qualify the result as estimated (J) due to potential lack of specificity.

XI. COMPOUND QUANTITATION

1. Were all analyte concentrations within the instrument calibration range? Yes No

If no, were appropriate dilutions performed? Yes No

If no, list associated samples and effect on sample data.

_____
_____
_____
_____

2. Were estimated detection limits (EDLs) calculated for all 2,3,7,8-substituted isomers that were not identified as positive values? Yes No

3. Example Calculation

The sample quantitation evaluation is to verify laboratory quantitation results. In the space below, please show a minimum of one sample calculation:

XII PERCENT SOLIDS

List samples that have ≤ 30% solids:

_____
_____
_____
_____

Actions:

If a soil sample has >10% solids but ≤30% solids, qualify positive results as estimated (J) and reject (R) non-detect results.

If a soil sample has <10% solids, reject (R) both positive and non-detect results.

Professional judgment may be applied if the laboratory used increased sample weights prior to extraction.

DATA REVIEW WORKSHEETS

Type of Validation Full: ____
Limited:____

ENSR Data Pkg#: _____
Site Name: _____
Project Number: _____

REVIEW OF SEMIVOLATILE ORGANIC DATA PACKAGE

The following guidelines for evaluating semivolatile organics data were created to delineate required validation actions. This document will assist the reviewer in using professional judgement to make more informed decisions and in better serving the needs of the data users. Quality control validation criteria were derived from the USEPA publications *Test Methods for Evaluating Solid Waste, Physical / Chemical Methods SW846* (Final Update III, December 1996), specifically SW-846 methods 8000B/8270C, and the project Quality Assurance Project Plan (QAPP). Validation actions were derived from *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review* (October 1999) and *Region 5 Standard Operating Procedure for Validation of CLP Organic Data* (USEPA Region 5 Superfund Technical Support Section, February 1997).

The hardcopy data package has been reviewed and the quality assurance and performance data summarized. The data review for semivolatile analytes included:

Laboratory Name/Location _____
Laboratory SDG No. _____
No. of Samples _____
Sample Matrix _____
Equipment/Field Blank ID _____
Field Duplicate IDs _____

The general criteria used to determine the performance were based on an examination of:

___ Data Completeness
___ Holding Times / Sample Preservation
___ GC/MS Tuning
___ Calibrations
___ Blank Analysis Results
___ Surrogate Spike Recoveries
___ Matrix Spike/Matrix Spike Duplicate (MS/MSD)
___ Laboratory Control Samples (LCS)
___ Field Duplicate Precision
___ Internal Standard Performance
___ Compound Identification
___ Quantitation Limits and Sample Results

Overall Comments: _____

Qualifiers:

J - Estimated result.
R - Reject data due to quality control criteria.
U - Compound not detected.
UJ - Estimated nondetect
N - Tentatively identified
JN - Estimated concentration, tentatively identified

Reviewer: _____ Date: _____

DATA REVIEW WORKSHEETS

I. DATA COMPLETENESS

A. Data Package:

_____ The tests requested on the COC or in subsequent communications were performed and reported

_____ The correct analyte list was reported

_____ The COCs (external and internal) are present and complete

_____ Sample receiving documentation is complete

Missing Information

A. Other Discrepancies:

DATA REVIEW WORKSHEETS

All criteria were met _____
Criteria were not met
and/or see below _____

II. HOLDING TIMES

The objective of this parameter is to ascertain the validity of results based on the holding time (HT) of the sample from the time of collection to the time of extraction, and subsequently from the time of extraction to the time of analysis.

Complete table for all samples and note the analysis and/or preservation dates not within criteria.

Sample ID	Date Sampled	Date Extracted	Date Analyzed	ACTION

Criteria:

- Extraction HT: Aqueous: Extract within 7 days from sample collection, Soil: Extract within 14 days.
- Analysis HT: Aqueous and Soil: Analysis within 40 days from date of sample extraction.
- Cooler Temperature (4°C ± 2°C): _____

Actions: Qualify detects/nondetects as follows:

1. For Holding Time exceedances:

Extraction from sampling (Days)		Analysis from Extraction (Days)	Action Detect/Nondetect
Water	Soil		
1-7	1-14	1-40	Accept
8-14	15-28	--	J/UJ
>14	>28	>40	J/R

2. If samples were > 10°C, use professional judgment to qualify results.

III. GC/MS TUNING

The assessment of the tuning results is to determine if the sample instrumentation is within standard tuning QC limits.

_____ The DFTPP performance results were reviewed and found to be within the specified criteria of the method. If ion abundance criteria were not met, use professional judgment to qualify results. If mass assignment is in error (e.g., m/z 199 as base peak instead of m/z 198), all associated data are rejected (R).

_____ All samples and CCVs were analyzed within 12 hrs of the DFTPP tunes. If no, use professional judgement to determine if qualification is appropriate.

DATA REVIEW WORKSHEETS

All criteria were met _____
Criteria were not met
and/or see below _____

I. CALIBRATIONS

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing and maintaining acceptable quantitative data.

Dates of Initial Calibration: _____

Dates of Continuing Calibrations: _____

Instrument ID Numbers: _____

DATE	Lab File ID#	Analyte	RFs, %RSD, %D, r	Samples Affected

ICAL	**Criteria**	**Action (Detects/Nondetects)**
RF	RF ≥ 0.05 for all target analytes, including SPCCs	J / R Note: Sample results negated (U) on the basis of blank contamination are not rejected, but estimated (UJ).
%RSD or correlation coefficient (r)	%RSD ≤ 30% for CCCs %RSD ≤ 15% for other analytes If %RSD > 15, line or curve must have r ≥ 0.99	J / UJ
CCV	**Criteria**	**Action (Detects/Nondetects)**
RF	RF ≥ 0.05 for all target analytes, including SPCCs	J / R Note: Sample results negated (U) on the basis of blank contamination are not rejected, but estimated (UJ).
%D	%D ≤ 20 for CCCs %D ≤ 25 for other analytes (20% if no CCCs)	J / UJ low recovery J / Accept high recovery

SPCCs: n-Nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol.
B/N CCCs: Acenaphthene, 1,4-dichlorobenzene, hexachlorobutadiene, diphenylamine, di-n-octylphthalate, fluoranthene, and benzo(a)pyrene
Acid CCCs: 4-Chloro-3-methylphenol, 2,4-dichlorophenol, 2-nitrophenol, phenol, pentachlorophenol, and 2,4,6-trichlorophenol

* A separate worksheet should be filled out for each initial curve.

V. BLANK ANALYSIS RESULTS (Sections 1 & 2)

The assessment of the blank analysis results is to determine the existence and magnitude of contamination problems. If problems with any blanks exist, all data associated with the case must 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.

1. Frequency Requirements

Was a preparation blank analyzed for each matrix, at the frequency stated in the method? Yes or No

If "No", data quality may be affected. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

_____

_____

2. Blanks: List the contamination in all of the blanks (laboratory and/or field QC blanks) below. High and low level blanks must be treated separately.

Date Analyzed	Lab ID or Field ID	Level/ Matrix	Compound	Conc. Unit:	Action Level Unit:	Affected Samples

3. **Blank Actions**

The action level (AL) for samples which have been diluted should be multiplied by the dilution factor.
No detected sample result should be reported unless the concentration of the compound in the sample exceeds the AL of 10x the amount in the blank for the common contaminants (phthalates), or 5x the amount for any other compound. Specific actions are as follows:

1. If sample result is ≤ the sample quantitation limit (SQL) and ≤ the AL, report the compound as not detected (U) at the SQL.
2. If sample result is > SQL but ≤ AL, report the compound as undetected (U) at the reported concentration.
3. If the concentration is > the AL, report the concentration unqualified.

DATA REVIEW WORKSHEETS

All criteria were met _____
Criteria were not met
and/or see below _____

VI. SURROGATE SPIKE RECOVERIES

Laboratory performance of individual samples is established by evaluation of surrogate spike recoveries. All samples are spiked with surrogate compounds prior to sample analysis. The effectiveness of the analysis is measured by the surrogate percent recovery (%R). Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the validation of data is frequently subjective and demands analytical experience and professional judgement.

List the %Rs which do not meet the criteria for surrogate recovery.

