

# **EPA Field Demonstration Quality Assurance Project Plan**

## Field Analysis of Mercury in Soil and Sediment



# **Field Demonstration Quality Assurance Project Plan**

## **Field Analysis of Mercury in Soil and Sediment**

Prepared by:

Science Applications International Corporation  
Idaho Falls, Idaho

Contract No. 68-C-00-179

Prepared for:

Dr. Stephen Billets  
Environmental Services Division  
National Exposure Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Las Vegas, Nevada 89193

### Concurrence Signatures

The primary purpose of the Demonstration is to evaluate innovative field technologies for the measurement of mercury in soil and sediment based on their performance and cost as compared to a conventional, off-site laboratory analytical method. The Demonstration will take place under the sponsorship of the United States Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program.

This document is intended to ensure that all aspects of the Demonstration are documented and scientifically sound and that operational procedures are conducted in accordance with quality assurance and quality control specifications and health and safety regulations.

The signatures of the individuals specified below indicate their concurrence with and agreement to operate in compliance with the procedures specified in this document.

Dr. Stephen Billets U.S. EPA Task Order Manager	Date	Mikhail Mensh Milestone Inc.	Date
George Brilis U.S. EPA NERL Quality Assurance Manager	Date	Volker Thomsen NITON LLC	Date
John Nicklas SAIC Task Order Manager	Date	Joseph Siperstein Ohio Lumex Co.	Date
Joseph Evans SAIC Quality Assurance Manager	Date	Felecia Owen MTI, Inc.	Date
Ray Martrano Analytical Laboratory Services, Inc.'s Laboratory Manager	Date	John I.H. Patterson Metorex	Date

Demonstration Plan Distribution List			
Organization	Mailing Address	Recipient	No. Of Copies
EPA-NERL/ESD	944 East Harmon Ave. Las Vegas, NV 89119	Dr. Steve Billets	2
		George Brilis	1
EPA-NRMRL/LRPCD QA Manager	26 W. Martin Luther King Drive Cincinnati, OH 45268	Ann Vega	1
EPA Office of Solid Waste	2800 Crystal Drive Arlington, VA 22202	Shen-yi Yang	1
DOE-ORNL	Oak Ridge Operations Office Oak Ridge, TN 37831	Elizabeth Phillips	1
UT-Battelle/ORNL	One Bethel Valley Road Oak Ridge, TN 37831	Roger Jenkins	1
TDEC Department of Energy Oversight	761 Emory Valley Road Oak Ridge, TN 37830	Dale Rector	1
Bechtel Jacobs	One Bethel Valley Road Oak Ridge, TN 37831	Janice Hensley	1
Metorex, Inc.	Princeton Crossroads Corp. Center 250 Phillips Blvd., Suite 250 Ewing, NJ 08618	John I.H. Patterson	1
Milestone	160B Shelton Road Monroe, CT 06468	Mikhail Mensh	1
NITON LLC	900 Middlesex Turnpike, Bldg. 8 Billerica, MA 01821	Volker Thomsen	1
Ohio Lumex Co.	9263 Ravenna Road, Unit A-3 Twinsburg, OH 44087	Joseph Siperstein	1
MTI, Inc.	1609 Ebb Drive Wilmington, NC 28409	Felecia Owen	1
Analytical Laboratory Services, Inc.	34 Dogwood Lane Middletown, PA 17057	Ray Martrano	1
Science Applications International Corporation	950 Energy Drive Idaho Falls, ID 83401	John Nicklas	1
		Joseph Evans	1
	11251 Roger Bacon Drive Reston, VA 20190	Maurice Owens	1
		Fernando Padilla	1
	411 Hackensack Ave. Hackensack, NJ 07601	Rita Schmon-Stasik	1
		Mike Bolen	1
		John King	1
		Andy Matuson	1
		Herb Skovronek	4
	2260 Park Ave., Suite 402 Cincinnati, OH 45206	Jim Rawe	1
		Joseph Tillman	1
Science Applications International Corporation	151 Lafayette Drive Oak Ridge, TN 37831	Allen Motley	1
		W. Kevin Jago	1
	595 East Brooks Ave, #301 Las Vegas, NV 89030	Nancy Patti	1
		Mark Pruitt	1

---

## Notice

This document was prepared for the EPA SITE Program under Contract No.: 68-C-00-179. It has been subjected to the Agency's peer and administrative reviews and has been approved for publication as an EPA document. Mention of corporation names, trade names, or commercial products does not constitute endorsement or recommendation for use.

---

## Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. Under the mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and scientific support that can be used to solve environmental problems, build the scientific knowledge base needed to manage ecological resources wisely, understand how pollutants affect public health, and prevent or reduce environmental risks.

The National Exposure Research Laboratory is the agency's center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. Goals of the laboratory's research program are to (1) develop and evaluate methods and technologies for characterizing and monitoring air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the scientific support needed to ensure effective implementation of environmental regulations and strategies.

The EPA's Superfund Innovative Technology Evaluation (SITE) Program evaluates technologies designed for characterization and remediation of contaminated Superfund and Resource Conservation and Recovery Act sites. The SITE Program was created to provide reliable cost and performance data in order to speed acceptance and use of innovative remediation, characterization, and monitoring technologies by the regulatory and user community.

Effective monitoring and measurement technologies are needed to assess the degree of contamination at a site, provide data that can be used to determine the risk to public health or the environment, and monitor the success or failure of a remediation process. One component of the EPA SITE Program, the Monitoring and Measurement Technology Program, demonstrates and evaluates innovative technologies to meet these needs.

Candidate technologies can originate within the federal government or the private sector. Through the SITE Program, developers are given the opportunity to conduct a rigorous demonstration of their technologies under actual field conditions. By completing the demonstration and distributing the results, the agency establishes a baseline for acceptance and use of these technologies. The Monitoring and Measurement Technology Program is managed by the Office of Research and Development's Environmental Sciences Division in Las Vegas, Nevada.

Gary Foley, Ph. D.  
Director  
National Exposure Research Laboratory  
Office of Research and Development

---

## Abstract

The Demonstration of innovative field devices for the measurement of mercury in soil and sediment is being conducted under the EPA's SITE Program in February 2003 at the United States Department of Energy's (DOE) Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee and the Tennessee Department of Environment and Conservation's Department of Energy Oversight facility in Oak Ridge, Tennessee. The primary purpose of the Demonstration is to evaluate innovative field devices for the measurement of mercury in soil and sediment based on their performance and cost as compared to a conventional, off-site laboratory analytical method. The five field measurement devices listed below will be demonstrated:

- Metorex's X-MET 2000 Metal Master Analyzer, X-Ray Fluorescence Analyzer
- Milestone Inc.'s Direct Mercury Analyzer (DMA-80), Thermal Decomposition Instrument
- NITON's XL-700 Series Multi-Element Analyzer, X-Ray Fluorescence Analyzer
- Ohio Lumex's RA-915+ Portable Mercury Analyzer, Atomic Absorption Spectrometer, Thermal Decomposition Attachment RP 91C
- MTI, Inc.'s PDV 5000 Hand Held Instrument, Anodic Stripping Voltammeter<sup>(1)</sup>.

This Demonstration Plan describes the procedures that will be used to verify the performance and cost of each field measurement device. The plan incorporates the quality assurance and quality control elements needed to generate data of sufficient quality to document each device's performance and cost. A separate Innovative Technology Verification Report (ITVR) will be prepared for each device. The ITVRs will present the Demonstration findings associated with the Demonstration objectives.

<sup>1</sup> MTI, Inc. participated in the Pre-Demonstration under the name Owen Scientific.

---

## Contents

Concurrence Signatures .....	ii
Demonstration Plan Distribution List .....	iii
Notice .....	iv
Foreword .....	v
Abstract .....	vi
Contents .....	vii
Tables .....	x
Figures .....	xi
Abbreviations, Acronyms, and Symbols .....	xii
Acknowledgments .....	xv
Executive Summary .....	xvi
1 Project Description and Objectives .....	1
1.1 Purpose of this Study .....	1
1.1.1 Background .....	1
1.1.2 SITE Demonstration .....	2
1.2 Vendor Technology Descriptions .....	2
1.2.1 Metorex Technology Description .....	2
1.2.2 Milestone Inc. Technology Description .....	4
1.2.3 NITON Technology Description .....	5
1.2.4 Ohio Lumex Co. Technology Description .....	6
1.2.5 MTI, Inc. Technology Description .....	6
1.3 Pre-Demonstration Activities .....	8
1.3.1 Site Descriptions .....	8
1.3.2 Site Sampling Activities .....	13
1.3.3 Soil and Sediment Homogenization .....	15
1.3.4 Pre-Demonstration Results .....	15
1.4 Project Objectives .....	17
1.4.1 Primary Objectives .....	17
1.4.2 Secondary Objectives .....	18
2 Project Organization .....	19
2.1 General Responsibilities .....	19
2.1.1 EPA .....	19
2.1.2 DOE .....	19
2.1.3 Tennessee Department of Environmental Conservation .....	19
2.1.4 SAIC .....	19
2.1.5 Referee Laboratory .....	20



---

## Contents (Continued)

	2.1.6	Vendors	20
2.2		Contact Information	20
3		Experimental Approach	25
	3.1	Experimental Design	25
		3.1.1 Field (Environmental) Sample Selection and Preparation	25
		3.1.2 SRM Sample Selection	26
		3.1.3 Spiked Samples	27
		3.1.4 Vendor Testing	27
		3.1.5 Independent Laboratory Confirmation	27
		3.1.6 Schedule	27
	3.2	Primary Project Objectives	27
		3.2.1 Statement of Primary Objectives	27
		3.2.2 Statistical Approach and Evaluation of Primary Objectives	29
	3.3	Secondary Objectives	34
		3.3.1 Secondary Objective # 1: Ease of Use	35
		3.3.2 Secondary Objective # 2: Health and Safety Concerns	35
		3.3.3 Secondary Objective # 3: Portability of the Device	36
		3.3.4 Secondary Objective # 4: Instrument Durability	36
		3.3.5 Secondary Objective # 5: Availability of Vendor Instruments and Supplies	38
4		Demonstration Activities	39
	4.1	Preparation of Test Material	39
		4.1.1 Homogenized Field Samples	39
		4.1.2 SRM Samples	44
	4.2	Field Analysis by Vendors	46
		4.2.1 Distribution of Samples	46
		4.2.2 Handling of Waste Material	47
	4.3	Field Observations	47
		4.3.1 Roles and Responsibilities	47
		4.3.2 Records	49
5		Referee Laboratory Testing and Measurement Protocols	51
	5.1	Referee Laboratory Selection	51
	5.2	Reference Method	53
		5.2.1 Laboratory Protocols	53
		5.2.2 Laboratory Calibration Requirements	55
	5.3	Additional Analytical Parameters	55
6		Referee Laboratory QA/QC Checks	56
	6.1	QA Objectives	56
	6.2	QC Checks	57
7		Data Reporting, Data Reduction, and Data Validation	59
	7.1	Referee Laboratory	59
		7.1.1 Data Reduction	59
		7.1.2 Data Validation	59