	Surrogate Compounds				Matrix: Aqueous/Soil		
Sample ID	NBZ	FBP	TPH	PHL	2FP	TBP	Actions
QC limits (LL - UL) must be filled in during validation.							
Aqueous	to	to	to	to	to	to	
Solid	to	to	to	to	to	to	

Notes:

Base / Neutral Surrogates		Acid Surrogates	
NBZ =	Nitrobenzene-d5	PHL =	Phenol-d5
FBP =	2-Fluorobiphenyl	2FP =	2-Fluorophenol
TPH =	Terphenyl-d14	TBP =	2,4,6-Tribromophenol

Criteria:

- Surrogate recoveries must fall between the QC limits established for the project. If any surrogate is out of QC limits, reanalysis is recommended to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

Actions: Data are not qualified unless

- Two or more surrogate %Rs within the same fraction (base/neutral or acid) are out of specification but >10% or
- One surrogate %R within the same faction <10%.

Surrogate action should be applied as follows:

Qualify results within the same fraction (base/neutral or acid)	%R		
	< 10%	10%-LL	> UL
Detected Results	J	J	J
Non-detected Results	R	UJ	Accept

Note: Sample results negated (U) on the basis of blank contamination are not rejected, but estimated (UJ).

VII. MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD)

This data is generated to determine long-term precision and accuracy of the analytical method for various matrices.

1. MS/MSD Recoveries and Precision (A separate worksheet should be used for each MS/MSD pair)

Sample ID: _____ Level / Matrix: _____

List the %Rs and relative percent differences (RPDs) of compounds that do not meet the project QC criteria.
Note: RPDs are calculated from MS and MSD concentrations, not recoveries.

MS or MSD	Compound	%R or RPD	QC Limits	Action

No action is taken on MS/MSD results **alone** to qualify an entire case. However, the reviewer may use MS/MSD results in conjunction with other QC criteria and determine the need for qualification of the data. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, then qualification should be limited to this sample alone. However, it may be determined through MS/MSD results that the laboratory is having a systematic problem in the analysis of one or more analytes (which affects all associated samples), then qualification should be applied to all samples in the analytical batch.

Actions: Qualify the unspiked sample as follows:

	MS, MSD %Rs			MS/MSD RPD
Qualify results	<10%	10%-LL	>UL	> QC Limit
Detected Results	J	J	J	J
Non-Detected Results	R	UJ	Accept	UJ

Note: Sample results negated (U) on the basis of blank contamination are not rejected, but estimated (UJ).

2. MS/MSD - Unspiked Compounds

List the concentrations of the unspiked compounds and determine %RSDs in the sample, MS and MSD.

Compound	Concentration			%RSD	Action
	Sample	MS	MSD		

Criteria: None specified, use % RSD ≤ 50 as professional judgment.
Action:
1. If the %RSD > 50, qualify the result in the unspiked sample as estimated (J).
2. If the %RSD is not calculable (NC) due to a nondetect value in the sample, MS, and/or MSD, use professional

judgment to qualify sample data.

VIII. LABORATORY CONTROL SAMPLE (LCS) or LCS/LCS DUPLICATE

This data is generated to determine accuracy of the analytical method for various matrices.

1. LCS or LCS/LCS Duplicate: List the %Rs and/or RPDs of compounds which do not meet the criteria.

LCS ID	Compound	%R or RPD	QC Limits	Action

Criteria:

- Project QC limits (LL = lower limit, UL = upper limit)

Actions: Actions on LCS %R and RPD should be based on both the number of compounds that are outside the %R criteria and the magnitude of the exceedance of the criteria.

	LCS, LCSD %R			LCS/LCSD
Qualify results	<10%	10%-LL	>UL	RPD > QC Limit
Detected Results	J	J	J	J
Non-Detected Results	R	Use professional judgement	Accept	UJ

Note: Sample results negated (U) on the basis of blank contamination are not rejected, but estimated (UJ).

- If ≤ half of LCS/LCSD compounds are outside the QC limits, qualification applies ONLY to the affected analytes.
- If more than half of LCS/LCSD compounds are outside the QC limits, qualification applies to ALL affected analytes.

2. LCS Frequency

Was an LCS analyzed at the proper frequency (1 per batch of 20 samples or less per matrix) ? Yes or No

If “no”, note in validation memo and use professional judgment in qualification of the data. Discuss any actions below:

DATA REVIEW WORKSHEETS

All criteria were met _____
Criteria were not met
and/or see below _____

IX. FIELD DUPLICATE PRECISION

Sample IDs: _____ _____ Matrix: _____

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and lab precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field duplicate samples.

Compound	SQL	Concentration (µg/L or µg/Kg)		RPD	Action
		Sample	Duplicate		

SQL = Sample quantitation limit

Criteria (in the absence of project-specific criteria):

- Soils RPD ≤ 50, Aqueous RPD ≤ 30, if both the sample and duplicate results are ≥ 5x SQL.
- The RPD criterion is doubled, if both the sample and duplicate results are < 5x SQL.

Actions:

- If the RPD criterion is exceeded, estimate detected results (J) in the sample and duplicate.

If the sample and/or duplicate are NDs, the RPD is not calculable:

- If both the sample and duplicate results are ND, precision is considered acceptable and no action is needed.
- If one sample result is ND and the other is ≥ 5x SQL, qualify both results (J/UJ).
- If one sample result is ND and the other is < 5x SQL, accept unqualified.

Note: If the SQLs for the sample and duplicate are significantly different, use professional judgment to determine if qualification is appropriate.

DATA REVIEW WORKSHEETS

All criteria were met _____
Criteria were not met
and/or see below _____

X. INTERNAL STANDARD PERFORMANCE

The assessment of the internal standard (IS) parameter is required for CCVs and recommended for samples to assist the data reviewer in determining the condition of the analytical instrumentation or effect of matrix on sample results.

List the IS area and/or retention times (RTs) which do not meet the criteria for IS performance.

Date	Sample ID	IS out	IS Area/RT	Acceptance Range	Action

Criteria:

- IS area of the CCV must fall between –50 and 100% of the IS area of the midpoint in the ICAL.
- IS RT of the CCV must fall between ±30 second of the IS RT of the midpoint of the ICAL.
- IS area of the sample must fall between –50% to +100% of the IS area in the associated CCAL.
- IS RT of the sample must fall between ± 30 seconds of the IS RT in the CCAL.

Actions:

If an IS is out of QC limits, reanalysis is recommended to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

1. Validation action should be applied to the compounds quantitated with the out-of control IS as follows:

Qualify results	Sample IS area compared to CCAL		
	Extreme low (< -10%)	-10% to -50%	> +100%
Detected Results	J	J	J
Non-Detected Results	R	UJ	Accept

2. 2.If RT of an IS varies more than 30 seconds from the CCV, reject (R) all nondetects in the affected samples.

Discuss any actions below:

_____

_____

XI. COMPOUND IDENTIFICATION

The compound identification evaluation is to verify that the laboratory correctly identified target analytes as well as the tentatively identified compounds (TICs).

1. Verify that the target analytes were within the retention time windows and spectra match.

2. Verify that target analytes and/or TICs were quantitated using the correct internal standards.

3. Verify that the target identification is supported by the mass spectral pattern.

DATA REVIEW WORKSHEETS

All criteria were met _____
Criteria were not met
and/or see below _____

I. QUANTITATION LIMITS and SAMPLE RESULTS

The sample quantitation evaluation is to verify laboratory quantitation results.

1. In the space below, please show a minimum of one sample calculation.

2. If dilutions performed, were the SQLs elevated accordingly by the laboratory? List the affected samples and dilution factor in the table below.

Sample ID	Dilution Factor	Reason for Dilution

If dilution was required but not performed, estimate results (J) for the affected compound.
List the affected samples/compounds: _____

3. If requested for the project, verify that results below the SQL and above the laboratory's method detection limits (MDLs) were reported.

4. Verify that the reporting limit is at or above the lowest calibration standard.

5. Verify that results were reported in dry weight for solid samples.

6. Are all sample percent solid ≥ 30? If not, list the affected samples/percent solids.

ENSR

DATA REVIEW WORKSHEETS

Type of Review Full:_____
Limited: ____

ENSR Data Pkg ID _____
Site Name: _____
Project Number: _____

REVIEW OF RADIOLOGICAL DATA PACKAGE

The following guidelines for evaluating radiological data were created to delineate required review actions. This document will assist the reviewer in using professional judgement to make more informed decisions and in better serving the needs of the data users. The radiological data will be reviewed based on method compliance and quality control (QC) results to provide a level of assurance that an nuclide is present or absent. The level of uncertainty (bias) associated with the reported result will be indicated, if applicable. The evaluation of the radiological data will be evaluated based on the Department of Energy *Evaluation of Radiochemical Data Usability (1997)*. However, the QC samples will not be evaluated based on a statistical level of confidence as discussed in the *Evaluation of Radiochemical Data Usability (1997)*, but rather to the laboratory QC acceptance criteria, unless otherwise indicated.