---

## Contents (Continued)

	7.1.3	Data Storage Requirements . . . . .	60
	7.1.4	Laboratory Reporting . . . . .	60
	7.2	Vendor Reporting . . . . .	60
	7.2.1	Field Reporting . . . . .	60
	7.2.2	Data Reduction/Validation . . . . .	60
	7.3	Final Technical Reports . . . . .	61
8		QA Assessments . . . . .	62
	8.1	Performance Audits . . . . .	62
	8.2	Systems Audits . . . . .	62
	8.2.1	Systems Audit - SAIC GeoMechanics Laboratory . . . . .	63
	8.2.2	Systems Audit - Referee Laboratory (ALSI) . . . . .	63
	8.2.3	Systems Audit - Vendor Technology Evaluation . . . . .	63
	8.3	Corrective Action . . . . .	64
	8.3.1	Corrective Action for Systems Audits . . . . .	65
	8.3.2	Corrective Action for Data Outside Control Limits . . . . .	65
9		References . . . . .	66
	Appendix A -	Laboratory Homogenization and Subsampling of Field Collected GeoMaterials Revision 1	
	Appendix B -	Analytical Laboratory Services, Inc.'s Standard Operating Procedures	

## Tables

Table	Page
1-1	Summary of Vendor Technologies . . . . . 3
1-2	Milestone DMA-80 Precision and Accuracy for Various Matrices . . . . . 5
1-3	Ohio Lumex RA-915+ Detection Limits for Various Matrices . . . . . 7
1-4	Mercury in Tailings Piles - Six Mile Canyon Area of Carson River Site . . . . . 10
1-5	Y-12 Mercury Concentration in Surface and Subsurface Soil at Building 8110 . . . . . 11
1-6	Mercury Concentration in Sediments - Upper East Fork of Poplar Creek at Y-12 . . . . . 11
1-7	Mercury in Subsurface Soils at the Confidential Manufacturing Site . . . . . 12
1-8	Mercury in Selected Test Plot Core Locations - Puget Sound . . . . . 13
1-9	Pre-Demonstration Analytical Results from Candidate Laboratories . . . . . 16
2-1	Vendors Selected for the Mercury Field Analysis Demonstration . . . . . 22
2-2	Demonstration Contact List . . . . . 23
3-1	Test Samples Collected from Each of the Four Field Sites . . . . . 26
3-2	Field Sample Contaminant Ranges for Vendor Technologies . . . . . 26
3-3	Projected Field Measurement Demonstration Schedule . . . . . 28
3-4	Estimated Sensitivities for Each Field Measurement Device . . . . . 28
3-5	Example Ease of Use Form . . . . . 35
3-6	Example Health and Safety Concerns Form . . . . . 36
3-7	Example Portability of the Device Form . . . . . 37
3-8	Example Instrument Durability Form . . . . . 38
4-1	Sample Volume, Containers, Preservation, and Holding Time Requirements . . . . . 43
4-2	Shipping Addresses and Contacts for Demonstration Samples . . . . . 46
5-1	Methods for Total Mercury Analysis . . . . . 54
5-2	Analytical Methods for Non-Critical Parameters . . . . . 54
6-1	QA Objectives for Mercury Measurements by SW-846 Method 7471B . . . . . 56
6-2	QC Checks for Mercury Measurements by SW-846 Method 7471B . . . . . 58

---

## Figures

Figure		Page
1-1	Experimental Design Flow Diagram. . . . .	9
2-1	Organizational Chart . . . . .	21
4-1	Test Sample Preparation at the SAIC GeoMechanics Laboratory . . . . .	40
4-2	Example Sample Homogenization Form . . . . .	42
4-3	Example Sample Label . . . . .	43
4-4	Example Chain-of-Custody Form . . . . .	45

---

## Abbreviations, Acronyms, and Symbols

%	Percent
%D	Percent difference
°C	Degrees Celsius
µg/kg	Microgram per kilogram
µg/l	Microgram per liter
AA	Atomic absorption
AAS	Atomic absorption spectrometry
AC	Alternating current
ALSI	Analytical Laboratory Services, Inc.
Ag	Silver
Am	Americium
As	Arsenic
ASV	Anodic stripping voltammetry
Au	Gold
bls	Below land surface
Cd	Cadmium
CIH	Certified Industrial Hygienist
Cl	Chlorine
cm	Centimeter
cm <sup>3</sup>	Cubic centimeter
COC	Chain of custody
CSV	Cathodic stripping voltammetry
Cu	Copper
CVAFS	Cold vapor atomic fluorescence spectrometry
DL	Detection limit
DMA-80	Direct Mercury Analyzer
DOE	Department of Energy
EPA	United States Environmental Protection Agency
EPA-NERL	Environmental Protection Agency's National Exposure Research Laboratory
FP	Fundamental parameters
FPXRF	Field portable x-ray fluorescence
g	Gram
g/cm <sup>3</sup>	Gram per cubic centimeter
gal	Gallon
hr	Hour

---

## Abbreviations, Acronyms, and Symbols (Continued)

Hg	Mercury
HgCl <sub>2</sub>	Mercury (II) chloride
ICAL	Initial calibration
ICP	Inductively coupled plasma
IDL	Instrument detection limit
IDW	Investigation-derived waste
Inc	Incorporated
ITVR	Innovative Technology Verification Report
kg	Kilogram
L	Liter
L/min	Liter per minute
LCS	Laboratory control sample
LEFPC	Lower East Fork Poplar Creek
LLC	Limited Liability Company
LRPCD	Land Remediation and Pollution Control Division
m <sup>3</sup>	Cubic meter
MDL	Method detection limit
mg	Milligram
mg/kg	Milligram per kilogram
mg/L	Milligram per liter
ml	Milliliter
mm	Millimeter
MMT	Measurement and Monitoring Technology
MSDS	Material safety data sheet
MS/MSD	Matrix spike/matrix spike duplicate
ND	Non-detectable, not detected, less than detection limit
NERL	National Exposure Research Laboratory
ng/L	Nanogram per liter
ng/m <sup>3</sup>	Nanogram per cubic meter
NIST	National Institute of Standards and Technology
nm	Nanometer
NRML	National Risk Management Research Laboratory
ORNL	Oak Ridge National Laboratory
Pb	Lead
PI	Prediction interval
POC	Point of contact
PPE	Personal protective equipment
PQL	Practical quantitation limit
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation

---

## Abbreviations, Acronyms, and Symbols (Continued)

SAIC	Science Applications International Corporation
Se	Selenium
Sec	Second
SITE	Superfund Innovative Technology Evaluation
SOP	Standard operating procedure
SOW	Statement of work
SRM	Standard reference material
SW-846	Test Methods for Evaluating Solid Waste; Physical/Chemical Methods
SWDA	Solid Waste Disposal Act
TD/AAS	Thermal decomposition / atomic absorption spectrometry
TDEC	Tennessee Department of Environment and Conservation
TOC	Total organic carbon
TOM	Task Order Manager
TP	Tailings pile
TSA	Technical system audit
UEFPC	Upper East Fork of Poplar Creek
VOC	Volatile Organic Compound
XRF	X-ray fluorescence
Y-12	Y-12 Oak Ridge Security Complex, Oak Ridge, Tennessee
Zn	Zinc

---

## **Acknowledgments**

Science Applications International Corporation (SAIC) acknowledges the support of the following individuals in preparing this document: Dr. Stephen Billets of the EPA National Exposure Research Laboratory (NERL); Ms. Elizabeth Phillips of the DOE ORNL; Mr. John Patterson of Metorex; Mr. Mikhail Mensh of Milestone, Inc.; Mr. Volker Thomsen, Ms. Debbie Schatzlein, and Mr. David Mercurio, of NITON LLC; Mr. Joseph Siperstein of Ohio Lumex; and Ms. Felecia Owen of MTI, Inc.

This document was QA reviewed by Ms. Ann Vega of the EPA National Risk Management Research Laboratory's Land Remediation and Pollution Control Division and Mr. George Brillis of NERL.



---

## Executive Summary

Performance verification of innovative environmental technologies is an integral part of the regulatory and research mission of the EPA. The SITE Program was established by the EPA Office of Solid Waste and Emergency Response and Office of Research and Development under the Superfund Amendments and Reauthorization Act of 1986. The program is designed to meet three primary objectives: (1) identify and remove obstacles to the development and commercial use of innovative technologies; (2) demonstrate promising innovative technologies and gather reliable performance and cost information to support site characterization and cleanup activities; and (3) develop procedures and policies that encourage use of innovative technologies at Superfund sites as well as other waste sites or commercial facilities. The intent of a SITE Demonstration is to obtain representative, high-quality performance and cost data on innovative technologies so that potential users can assess a given technology's suitability for a specific application.

The Demonstration of innovative field devices for the measurement of mercury in soil and sediment is to be conducted under the SITE Program in February 2003 at DOE ORNL in Oak Ridge, Tennessee and the Tennessee Department of Environment and Conservation's Department of Energy Oversight facility in Oak Ridge, Tennessee. The Demonstration is being conducted under the Monitoring and Measurement Technology Program, which is administered by the Environmental Sciences Division of the EPA NERL in Las Vegas, Nevada. The primary purpose of the Demonstration is to evaluate innovative field measurement devices for mercury in soil and sediment based on comparison of their performance and cost to those of a conventional, off-site laboratory analytical method. Laboratory and method selection followed a carefully documented procedure to ensure the best data quality possible for the collected samples.