The hardcopied (laboratory name) _____ data package received has been reviewed and the quality control (QC) and performance data summarized. The review of radiological data included:

Lab Project/SDG No.: _____
Sample Matrix: _____
No. of Samples: _____
Field Blank ID: _____
Equipment Blank ID.: _____
Field Duplicate IDs.: _____

List analyses reviewed and analytical method: _____ _____
_____ _____
_____ _____

The general criteria used to determine performance were based on an examination of (check all that apply):

____ Data Completeness
____ Holding Times/Sample Preservation
____ Method Blank
____ Chemical Yield (Tracers and Carriers)
____ Laboratory Control Sample (LCS)
____ Calibration
____ Matrix Spike/Matrix Spike Duplicate (MS/MSD)
____ Laboratory Duplicates
____ Field Duplicates
____ Sample Identification and Quantitation
____ Reporting Limits

Overall Comments: _____
_____
_____

Definitions and Qualifiers:

U - Nuclide considered not detected above the reported Minimum Detectable Concentration (MDC) or 2 sigma counting uncertainty
J - Nuclide identified; the associated numerical value is estimated
UJ - Nuclide is not detected above the reported MDC or 2 sigma counting uncertainty; the reporting limit may be inaccurate or imprecise
R - Result is rejected and is not usable for project objectives

In general, only one qualifier is permitted with each result. Qualifiers relating to identification (U or R) take precedence over qualifiers relating to quantitation (J or UJ). Whenever an "R" is used for nondetects, "UJ" is not used. Within each category of qualifiers, use the qualifier that indicates a more serious problem.

Reviewer: _____ Date: _____

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

I. DATA COMPLETENESS

A. Data Package:

_____ The tests requested on the COC or in subsequent communications were performed and reported

_____ The correct nuclide list was reported

_____ The COCs (external and internal) are present and properly completed

_____ Sample receiving documentation is complete

Missing Information	Date Lab Contacted	Date Received

B. Other Discrepancies

Codes

SR – Sample Results
BR – Blank Result
MDC – Minimum Detectable Concentration
TPU – Total Propagated Uncertainty
RL- Reporting Limit

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

II. HOLDING TIMES

The objective of this parameter is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of sample analysis (activity detection). Samples must be analyzed prior to significant decay of short-lived target radionuclides. Complete the table for all samples and circle the analysis date for samples not within criteria.

SAMPLE ID	DATE SAMPLED	GROSS ALPHA DATE ANALYSIS	GROSS BETA DATE ANALYSIS	ISOTOPIC URANIUM DATE ANALYSIS	ISOTOPIC THORIUM DATE ANALYSIS	pH	ACTION

Cooler Temperature: _____

Criteria:

- Analysis Holding Times: no technical holding times due to long half lives, but 6 months from sample collection (for contractual reasons)
- Sample Preservation: Concentrated HCL or HNO_3 to pH $\leq$ 2

Actions:

If samples not preserved properly in the field or laboratory and/or stored in improper container, then:

- SR < sample MDC qualify as estimated "UJ".
- SR $\geq$ sample MDC use professional judgment to qualify as estimated "J"

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

II. HOLDING TIMES (continued)

The objective of this parameter is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of sample analysis (activity detection). Samples must be analyzed prior to significant decay of short-lived target radionuclides. Complete the table for all samples and circle the analysis date for samples not within criteria.

SAMPLE ID	DATE SAMPLED	Ra-226 DATE ANALYSIS	Ra-228 DATE ANALYSIS	Tc-99 DATE ANALYSIS	Tritium DATE ANALYSIS	pH	ACTION

Cooler Temperature: _____

Criteria:

- Analysis Holding Times: no technical holding times due to long half lives, but 6 months from sample collection (for contractual reasons)
- Sample Preservation: Concentrated HCL or HNO_3 to pH $\leq$ 2 for gross alpha or beta, Ra-226, Ra-228, isotopic uranium, isotopic thorium, and Tc-99

Actions:

If samples not preserved properly in the field or laboratory and/or stored in improper container, then:

- SR < sample MDC qualify as estimated "UJ".
- SR $\geq$ sample MDC use professional judgment to qualify as estimated "J"

All criteria were met: _____
Criteria were not met,
and/or see below: _____

III. BLANK ANALYSIS RESULTS

The assessment of the blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples, including equipment, field, and laboratory blanks.

If problems with any blanks exist, all data associated with the case must 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.

1. Frequency Requirements

Was a method blank analyzed at the frequency stated in the method or by the project? Yes or No
Was the method blank the same matrix as the sample in the batch? Yes or No

If no, the data may be affected. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions below, and list the samples affected.

_____

_____

2. Blank Actions

The method blank activities must be less than their MDC and 2 sigma counting uncertainty.

Blanks must be evaluated in the following order:
- Method blanks must first be used to qualify equipment/field blanks and samples.
- Contamination remaining in the equipment/field blanks will be used to qualify the associated samples.

Actions:
- if blank results < MDC or < 2 sigma counting uncertainty – no action
- if blank results > MDC , but SR < sample MDC – no action
- if blank results > MDC and SR > sample MDC or 2 sigma counting uncertainty, then
  - determine normalized absolute difference between blank and SR using

$$\frac{\text{Absolute Difference (SR – BR)}}{\text{Square Root } (TPU^2_{SR} + TPU^2_{BR})}$$

If normalized absolute difference > 2.58, no qualification
If normalized absolute difference between 1.96 and 2.58, qualify SR ≥ MDC as estimated "J"
If normalized absolute difference between 0 and 1.96, use professional judgment to "R"

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

III. BLANK ANALYSIS RESULTS (continued)

List the contamination > MDC or RL in Sections A & B below.

A. Method blanks

Matrix: _____ Unit _____

Date Analyzed	MB ID	Nuclide	Concentration	RL	Affected Samples

B. Field/Equipment blanks

Date Collected	Field ID	Nuclide	Concentration	RL	Affected Samples

C. Normalized Absolute Difference

Sample ID	Nuclide	SR + TPU	BR + TPU	Normalized Absolute Difference	Action

All criteria were met: _____
Criteria were not met,
and/or see below: _____

IV. CHEMICAL YIELD (TRACERS AND CARRIERS)

Tracers and carriers used in radiochemical separation methods are used to evaluate chemical separation.

1. Frequency Requirements

Were carrier or tracer percent recoveries reported for each sample? Yes or No

If no, the data may be affected. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

2. Carrier or Tracer Recovery

List samples that have carrier or tracer percent recoveries (%Rs) outside criteria.

Sample ID	Nuclide	%R	Action

Criteria: %R = 25-125% for isotopic uranium

Actions: Do not qualify data on yield results alone. If carrier or tracer %Rs are low, there may be increased uncertainty in the SR (MDC > RL). If the yield is low, but the LCS %Rs are acceptable, then accept data without qualification.

All criteria were met: _____
Criteria were not met,
and/or see below: _____

V. LABORATORY CONTROL SAMPLE (LCS)

The assessment of the LCS(s) is to monitor the accuracy of preparation and analysis.

1. Recovery Criteria

List LCS percent recoveries (%Rs) or normalized differences not within the criteria and the samples affected.

Date	Nuclide	%R/Normalized Difference	Action	Sample Affected

Criteria: ____ %R = 75-125% or _____ list other %R or ____ Normalized Difference

Actions:

If %R criteria used then follow the actions stated below:

LCS	%R < 10%	%R = 10 – LL%	%R > UL%
Detected Sample Results	R	J	J
Nondetected Results	R	UJ	Accept

LL – lower limit UL – upper limit

If normalized difference criteria used then follow the actions stated below:

LCS	Negative bias less than -2.58	Negative bias between -1.96 and -2.58	Between -1.96 and 1.96	Positive bias between 1.96 and 2.58	Positive bias greater than 2.58
Sample Results ≥ MDC	R*	J	Accept	J	R*
Sample Results < MDC	R*	UJ	Accept	Accept	Accept

* Consider the effects of other QC samples prior to qualifying

2. Frequency Criteria

Was an LCS analyzed with each batch? Yes or No
Was the LCS analyzed on the same detection system as the samples? Yes or No

If no, data quality may be jeopardized. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions and list affected samples.