The following five field measurement devices will be demonstrated and evaluated:

- Metorex's X-MET 2000 Metal Master Analyzer, X-Ray Fluorescence Analyzer
- Milestone Inc.'s Direct Mercury Analyzer (DMA-80), Thermal Decomposition Instrument
- NITON LLC's XL-700 Series Multi-Element Analyzer, X-Ray Fluorescence Analyzer
- Ohio Lumex's RA-915+ Portable Mercury Analyzer, Atomic Absorption Spectrometer, Thermal Decomposition Attachment RP 91C
- MTI, Inc.'s PDV 5000 Hand Held Instrument, Anodic Stripping Voltammeter.

The mission of this program is to obtain high quality performance data. The performance and cost of each device will be compared to those of a conventional, off-site laboratory analytical method - that is, a reference method. The performance and cost of one device will not be compared to those of another device. The reference method that will be used for the Demonstration is EPA's "Test Methods for Evaluating Solid Waste; Physical/Chemical Methods" (SW-846) Method 7471B. SW-846 methods are intended as performance-based methods and, therefore, specified objectives have been designated in this Demonstration Plan. A separate ITVR will be prepared for each device. The Demonstration has both primary and secondary objectives. The primary objectives are critical to the technology evaluations and require use of quantitative results to draw conclusions regarding technology performance. The secondary objectives pertain to information that is useful but do not necessarily require use of quantitative results to draw conclusions regarding technology performance. The primary objectives for the Demonstration of the individual field measurement devices are as follows:

**Primary Objective # 1.**      *Determine the sensitivity of each field instrument with respect to the Method Detection Limit and Practical Quantitation Limit generated by each vendor.*

- 
- |                               |   |
|-------------------------------|---|
| <b>Primary Objective # 2.</b> | <i>Determine the potential analytical accuracy associated with the field measurement technologies.</i>  |
| <b>Primary Objective # 3.</b> | <i>Evaluate the precision of the field measurement technologies.</i>  |
| <b>Primary Objective # 4.</b> | <i>Measure the amount of time required for performing five functions related to mercury measurements: 1) mobilization and setup; 2) initial calibration; 3) daily calibration, 4) demobilization; and 5) sample analysis.</i> |
| <b>Primary Objective # 5.</b> | <i>Estimate the costs associated with mercury measurements for the following four categories: 1) capital; 2) labor; 3) supplies; and 4) investigation-derived waste.</i>  |

The secondary objectives for the Demonstration of the individual field measurement devices are as follows:

- |                                 |  |
|---------------------------------|--|
| <b>Secondary Objective # 1.</b> | <i>Document the ease of use, as well as the skills and training required to properly operate the device.</i> |
| <b>Secondary Objective # 2.</b> | <i>Document potential health and safety concerns associated with operating the device.</i>                   |
| <b>Secondary Objective # 3.</b> | <i>Document the portability of the device.</i>   |
| <b>Secondary Objective # 4.</b> | <i>Evaluate the durability of the device based on its materials of construction and engineering design.</i>  |
| <b>Secondary Objective # 5.</b> | <i>Document the availability of the device and spare parts.</i>  |

It is not an objective of the Demonstration to characterize the concentration of mercury in soil at specific sampling sites. It is, however, necessary to ensure comparability between vendor results and the referee laboratory results by utilizing a homogenous matrix, such that, all sub-samples have consistent mercury concentrations. For this reason some conditions of field samples have been sacrificed to obtain sub-samples with a consistent mercury concentration.

To address the Demonstration objectives, both environmental and standard reference material (SRM) samples will be analyzed during the Demonstration. The environmental samples were collected from four sites contaminated with mercury. The SRMs will be obtained from commercial providers. Collectively, the environmental and SRM samples will have the range of physical (sand, silt, and clay) and chemical (mercury concentration) characteristics necessary to properly evaluate the field measurement devices. In addition to SRMs and environmental samples, environmental spike samples using a known concentration of mercury (II) chloride will be prepared in an environmental matrix. This will be done as an additional test of each technology.

Upon completion of the Demonstration, field measurement device and reference method results will be compared to evaluate the performance and associated cost of each device. The ITVRs for the five devices are scheduled for completion in October 2003.

---

# Chapter 1

## Project Description and Objectives

### 1.1 Purpose of this Study

This Demonstration project is being performed to evaluate vendor field analytical equipment for the measurement of mercury (Hg) concentrations in soil and sediment. The Hg concentration results from the field analytical equipment of five vendors will be compared to results from a selected referee laboratory. In addition, factors such as the ease of use, cost, safety, portability, and durability of the vendor equipment will be evaluated.

#### 1.1.1 Background

Performance evaluation of innovative environmental technologies is an integral part of the regulatory and research mission of the United States Environmental Protection Agency (EPA). The Superfund Innovative Technology Evaluation (SITE) Program was established by EPA's Office of Solid Waste and Emergency Response and Office of Research and Development under the Superfund Amendments and Reauthorization Act of 1986.