_____

_____

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

VI. MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD)

1. Recovery Criteria

Sample # _____ Matrix: _____ Units: _____

This data is generated to determine long-term precision and accuracy of the analytical method for various matrices.

List MS/MSD percent recoveries (%Rs) or normalized differences not within the criteria and the samples affected.

Nuclide	Spiked Sample Result (SSR)	Sample Result (SR)	Spike Added (S)	%R	%RPD	Normalized Difference	Action

Criteria: ____ %R = 75-125% or _____ list other %R or ____ Normalized Difference

Actions: MS/MSD actions apply to the field sample used for the MS/MSD analyses. This qualification may also be applied to the results of all samples within a given area of the site or preparation batch, if deemed appropriate.

If %R criteria used then follow the actions stated below:

Qualify Results	MS and/or MSD %R			-20%< %RPD >20%
	%R < 10%	%R = 10 - LL%	%R > UL%	
Detected Results	J	J	J	J
Nondetected Results	R	UJ	Accept	UJ

LL – lower limit UL – upper limit

If normalized difference criteria used then follow the actions stated below:

LCS	Negative bias less than -2.58	Negative bias between -1.96 and -2.58	Between -1.96 and 1.96	Positive bias between 1.96 and 2.58	Positive bias greater than 2.58
Sample Results ≥ MDC	R*	J	Accept	J	R*
Sample Results < MDC	R*	UJ	Accept	Accept	Accept

* Consider the effects of other QC samples prior to qualifying

2. Frequency Criteria

Was a matrix spike prepared at the frequency stated in the method or by the project? Yes or No
Were all nuclides or interest spiked into the MS/MSD? Yes or No or NA

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

VII. LABORATORY DUPLICATES*

Sample #_____ Matrix: _____ Units: _____

Laboratories run duplicate samples to verify laboratory consistency and precision. They are a measure of laboratory performance. It is expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with preparing identical duplicate samples.

List nuclide not meeting the RPD or Normalized Absolute Difference (circle criteria used).

Nuclide	MDC	RL	Sample Results	Duplicate Results	RPD (%)	Normalized Absolute Difference	Action

Laboratory duplicate actions should be applied to the field sample used as the laboratory duplicate. This qualification may also be applied to the results of all samples within a given area of the site and/or preparation batch, if deemed appropriate.

Criteria:

- RPD ± 20% for aqueous, RPD ± 35% for soil samples, if sample and duplicate results ≥ 5x RL or MDC.
- QC limits ± RL or MDC for aqueous, ± 2x RL or MDC for soil samples, if sample/duplicate results < 5x RL or MDC.
- Normalized absolute difference less than or equal to 1.96

Actions: Indicate which criteria were used to evaluate precision by circling RPD, RL, or MDC. If both samples are nondetected, precision is considered acceptable. No action is needed.

- If RPD is exceeded and sample results are ≥ 5x RL or MDC, estimate detected results and nondetects (J/UJ).
- RPD is exceeded and sample or duplicate result is < 5x RL or MDC, estimate detected results and nondetects (J/UJ) for nuclides whose absolute difference is > RL or MDC for waters or > 2x RL or MDC for soils.
- If normalized absolute difference is greater than 1.96, estimate results (J/UJ)

2. Frequency Criteria

Was a laboratory duplicate prepared and analyzed with each batch of up to 20 samples? Yes or No

*A separate worksheet page should be used for each laboratory duplicate

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

VIII. FIELD DUPLICATES*

Sample #_____ Matrix: _____ Units: _____

Field duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and lab precision; therefore, the results may have more variability than lab duplicates which measure only lab performance. It is also expected that solid matrices will have a greater variance than water matrices due to difficulties associated with collecting identical field duplicate samples.

List nuclide not meeting the RPD or Normalized Absolute Difference (circle criteria used).

Nuclide	MDC	RL	Sample Results	Field Duplicate Results	RPD (%)	Normalized Absolute Difference	Action

Field duplicate actions should be applied to the field duplicate pair. This qualification may be applied to the results of all samples within a given area of the site and/or preparation batch, if deemed appropriate.

Criteria:

- RPD ± 30% for aqueous, ± 50% for soils, if sample and duplicate results ≥ 10x RL or MDC.
- Absolute difference ± 4x RL or MDC for aqueous, ± 8x RL or MDC for soils, if sample and duplicate < 10x RL or MDC.
- RPD and absolute difference must be exceeded if one result ≥ 10x RL and one < 10x RL.
- Normalized absolute difference less than or equal to 1.96

Actions: Indicate which criteria were used to evaluate precision by circling RPD, RL, or MDC. If both samples are nondetected, precision is considered acceptable. No action is needed.

- If RPD is exceeded and sample results are ≥ 10x RL or MDC, estimate detected results and nondetects (J/UJ).
- If RPD is exceeded and sample or duplicate result is < 10x RL or MDC, estimate detected results and nondetects (J/UJ) for elements whose absolute difference is > 4x RL or MDC for waters or > 8x RL or MDC for soils.
- If RPD is NC because one result ≥ 10x RL or MDC and one nondetect, estimate detected and nondetects (J/UJ).
- If RPD is NC because one result < 10x RL or MDC and one nondetect, use professional judgment. Laboratory duplicate actions should be applied to the field sample used as the laboratory duplicate.
- If normalized absolute difference is greater than 1.96, estimate results (J/UJ)

2. Frequency Criteria

Was a laboratory duplicate prepared and analyzed with each batch of up to 20 samples? Yes or No

*A separate worksheet page should be used for each laboratory duplicate

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

IX. CALIBRATION

1. Standard Traceability

a. Were certificates included for calibration standards, LCS, and/or MS/MSD? Yes or No
b. Did certificate serial numbers match referenced standards? Yes or No
c. Were the standards within the expiration dates? Yes or No

If no, list standards affected

Standard ID	Nuclide	Lab ID	Certificate ID	Expiration Date

2. Calibration Verification

a. Are the efficiencies within the appropriate control criteria? Yes or No
b. Are instrument backgrounds within the appropriate control criteria? Yes or No
c. Are energies within the appropriate control criteria? Yes or No
d. Peak resolution within appropriate control criteria? Yes or No

If no, list standards affected

Standard ID	Nuclide	Lab ID	Certificate ID	Expiration Date

DATA REVIEW WORKSHEETS

All criteria were met: _____
Criteria were not met,
and/or see below: _____

X. SPECTRAL INTERPRETATION

1. Gamma Analyses

a. Do isotopes of the same radionuclide show secular equilibrium? Yes or No
b. Soil samples: are peaks at 511 keV (annihilation peak) and 1460 keV (K-40) present? Yes or No
c. Are all detected peaks correctly identified? Yes or No
d. Do peaks overlap? Yes or No

If yes, list affected samples and nuclides

Sample ID	Nuclide	Peak Energy	Estimated % Overlap	Action

2. Alpha Spectra

a. Are target peaks within the energy range of interest (ROI)? Yes or No
b. Does peak overlap exist through tailing from other nuclides? Yes or No
If yes, list samples and nuclides affected by tailing below:

Sample ID	Nuclide	Issue

All criteria were met: _____
Criteria were not met,
and/or see below: _____

XI. SAMPLE IDENTIFICATION AND QUANTITATION

1. Are sample results > sample MDCs? Yes or No
If no, qualify SRs as "U". List samples and nuclides below

Sample ID	Nuclide	SR	SR MDC	Action

2. Are sample results > 2 sigma counting uncertainty? Yes or No
If no, qualify SRs as "U". List samples and nuclides below

Sample ID	Nuclide	SR	SR MDC	Action

Use Professional judgment in cases where:
- SR < MDC, but > 2 sigma counting uncertainty may have been counted long enough to be considered detected.
- SR > MDC, but < 2 sigma counting uncertainty may NOT have been counted long enough to be considered detected.

3. Are sample results > 2 TPU? Yes or No
If no, qualify sample results (SRs) as "U". List samples and nuclides below

Sample ID	Nuclide	SR	SR TPU	Action

Use Professional judgment in cases where:
- SR < MDC, but > 2 sigma counting uncertainty may have been counted long enough to be considered detected.
- SR > MDC, but < 2 sigma counting uncertainty may NOT have been counted long enough to be considered detected.

All criteria were met: _____
Criteria were not met,
and/or see below: _____

4. Negative Sample Results

Negative results with absolute values greater than their 2 sigma counting uncertainty indicate that the instrument background may have shifted. Use professional judgment to qualify data.