The overall goal of the SITE Program is to conduct performance evaluation studies and to promote the acceptance of innovative technologies that may be used to achieve long-term protection of human health and the environment. The SITE Program includes the following elements:

- Measurement and Monitoring Technology (MMT) Program - evaluates innovative technologies that sample, detect, monitor, or measure hazardous and toxic substances. These technologies are expected to provide better, faster, or more cost-effective methods for producing real-time data during site characterization and remediation studies than do conventional technologies.
- Remediation Technology Program - conducts demonstrations of innovative treatment technologies to provide reliable performance, cost, and applicability data for site cleanups.
- Technology Transfer Program - provides and disseminates technical information in the form of updates, brochures, and other publications that promote the SITE Program and participating technologies. The Technology Transfer Program also offers technical assistance, training, and workshops to support the technologies. A significant number of these activities are performed by EPA's Technology Innovation Office.

This Demonstration is being performed under the MMT Program. The primary objectives of the MMT Program are as follows:

- Test and verify the performance of innovative field sampling and analytical technologies that enhance sampling, monitoring, and site characterization capabilities.
- Identify performance attributes of innovative technologies that address field sampling, monitoring, and characterization problems in a more cost-effective and efficient manner.
- Prepare protocols, guidelines, methods, and other technical publications that enhance acceptance of these technologies for routine use.

The MMT Program is administered by the Environmental Sciences Division of the EPA National Exposure Research Laboratory (NERL), in Las Vegas, Nevada. Science Applications International Corporation (SAIC) has prepared this

---

Quality Assurance Project Plan (QAPP) under the MMT Program to evaluate field analytical techniques for detecting Hg in soil and sediment. The EPA Task Order Manager (TOM) is Dr. Stephen Billets.

### 1.1.2 SITE Demonstration

This SITE Demonstration is divided into two phases: 1) Pre-demonstration and 2) Demonstration. The Pre-demonstration activities were completed in the Fall of 2002 and are described in Subchapter 1.3. Planned Demonstration activities are summarized in this subchapter and presented in detail throughout the remainder of this document.

The Demonstration will involve evaluating the capabilities of five vendors to measure mercury concentrations in soil and sediment. During the Demonstration, each vendor will receive field samples for analysis. Each sample will be analyzed in replicate. The samples were obtained during the Pre-demonstration phase from the following locations:

- Carson River Mercury Site (soil and sediment)
- Oak Ridge Y-12 National Security Complex (Y-12) (soil and sediment)
- A Confidential Manufacturing Facility (soil)
- Puget Sound (sediment).

In addition, each vendor will analyze certified standard reference material (SRM) samples and spikes prepared using environmental samples spiked with mercury (II) chloride ( $\text{HgCl}_2$ ). Together, the field samples, SRMs, and spikes will be called "Demonstration samples" for the purpose of this Demonstration. Each vendor will receive between 150 and 200 Demonstration samples. All Demonstration samples will be independently analyzed by a carefully selected referee laboratory. It is the intention of this program to compare results to a suitable analytical method. Samples will be in replicates of up to seven. The experimental design is fully described in Chapter 3.

## 1.2 Vendor Technology Descriptions

The following paragraphs provide details on each of the field technologies to be evaluated during this Demonstration. Information was provided by the vendors via responses to questionnaires, instrument manuals, brochures, and/or vendor web sites. This information has not been independently verified by SAIC; however, vendor claims (e.g., accuracy, precision, and sensitivity) will be evaluated as part of this Demonstration. Table 1-1 summarizes much of this information. Actual vendor operating conditions will be observed and recorded by SAIC during the Demonstration.

### 1.2.1 Metorex Technology Description

The Metorex X-2000 Metal Master analyzer is based on x-ray fluorescence (XRF) technology (Metorex, 2002). The sample to be measured is irradiated with a radioactive isotope. The isotopes most commonly used in soil analysis are cadmium ( $^{109}\text{Cd}$ ) and americium ( $^{241}\text{Am}$ ). If the energy of radiation from the source is higher than the absorption energy of a target element, the atoms of that element will be excited, and fluorescent x-ray radiation from that element can be detected with the instrument. The x-ray energies for specific elements are well defined. The instrument's detector converts the energies of x-ray quanta to electrical pulses. The pulses are then measured and counted. The intensity (counts in a certain time) from the measured element is proportional to the concentration of the element in the sample. The measurement technique is fast and nondestructive, and multiple elements can be measured simultaneously. The chemical or physical form of the atom does not affect the x-ray energy, because the electrons producing x-rays are not valence (outer) shell electrons. Both identification and quantitation can be accomplished from a single measurement. The high-resolution silicon-PIN (as in diode which is positive, intrinsic, negative) detector is stable and accurate, and continuous self-testing and automatic source decay correction insure the reliability and accuracy of the measurement results.

**Application and Specifications** - The Metorex analyzer can reportedly perform analysis on solids, powders, waste water, solutions, slurries, sludge, air particulate matter collected on filter, coating materials, and paste samples. The main unit weighs 5.67 kilograms (kg) and has dimensions of 44.96 centimeters (cm) by 33.53 cm by 10.16 cm. The probe has a weight of 1.36 kg and measures 22.35 cm by 24.89 cm by 7.62 cm. Required accessories include battery, battery charger, and field case for carrying the unit on the shoulder. The battery operates for approximately 4 hours before needing to be charged. For sample preparation, required accessories include sample cups, film, and a tool for compressing powder samples (pressing tool).