Do negative sample results have absolute values > 2 sigma counting uncertainty? Yes or No
If yes, list samples and nuclides below:

Sample ID	Nuclide	SR	SR 2 sigma uncertainty	Action

5. Gross values vs total of individual nuclides

Are gross alpha results > total of individual uranium results Yes or No
If no, list samples with gross alpha < total of individual uranium isotopes

Sample ID	Gross alpha SR	Total of individual uranium isotopes	Action

Action

- if gross alpha < total of individual isotopic uranium, then estimate (J) detected individual U results if applicable in affected sample.

All criteria were met: _____
Criteria were not met,
and/or see below: _____

XII. REPORTING LIMITS

1. Minimum Detectable Concentration (MDC)

   A. Were sample MDCs < RLs? Yes or No

   B. Determine why the MDC> RL (ex. small sample size, inadequate count time, or matrix problems). If sample MDC > RL and SR < sample MDC or ± 2 sigma counting uncertainty, and there is no justification for not reanalyzing at a longer count time or greater sample aliquot, then data are noncompliant with RL – note in report. The data may be affected. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

_____
_____
_____
_____
_____
_____
_____
_____
_____

2. Aliquot Size

   List samples and nuclides that required adjusted aliquot size.

Sample ID	Nuclide	Aliquot Size

A representative sample aliquot must be chosen to ensure the dissolved solid content of the sample falls within the mass range of the appropriate curve. Sample results for which aliquot weight is outside the attenuation curve should be qualified as estimated (J) if not reanalyzed with a smaller aliquot.

DATA REVIEW WORKSHEETS

Type of Validation Full: ____
Limited:____

ENSR Data Pkg#: _____
Site Name: _____
Project Number: _____

REVIEW OF METALS ANALYSIS DATA PACKAGE

The following guidelines for evaluating metals were created to delineate required validation actions. This document will assist the reviewer in using professional judgement to make more informed decisions and in better serving the needs of the data users. Quality control validation criteria were derived from USEPA publications: "Test Methods for Evaluating Solid Waste, Physical / Chemical Methods SW846" (3RD Edition and subsequent Updates), specifically SW-846 methods 6010B, 7470A, and 7471A. Validation actions were derived from "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (Final, October 2004) and were modified to accommodate the non-CLP methods and professional judgment. The project QAPP should be reviewed for project-specific information.

The hardcopy data package received from (laboratory name/location) _____ has been reviewed and the quality assurance and performance data summarized.

The data review for metals included:
Lab Project/SDG No. _____ No. of Samples: _____ Sample Matrix: _____
Field Blank IDs: _____
Equipment Blank IDs.: _____
Field Duplicate IDs.: _____

The general criteria used to determine the performance were based on an examination of (check all that apply):

_____ Data Completeness
_____ Holding Times and Sample Preservation
_____ Calibrations
_____ Blanks
_____ ICP Interference Check Sample
_____ Matrix Spike Results
_____ Laboratory Duplicate Results
_____ Field Duplicate Results
_____ Laboratory Control Sample
_____ ICP Serial Dilution Results
_____ Sample Quantitation Assessment
_____ GFAA Results (Addendum)

NOTE: If GFAA methods (SW-846 7000 series) were used to analyze samples, the data validation of these analyses should be attached as an addendum to these Data Review Worksheets.

If spreadsheets are used to automate calculations, they must be attached to these worksheets.

Overall Comments: _____

Definitions and Qualifiers:

J - Estimated result with undetermined bias
J+ - Estimated result, result may be biased high
J- - Estimated result, result may be biased low
QL – quantitation limit (the laboratory may use reporting limit, practical quantitation limit, detection limit)
U - analyte not detected
UJ - Estimated nondetect – quantitation limit is estimated
R - Rejected data (unusable)
MDL or IDL – Method detection limit or instrument detection limit, respectively

Actions based on MS, laboratory duplicate, field duplicate, serial dilution analyses should be applied to all samples of the same matrix or to the results of all samples within a given area of the site, if deemed appropriate. Any validation action based upon professional judgement or any deviation from the validation guidelines presented in these worksheets needs to be described in detail in an attached narrative or memo.

Reviewer: _____ Date: _____

All criteria were met: ____
Criteria were not met, and/or see below: ____

I. DATA COMPLETENESS

A. Data Package:

_____ The tests requested on the COC or in subsequent communications were performed and reported.

_____ The correct analyte list was reported.

_____ The COCs (external and internal) are present and complete.

_____ Sample receiving documentation is complete.

Missing Information	Date Lab Contacted	Date Received

B. Other Discrepancies

All criteria were met: ____
Criteria were not met, and/or see below: ____

II. HOLDING TIMES (HT) and SAMPLE PRESERVATION

The objective of this parameter is to ascertain the validity of results based on the sample condition, and holding time of the sample from the time of collection to the time of preparation, and subsequently from the time of preparation to the time of analysis. Complete the table for all samples and circle the analysis date for samples not within criteria.

Sample ID	Date Sampled	Mercury (Hg) 7470A/7471A Date Analyzed	Metals by ICP 6010B Date Analyzed	pH	ACTION

Cooler temperatures: _____

Criteria (professional judgement):

- Analysis HT: Mercury – 28 days from sample collection; Other metals - 180 days from sample collection
- Aqueous Preservation: pH ≤ 2 with nitric acid for all metals.
- Cooler/Storage Temperature: 4°C ± 2°C for aqueous and solid matrices until preparation and analysis

Actions (to be used as professional judgement):

1. If aqueous samples were not properly preserved in the field or upon receipt (within 24 hours of sample collection) or if samples were not digested within 24 hours, qualify detected results as estimated low (J-) and reject nondetects (R).
2. If holding times are exceeded, qualify detected results as estimated low (J-) and reject nondetects (R).
3. If HTs are grossly exceeded (> 2x), notify the Project Chemist for action.
4. If samples were not at the proper temperature (>10°C), the validator should document all justifications for qualifying or not qualifying sample data in the validation memo. For example, SW-846 only requires thermal preservation for mercury in soils.

All criteria were met: ____
Criteria were not met, and/or see below: ____

III. INSTRUMENT CALIBRATION

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrumentation is capable of producing and maintaining acceptable quantitative data.

1. Analytical Sequence

A. Did the laboratory use the proper number of standards for calibration as described in the method or per manufacturer's recommendation? (ICP metals = a blank and at least one standard, Hg = a blank and at least five standards) — Yes or No

B. Were initial calibrations performed successfully on a daily basis or once/24 hours and each time the instrument was set up? — Yes or No

C. Were all measurements the average of at least two replicate exposures? — Yes or No

D. Was an initial calibration verification standard (ICV) analyzed for all analytes at the proper concentration (e.g., within the linear range for 6010B) and at the beginning of sample analysis? — Yes or No

Was the ICV made from a second source (different than calibration standards)? — Yes or No

E. Were continuing calibration verification standards (CCVs) analyzed for all analytes immediately following daily calibration, every 10 samples, and at the end of the run at a mid-range concentration? — Yes or No

F. Although not required by SW-846, if a Contract Required Quantitation Limit (CRQL) check standard was analyzed, was the concentration of this CRQL standard at or comparable to the QL reported by the laboratory? Note: for ICP analysis, the CRQL check standard is often referred to as CRI standard. For CVAA, the CRQL check standard is often referred to as CRA — Yes or No

Actions:

1. If the calibration was not performed, qualify all results as unusable (R).
2. If the calibration is incomplete or if any of the above answers are "No", data quality may be affected.

Use professional judgment to determine the severity of the effect. Discuss any actions below and list the samples affected.

_____

_____

_____

_____

_____

All criteria were met: ____
Criteria were not met, and/or see below: ____

III. INSTRUMENT CALIBRATION (continued)

2. Recovery Criteria

List the analytes which did not meet the percent recovery (%R) criteria for the ICV, CCV, CRI, or CRA.

Date	ICV, CCV CRI, or CRA	Analyte	%R	Action	Samples Affected

Criteria:

Calibration standard	**%R**	**CRI/CRA standard**	**%R**
ICP Metals ICV or CCV	100 ± 10	ICP Metals (except Sb, Pb, Tl) CRI	100 ± 30
Mercury ICV	100 ± 10	Sb, Pb, Tl CRI	100 ± 50
Mercury CCV	100 ± 20	Mercury CRA	100 ± 30

Actions*: If any analyte does not meet the %R criteria, follow the actions stated below:

Full Validation:
1. For ICV nonconformance, apply action to all samples in the analytical sequence.
2. For CCV nonconformance, apply action to samples analyzed between the previous in-control CCV and the subsequent in-control CCV.