**Table 1-1.** Summary of Vendor Technologies.

INSTRUMENT PARAMETER	VENDOR NAME				
	Metorex, Inc.	Milestone Inc.	NITON LLC	Ohio Lumex Co.	MTI, Inc.
<b>Principle of Operation</b>	XRF	TD/AAS	EDXRF	AAS	ASV
<b>Analytical Range</b> <sup>1</sup>	10 to 1,000 mg/kg	50 µg/kg-5 mg/kg (8 µg/kg with larger sample aliquot)	20 to 1,000 mg/kg	5 µg/kg to 100 mg/kg	100 µg/kg to 1,000 mg/kg
<b>MDL</b> <sup>2</sup>	10 mg/kg	50 µg/kg	20 mg/kg	5 µg/kg	100 µg/kg
<b>Potential Interferences</b>	High Pb, As, Se, & Zn	VOCs, concentrated inorganic acids, & heavy metals	Pb, As, and Zn > 500 mg/kg	None Identified	High Ag
<b>Accuracy</b> <sup>1</sup>	15-20%	+/- 10%	At 100 mg/kg +/- 15%	+/- 10%	+/- 10%
<b>Precision</b> <sup>1</sup>	5-20%	+/- 5%	10% RSD @ 60 ppm to 20% for environmental samples	+/- 10%	+/- 15%
<b>Required Sample Size</b>	8 g	0.01 to 5 g	5 to 10 g	0.01 to 0.2 g	2 to 5 g
<b>Expected Throughput</b> <sup>3</sup>	10/hr	12/hr	25/hr - direct analysis; 10/hr with preparation	10/hr	10/hr

<sup>1</sup> This information is based solely upon vendor claims. These claims will be evaluated during the Demonstration.

<sup>2</sup> MDL for soil and sediment.

<sup>3</sup> Sample analyses based upon multiple hours of operation

µg/kg - micrograms per kilogram

mg/kg - milligrams per kilogram

AAS - Atomic Absorption Spectrometry

As, Cu, Hg, Pb, Se, and Zn - Arsenic, Copper, Mercury, Lead, Selenium and Zinc, respectively

ASV - Anodic Stripping Voltammetry

EDXRF - Energy Dispersive X-Ray Fluorescence

g - gram

hr - Hour

LLC - Limited Liability Company

MDL - Method Detection Limit

RSD - Relative Standard Deviation

TD - Thermal Decomposition

VOCs - Volatile Organic Compounds

XRF - X-Ray Fluorescence

---

**Operation** - The Metorex X-MET 2000 comes factory calibrated. When measuring with the Metal Master, calibration can utilize either fundamental parameters (FPs) or empirical calibration. FP calibration is reportedly fast and easy and does not require user interaction or calibration standards. The standard version analyzes the 25 most common elements from titanium to uranium, including, for example, arsenic, selenium, tin, lead, iron, and chromium. The elements analyzed can be customized according to the user needs. Empirical calibration is used when maximum accuracy is required; for example, when measuring trace elements. For site-specific analysis, the instrument needs to be calibrated either with site-specific or site-typical samples. The number of samples for calibration should be between 5 to 20, and must be an accurate analysis available for the elements of interest. The calibration sample must cover the concentration range for each element the user wants to measure.

The measurement is done either by placing the probe on the sample or placing the sample in a sample cup and placing the cup on the probe. The trigger is pressed, and the sample is measured for a preset time. One analysis takes from 30 seconds to 10 minutes, depending on the desired accuracy. On completion of the measurement an assay is displayed. Data collection, analysis, and management are completely automated. Connection to a remote computer allows transfer of the collected data for further evaluation and report generation.

When measuring soil, oversize materials and plants should be removed. If sample cups are used, it is advantageous to sieve the sample so that the particle size is homogenous. The water content difference between calibration samples and samples to be analyzed should be less than 25 percent (%) to minimize error. If the difference is larger than 25%, samples should be dried for accurate analysis.

Elements with energies close to mercury may interfere with the analysis if they are present in large quantities (approximately 5 times the mercury concentration). Large quantities of lead, arsenic, selenium, and zinc, for example can cause interference.

### 1.2.2 Milestone Inc. Technology Description

The thermal decomposition, atomic absorption (AA) spectrometry technique employed by Milestone Inc.'s Direct Mercury Analyzer (DMA-80) analyzes samples directly, eliminating digestion, chemical pretreatment, and waste disposal (Milestone, 2002). Samples are introduced to the DMA-80, dried, and then thermally decomposed in a continuous flow of oxygen. Combustion products are carried off and further decomposed in a hot catalyst bed. Mercury vapors are trapped on a gold amalgamator and subsequently desorbed for quantitation. The mercury content is determined using AA spectrophotometry at 254 nanometers (nm). The DMA-80 analyzes liquid and solid samples with no sample preparation and no waste disposal. The vendor notes that the DMA-80 can automatically process 40 samples in about 4 hours, start to finish. An intuitive controller uploads sample weights, controls the analysis, and processes data with built-in report generation and networking capabilities.

As per Milestone, the thermal decomposition technique eliminates the sample digestion step since the sample is thermally decomposed. In addition, the DMA-80 eliminates a chemical pretreatment step since the mercury is reduced by the catalysts in the decomposition tube. The use of the DMA-80 eliminates waste disposal because no reagents are required. Milestone notes that it has validated results for solid and liquid matrices.