* As stated in the NFGs, use professional judgement to qualify.

	%R of Analyte in the ICV/CCV and Recommended Actions				
ICP Metals ICV/CCV and Mercury (ICV)	**< 75%**	**75 to 89%**	**111 to 125%**	**126 to 160%**	**> 160%**
Mercury (CCV)	**< 65%**	**65 to 79%**	**121 to 135%**	**136 to 170%**	**> 170%**
Detected Results	J- or R	J-	J	J+ or R	R
Nondetects	R	UJ	A	A	A

Qualification based on CRI/CRA	**%R of Analyte in the CRI/CRA and Recommended Actions**			
ICP Metals (except Sb, Pb,Tl) and Mercury	**< 50%**	**50 to 69%**	**130 to 180%**	**> 180%**
Sb, Pb,Tl	**< 30%**	**30 to 49%**	**150 to 200%**	**> 200%**
Detected Results > 2X the CRI/CRA	J	A	A	R
Detected Results < 2X the CRI/CRA	R	J-	J+	R
Nondetects	R	UJ	A	A

All criteria were met: ____
Criteria were not met,
and/or see below: ____

IV. BLANK ANALYSIS RESULTS

The objective of blank analysis results assessment is to determine the existence and magnitude of contamination resulting from laboratory or field activities. The criteria for evaluation of blanks apply to any blank associated with the samples, (e.g., equipment blank [EB], field blank [FB], preparation blank [PB], initial and continuing calibration blanks [ICB/CCB], etc.). If problems with any blank exist, all data associated with the case must be carefully evaluated to determine if there is an inherent variability in the data for the case, or if the problem is an isolated occurrence not affecting samples.

A.	Was a PB analyzed for each matrix or with each batch of samples digested (≤ 20 samples)?	Yes or No
B.	Was an ICB analyzed after the calibration standards ?	Yes or No
C.	Was a CCB analyzed after ever ten samples and at the end of the run?	Yes or No

Data quality may be affected if any of the above answers are "No". Use professional judgment to determine if the associated sample data should be qualified. Discuss any actions on a separate attached shseet, and list the samples affected.

Actions

Blanks must be evaluated in the following order:

- Lab blanks (preparation and calibration) must first be used to qualify equipment/field blanks and samples.
- Any contamination remaining in the equipment/field blanks will be used to qualify the associated samples.

Full Validation:

1. For PB nonconformance, apply action to all samples in the analytical batch.
2. For ICB nonconformance, apply action to all samples in the analytical sequence.
3. For CCB nonconformance, apply action to samples analyzed between the previous in-control CCB and the subsequence in-control CCB.

Limited Validation: Use the highest blank PB, ICB, or CCB in the analytical batch or sequence.

The blank actions/qualifications on the following page are written for CLP methods and not SW-846. Therefore, professional judgment may be used to modify some of the actions (e.g., in the case where QLs are extremely high or not technically supported). It may be appropriate to use actions for blanks from the 1994 National Functional Guidelines (e.g., if the laboratory reports nondetects at the MDL/IDL). Justification for using this approach must be documented in the worksheets and in the validation memorandum.

The guidelines below should be followed when using the 1994 National Functional Guidelines and the "5x rule".

Establish an Action Level (AL) for any analyte equal to five times (5x) the highest concentration of that element's contamination in any blank. Any blank with a negative result whose absolute value > IDL or MDL (or lowest quantitation limit) must be carefully evaluated to determine its affect on the sample data. Use professional judgment to assess the data.

Blanks must be evaluated in the following order:

- Lab blanks (preparation and calibration) must first be used to qualify equip/field blanks and samples.
- Any contamination remaining in the equip/field blanks will be used to qualify the associated samples.

Actions:

1. For positive blank contamination:
   - results ≤ AL are qualified as undetected (U) at the reported concentration.
   - results > AL or nondetects are accepted unqualified.

2. For negative blank contamination:
   - results ≤ absolute value of negative AL are estimated (J).
   - nondetects are estimated (UJ).
   - results > AL are accepted unqualified.

3. When both positive and negative blank contaminations exist, use professional judgment to assess data.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

October 2004 National Functional Guidelines

Blank Actions

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB (Positive)	≥ MDL but ≤ QL	Nondetect	No action
		≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL	Use professional judgement (see below [1])
	>QL	≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL but < Blank Result	Qualify as nondetect (U) at the blank level Or qualify result as unusable (R).
		> Blank Result	Use professional judgement (see below [1])
ICB/CCB (Negative)	≤ (-MDL) but ≥ (-QL)	≥ MDL or nondetect	Use professional judgement (see below [2])
	< (-QL)	< 10x QL	Quality results ≥ QL as estimated low (J-) and nondetects as estimated (UJ)
		> 10x QL (professional judgment)	No action (professional judgment)
PB / EB / FB (Positive)	> QL	≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL but < 10x Blank Result	Qualify results as unusable (R) or estimated high (J+)
		≥ 10x Blank Result	No action
	≥ MDL but ≤ QL	Nondetect	No action
		≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL	Use professional judgement (see below [1])
PB (Negative)	< (-QL)	< 10x QL	Qualify results ≥ QL as estimated low (J-), non-detects as estimated (UJ)
		> 10x QL (professional judgment)	No action (professional judgment)

[1] Consider establishing an action level (AL) at 5x the blank contamination. If sample result is <AL, qualify the reported result with a "U".

[2] Consider estimating positive results and nondetects (J-/UJ).

All criteria were met: ____
Criteria were not met, and/or see below: ____

IV. BLANK ANALYSIS RESULTS (continued)

Laboratory blanks

Matrix: Solid / Aqueous

Date Analyzed	Prep/ ICB/CCB	Analyte	Concentration (circle highest)	Units	Actions for Samples	Affected Samples

Field/Equipment blanks

Date Collected	Field ID	Analyte	Concentration	Units	Actions for Samples	Affected Samples

The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. For example, soil sample results will not be in the same units as the ICB, CCB, EB, or FB data. It may be easier to work with the raw data or use the following equation to convert results in µg/L to mg/Kg.

ICB, CCB, EB, or FB concentration in µg/L must be converted to mg/kg in order to compare with sample results.

$$\text{Concentration in } \mu g/L \times \frac{\text{Volume diluted to (} \quad \text{ml)}}{\text{Weight digested (} \quad \text{g)}} \times \frac{1L}{1000ml} \times \frac{1000\ g}{1kg} \times \frac{1mg}{1000\ \mu g} = \text{wet weight (mg/kg)}$$

For each sample, the concentrations are converted to dry weight using the % solids calculation:

$$\frac{\text{Wet weight conc}}{\%\ \text{Solids}} \times 100 = \text{Concentration in dry weight (mg/kg)}$$

All criteria were met: ____
Criteria were not met,
and/or see below: ____

V. ICP INTERFERENCE CHECK SAMPLE

The ICP interference check sample (ICS) verifies the analytical instrument's ability to overcome interferences typical of those found in samples and verifies the laboratory's interelement and background correction factors.

1. Frequency Requirements

A. Was the ICS solution analyzed at the beginning of each sample analysis run? Yes or No

If no, the data may be affected. Use professional judgement to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

_____

_____

_____

B. Did the laboratory analyze an ICS A solution (not required in 6010B)? Yes or No

2. Recovery Criteria

List any elements in the ICS solution, which did not meet the %R criteria. Also evaluate the ICS A if the laboratory performed this analysis. Use professional judgment for actions or use those listed below.

Date	Analyte	%R	Action	Samples Affected

Criteria: %R = 100 ± 20% the true value or the true value ± 2x the RL (whichever is greater).

Actions: If any analyte does not meet the %R criteria, follow the actions stated below:

Full Validation: Use %R = 100 ± 20% and apply action to samples analyzed between the previous in-control ICS and the subsequent in-control ICS (if the ICS was analyzed more frequently than the method requirement) if samples contain interferents at levels comparable to or greater than the levels in the ICS.

Limited Validation: Use %R = 100 ± 20% and apply actions to all samples in the analytical sequence if samples contain interferents at levels comparable to or greater than the levels in the ICS..

Qualify results	**%R of Analyte in the ICS Solution**		
	%R < 50%	**%R = 50%-79% or < true value - 2x RL**	**%R > 120% or > true value + 2x RL**
Detected Results	J-	J-	J+
Nondetects	R	UJ	A

All criteria were met: ____
Criteria were not met, and/or see below: ____

V. ICP INTERFERENCE CHECK SAMPLE (continued)

3. ICS A Analysis Results (using ENSR professional judgment and guidance from the NFGs since analysis of the ICS A solution is not required in 6010B)

List the concentration of any elements ≥ MDL (or lowest quantitation limit used) in the ICS A solution that should not be present. For soil samples, results might not be in the same units as the ICS solutions; it may be easier to work with the raw data.

List the samples affected by interferences below:

Interferent	Concentration in ICS A (ug/L)	Sample ID	Sample ID	Sample ID	Sample ID	Sample ID
Al						
Ca						
Fe						
Mg						
Element						

Criteria: No target analytes should be present in the ICS A solution at concentration ≥ MDL.

Actions:

1. If an element was detected ≥ MDL but should not be present in the ICS A and sample concentrations of the interferents (Al, Ca, Fe, and Mg) are < ICS A; accept results unqualified.

2. If an element was detected ≥ MDL but should not be present in the ICS A and sample concentrations of the interferents (Al, Ca, Fe, and Mg) are comparable or higher than those found in the ICS A, qualify detected results for the affected element as estimated biased high (J+) and accept nondetects.

3. If an element was detected as negative interference, (i.e., the absolute value ≥ MDL) but should not be present in the ICS A and sample concentrations of the interferents (Al, Ca, Fe, and Mg) are comparable or higher than those found in the ICS A, qualify detected results < 10x the absolute value of the negative result for the affected element as estimated biased low (J-) and nondetects (UJ).

Note: If the levels of interferents in the samples are comparable to or higher than those found in the samples, it may be appropriate to calculate the estimated interference for the analytes of interest using the following equation. Information on the impact of the calculated interference on the results for the analytes of interest may be included in the validation memorandum.

$$\text{Calculated Estimated Intereference} = \frac{\text{Interferent in sample}}{\text{Interferent in ICS A}} \times \text{element concentration in ICSA}$$

All criteria were met: ____
Criteria were not met,
and/or see below: ____

VII. MATRIX SPIKE (MS) RESULTS

This data is generated to determine the effect of each sample matrix on sample preparation procedures and the measurement methodology.

1. Frequency Criteria

A. Was the MS analysis performed on a site-specific sample? Yes or No
If no, results are not evaluated due to potential differences in sample matrix.

B. Was an MS prepared at the required frequency (1 / batch / 20 samples / matrix)? Yes or No

C. Was a Post digestion spike (PDS) performed for any analytes that fail MS %R criteria? Yes or No
(recommended for a new or unusual matrix and NA for CVAA)

D. Was a matrix spike/matrix spike duplicate (MS/MSD) analyzed in place of or in addition to a laboratory duplicate analysis? If yes, refer to Section VIII for calculations of RPDs from MS/MSD results. Yes or No

2. Recovery Criteria

List the %Rs for analytes, which did not meet the criteria.

Sample # _____ Matrix: _____ Units: _____

Analyte	MS/MSD Spiked Sample Result (SSR)	Sample Result (SR)	Spike Added (S)	MS/MSD %R	Action

Criteria: %R = 75-125% or project-specific QC limits (LL – lower limit, UL – upper limit).

Actions: MS actions apply to all samples of the same matrix. This qualification will also be applied to the results of all samples within a given area of the site, if deemed appropriate.

1. If the sample result (SR) > 4x the spike concentration (S), no action is taken.
2. If any analyte does not meet the %R criteria and a Post Digestion Spike analysis was performed, use professional judgement to assess the results. Refer to the National Functional Guidelines for recommended actions.
3. If either the MS or MSD does not meet %R criteria, qualify all associated samples.

Qualify results	MS %R in the Sample		
	%R < 30%	%R = 30%- 74% or 30% to LL	%R > 125% or > UL
Detected results	J-	J-	J+
Nondetects	R	UJ	A

All criteria were met: ____
Criteria were not met, and/or see below: ____

VIII. LABORATORY DUPLICATE RESULTS

Laboratories run duplicate samples to verify laboratory consistency and precision. They are a measure of laboratory performance. It is expected that soil/sediment duplicate results will have a greater variance than water matrices due to difficulties associated with preparing identical duplicate samples.

1. Frequency Criteria

A. Was the duplicate analysis or MSD analysis performed on a site -specific sample? Yes or No
If no, results are not evaluated due to potential differences in sample matrix.

B. Was a duplicate or MSD analysis prepared at the required frequency (1 /batch /20 samples /matrix)? Yes or No

2. Precision Criteria: List the RPDs for analytes which did not meet the criteria.

Sample # _____ Matrix: _____ Units: _____

For the soil matrix, calculate the sample quantitation limit (RL based on PQL) in mg/kg using the amount, volume, and % solids data for the sample. In some cases the lab may run an MS/MSD in place of a duplicate. Calculate RPDs from MS/MSD results.

Element	QL (ug/L)	QL (mg/Kg)	Sample or MS Result	Duplicate or MSD Result	RPD (%)	Action
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						
Tin						

Attach a separate sheet for additional metals

Criteria:
RPD ± 20% for aqueous, RPD ± 35% for soil samples, if sample and duplicate results ≥ 5x QL.
QC limits of ± QL for aqueous, ± 2x QL for soil samples, if sample or duplicate result < 5x QL.

Actions: Indicate which criteria were used to evaluate precision by circling either the RPD or QL. If both samples are nondetected, the RPD is not calculated (NC), precision is considered acceptable. No action is needed.
If RPD is exceeded and sample or duplicate results are ≥ 5x QL, estimate detected results and nondetects (J/UJ).
If RPD is exceeded and sample or duplicate result is < 5x QL (including nondetects) and absolute difference between sample and duplicate is > QL for waters or > 2x QL for soils, estimate detected results and nondetects (J/UJ).

All criteria were met: ____
Criteria were not met,
and/or see below: ____

IX. FIELD DUPLICATE RESULTS

Field duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and lab precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field duplicate samples.

If appropriate, list the analyte concentration not meeting RPD criteria. For soil matrix, calculate the sample quantitation limit in mg/kg using the amount, volume, and %solids data for the sample.

Sample#_____Duplicate#_____Matrix:_____Units:_____

Element	QL (ug/L)	QL (mg/Kg)	Sample Result	Duplicate Result	RPD (%)	Action
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						
Tin						

Attach a separate sheet for additional metals

Field duplicate actions should be applied to all other samples of the same matrix type. This qualification will also be applied to the results of all samples within a given area of the site, if deemed appropriate.

Criteria:
RPD ± 30% for aqueous, ± 50% for soils, if sample and duplicate results ≥10x QL.
Absolute difference of ± 4x QL for aqueous, ± 8x QL for soils if sample and duplicate <10x QL.
RPD and absolute difference must be exceeded if one result ≥ 10x QL and one <10x QL.

Actions:
Indicate which criteria were used to evaluate precision by circling either the RPD or QL. If both samples are nondetected, the RPD is not calculated (NC), no action is needed.

If RPD is exceeded and sample results are ≥ 10x QL, estimate detected results and nondetects (J/UJ).
If RPD is exceeded and sample or duplicate result is < 10x QL, estimate detected results and nondetects (J/UJ) for elements whose absolute difference is > 4x QL for waters and > 8x QL for soils.
If RPD is NC because one result is ≥ 10x QL and one nondetect, estimate detected results and nondetects (J/UJ).
If RPD is NC because one result is < 10x QL and one nondetect, use professional judgement.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

X. LABORATORY CONTROL SAMPLE (LCS) RESULTS

The assessment of the LCS(s) is to monitor the overall performance of each step during the analysis, including the sample preparation and determine matrix specific precision and accuracy.

Recovery Criteria: List any LCS results not within project-specific criteria, laboratory established control limits or National Functional Guideline recovery criteria.

Indicate which criteria were used: _____

AQUEOUS LCS

Date	Analyte	%R	Action	Samples Affected

Note: NFGs have no control limits for Ag and Sb; however, include Ag and Sb in professional judgment. Apply actions to all samples in the same preparation batch.

Actions:

Aqueous LCS:	%R < 50%	%R = 50 – lower limit or 80%	%R > upper limit or 120%	%R >150%
Positive Sample Results	J-	J-	J+	R
Nondetects	R	UJ	A	R

SOLID LCS

Date	Analyte	LCS Conc.	QC Windows	Action	Samples Affected

Criteria: LCS results must be within the QC windows provided by the vendor. In absence of vendor limits use aqueous LCS control limits.

Note: Apply actions to all samples in the same preparation batch.

Actions:

Solid LCS	Less than Lower Acceptance Limit	Greater than Upper Acceptance Limit
Positive Sample Results	J-	J+
Nondetects	UJ	Accept

2. Frequency Criteria

Was an aqueous LCS analyzed with each batch of aqueous samples digested or for every group of aqueous samples in an SDG, whichever is more frequent? Yes or No

Was an solid LCS analyzed with each batch of solid samples digested or for every group of soil/sediment samples in an SDG ,whichever is more frequent? Yes or No

If no, data quality may be jeopardized. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions and list affected samples.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

XI. SERIAL DILUTION ANALYSIS

The assessment of the serial dilution analysis is to determine the effect of the sample matrix on the accuracy of the results.

Were serial dilutions (1:5 dilutions) performed for each matrix and the results of the diluted sample analysis agreed within 10% difference (%D) of the original undiluted analysis for analyte concentrations >50x the IDL or MDL before dilution? Yes or No

Serial dilutions were not performed for the following target analytes: (optional for Hg) Yes or No

Was the serial dilution anlaysis performed on a site-specific sample? If no, results are not evaluated due to potential differences in sample matrix. Yes or No

List the % Ds for analytes which did not meet the %D criterion (10%).

Sample #:_____ Matrix:_____ Units:_____

Element	IDL/MDL	50x IDL/MDL	Sample Results	Corrected Serial Dilution Results	%D	Action
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						
Tin						

Attach a separate sheet for additional metals

Actions: Actions apply to all samples of the same matrix. This qualification will also be applied to the results of all samples within a given area of the site, if deemed appropriate.

Estimate detected results and nondetects (J/UJ) for elements with %Ds > 10.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

XII. SAMPLE QUANTITATION ASSESSMENT

The objective is to ensure that the reported sample quantitation results are accurate. Evaluate any technical problems not previously addressed, examine the raw data for any anomalies, verify that there were no transcription or reduction errors on one or more samples and that results fall within the linear range for ICP and within the calibration range for CVAA.

1. Instrument Detection Limits/Method Detection Limits (IDL/MDL)/Quantitation Limits (QLs):

   A. Were results reported down to IDL/MDL or QL? (Circle one) IDL/MDL or QL

   B. Were IDL/MDL or QL results for all elements reported at levels that meet project objectives? Yes or No
   If not, indicate affected elements:

   C. If appropriate, estimate (J) results between the IDL/MDL and QL (refer to project-specific QAPP). Attach a separate sheet listing the qualified samples and analytes.

2. Reporting requirement:

   A. Were sample weights (including dry weights), volumes, and dilutions taken into account when reporting results (positive and nondetects)? If no, the reported results may be inaccurate. Request that the laboratory resubmit the corrected data. Yes or No

   B. Did sample results fall within the linear dynamic range for ICP and within the calibration range for CVAA? Yes or No
   If no, were dilutions performed? Yes or No
   List the affected samples/elements/dilution factor :

   If no, and dilution was not performed, estimate results (J).
   List the affected samples/elements:

All criteria were met: ____
Criteria were not met,
and/or see below: ____

XII. SAMPLE QUANTITATION ASSESSMENT (continued)

Sample Quantitation (full validation only): The sample quantitation evaluation is to verify that there were no transcription or reduction errors and to verify laboratory sample quantitation on one or more samples. In the space below, please show a minimum of one sample calculation.

ICP by 6010B

Mercury by 7470A/7471A

For soil samples, the following equation may be necessary to convert raw data values reported in µg/L to actual sample concentrations (mg/kg):

$$\text{Conc. in } \mu g/L \times \frac{\text{Volume diluted to (} \quad \text{ml)}}{\text{Weight digested (} \quad \text{g)}} \times \frac{1L}{1000ml} \times \frac{1000\,g}{1kg} \times \frac{1mg}{1000\,\mu g} = \text{concentration in wet weight (mg/kg)}$$

In addition, the concentrations are converted to dry weight using the % solids calculation:

$$\frac{\text{Wet weight conc}}{\% \text{ Solids}} \times 100 = \text{Concentration in dry weight (mg/kg)}$$

Laboratory/Location:	ENSR Data Package #:	
Laboratory SDG/Job No:	Client/Site Name:	
No. of Samples-Matrix:	Project Number:	
Acceptance Criteria: QAPP/Method	Validation Actions:	
Validator:	Date Checked:	Full / Limited Validation (circle one)

DATA PACKAGE COMPLETENESS CHECKLIST

ITEM	YES	NO	N/A	COMMENTS
Sample results included?				
Detection levels included?				
Field I.D. included?				
Laboratory I.D. included?				
Sample matrix included?				
Sample receipt temperature 2-6°C?				
Sample preservation acceptable?				
Signed COCs included?				
Date of sample collection included?				
Date of sample prep. included?				
Date of analysis included?				
Method reference included?				
QC Documentation included?				
Case Narrative included				
Equipment/Field Blank IDs				
Field Duplicate IDs				

Definitions: IDL – Instrument Detection Limit; MDL – Method Detection Limit; RL – Reporting Limit; SQL = Sample Quantitation Limit; %RSD – Percent Relative Standard Deviation; %D – Percent Difference; %R – Percent Recovery; RPD – Relative Percent Difference; r – correlation coefficient; LCS – Laboratory Control Sample; NFG – National Functional Guidelines

Comments	Review Element	Criteria*	Action
	Preserv.:	See method	Use prof. judgment
	HT:	See method	J-/UJ if exceeded
	Calib. curve Cyanide Other	r ≥ 0.995 100 ±15% 100 ±10%	Use prof. judgement J+ if exceeded J-/UJ if below
	Blank	< RL	Refer to NFG
	MS/MSD	%R= 75-125% RPD ±20%	J+ if %R > 125 J-/UJ if %R < 75 J if RPD exceeded
	Lab Dup	Aq. RPD ±20% So. RPD ±35%	J if RPD exceeded
	Field Dup (ENSR)	Aq. RPD ±30% So. RPD ±50%	See ENSR DV actions
	LCS/LCSD	%R= 75-125% RPD ±30%	J+ if %R > 125 J-/UJ if %R < 75 J if RPD exceeded
	* If no criteria specified by the method, lab, or QAPP, use these QC limits as guidance.		

QA/QC CHECKLIST FOR GENERAL CHEMISTRY ANALYSIS

ITEM	YES	NO	N/A	COMMENTS
PARAMETER:		**METHOD:**		
Calibration Info Included in Lab Package?				
Criteria met? (%RSD, r, %Rs)				
Method Blank Data Included in Lab Package?				
Criteria met? (< RL)				
Field/Equipment Blank Included in Lab Package?				
Criteria met? (< RL)				
Matrix Spike (MS) Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
MS Duplicate or Lab Dup Data Included in Lab Package?				
%R or RPD criteria met? (Method or Lab or QAPP)				
Field Duplicate Included in Lab Package?				
RPD criteria met? (QAPP OR ENSR)				
QC Check Samples/LCS Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
PARAMETER:		**METHOD:**		
Calibration Info Included in Lab Package?				
Criteria met? (%RSD, r, %Rs)				
Method Blank Data Included in Lab Package?				
Criteria met? (< RL)				
Field/Equipment Blank Included in Lab Package?				
Criteria met? (< RL)				
Matrix Spike (MS) Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
MS Duplicate or Lab Dup Data Included in Lab Package?				
%R or RPD criteria met? (Method or Lab or QAPP)				
Field Duplicate Included in Lab Package?				
RPD criteria met? (QAPP OR ENSR)				
QC Check Samples/LCS Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
PARAMETER:		**METHOD:**		
Calibration Info Included in Lab Package?				
Criteria met? (%RSD, r, %Rs)				
Method Blank Data Included in Lab Package?				
Criteria met? (< RL)				
Field/Equipment Blank Included in Lab Package?				
Criteria met? (< RL)				
Matrix Spike (MS) Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
MS Duplicate or Lab Dup Data Included in Lab Package?				
%R or RPD criteria met? (Method or Lab or QAPP)				
Field Duplicate Included in Lab Package?				
RPD criteria met? (QAPP OR ENSR)				
QC Check Samples/LCS Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				

Use this space for notes/comments and/or spot check calculation (if required)