**Application and Specifications** - The DMA-80 permits direct analysis of trace level mercury in several matrices, including solids (sediment, soil, sludge, food/feed, plant and animal tissues, coal, oil, fish, cement, paints) and liquids (wastewater, beverages, biological fluids). Milestone indicates that the DMA-80 has application in various industries including environmental, agriculture, petrochemical, food and feed, power plant, mines, and resources laboratories.

The Milestone system requires bench space measuring 150 cm in length and 80 cm deep. The dimensions of the unit itself are 80 cm by 42 cm by 30 cm (height) and the terminal measures 33 cm by 27 cm by 26 cm (height). The total weight is 56 kg. The DMA-80 can interface with any Windows® compatible printer. The unit requires alternating current (AC) power (110 volts, 60 hertz, 10-15 amperes). Standard grade oxygen is required with a gas regulator having a capacity of 60 pounds per square inch. The unit exhaust is connected to a fume hood. The DMA-80 is equipped with a 40-position autosampler and can optionally be interfaced to an analytical balance.

**Operation** - Instrument calibration is achieved using applicable SRMs, as recommended in the Milestone installation guide. These standards can be soil or other solids, tissue samples, or a certified liquid standard. Calibration is based on a second order calibration. The DMA-80 has dual measuring cells for an extended analysis range of 0-600 nanograms mercury. The method analytical range is 50 micrograms per kilogram ( $\mu\text{g/kg}$ ) to 5 milligrams per kilogram ( $\text{mg/kg}$ ) using a 100 milligram (mg) sample size. Using a 500 mg sample, a quantitation limit of 8  $\mu\text{g/kg}$  is expected with a detection limit of 0.04  $\mu\text{g/kg}$ . Maximum sample size is 500 mg. It is expected that approximately 12 samples per hour can be analyzed

during the Demonstration. Expected variability for the DMA-80 is +/- 5% with expected accuracy 90-110%. Milestone presents the following information on precision and accuracy in its manual for the DMA-80 (Table 1-2).

**Table 1-2.** Milestone DMA-80 Precision and Accuracy for Various Matrices.

Matrix (SRM Material)	Certified Results	DMA-80 Results*
Rice Flour (NIST 1568a)	5.8 ± 0.5 µg/kg	5.5 ± 0.8 µg/kg
Tomato Leaves (NIST 1573a)	34 ± 4 µg/kg	31.7 ± 1.4 µg/kg
Coal (NIST 1630a)	93.8 ± 3.7 µg/kg	93.4 ± 2.4 µg/kg
Fly Ash (NIST1633b)	141 ± 19 µg/kg	148.6 ± 1.8 µg/kg
Soil (NIST 2709)	1400 ± 80 µg/kg	1460 ± 20 µg/kg
Soil (NIST 2711)	6250 ± 190 µg/kg	6240 ± 70 µg/kg

\*Source: The DMA-80 Direct Mercury Analyzer Manual (Milestone, 2002)

NIST - National Institute of Standards and Technology

µg/kg - microgram/kilogram

### 1.2.3 NITON Technology Description

The NITON XL 700 series sample analyzer is an energy dispersive XRF spectrometer that uses either a <sup>109</sup>Cd radioactive isotope (XLi model) or a low-powered miniature x-ray tube with a silver target (XLt model) to excite characteristic x-rays of a test sample's constituent elements (NITON, 2002). These characteristic x-rays are continuously detected, identified, and quantified by the spectrometer during sample analysis. Stated simply, the energy of each x-ray detected identifies a particular element present in the sample, and the rate at which x-rays of a given energy are counted provides a determination of the quantity of that element that is present in the sample.

Detection of the characteristic mercury x-rays is achieved using a highly-efficient, thermo-electrically cooled, solid-state detector. Signals from this detector are amplified, digitized, and then quantified via integral multichannel analysis and data processing units. Sample test results are displayed in parts per million (ppm) of total elemental mercury.

**Application and Specifications** - The NITON XLt 700 series analyzer with x-ray tube excitation provides the user with the speed and efficiency of x-ray tube excitation, while reducing the regulatory demands typically encountered with isotope-based systems. In most cases, the x-ray tube equipped 700 analyzer can be shipped from state to state and country to country with minimal paperwork and expense. The XLi and XLt 700 Series analyzers offer testing modes for soil and other bulk samples; filters, wipes, and other thin samples; and lead-based paint. Testing applications include management of remediation projects, site assessments, and compliance testing. They provide simultaneous analysis of up to 25 elements, including all eight of the metals listed under the Resource Conservation and Recovery Act. XRF analysis is non-destructive, so screened samples can be sent to an accredited laboratory for confirmation of results obtained on-site.

NITON's software corrects automatically for variations in soil matrix and density making it applicable for both *in-situ* and *ex-situ* testing.

**Operation** - For *in-situ* analysis, the analyzer is placed directly on the ground or on bagged soil samples. Because contamination patterns tend to be heterogeneous, a large number of data points can be produced using *in-situ* testing to delineate contamination patterns. *In-situ* testing with either the XLi or XLt 700 Series instrument is in full compliance with EPA Method 6200. *In-situ* testing allows for testing many locations in a short time and is ideal for rapid site-profiling, locating sources of contamination, and monitoring and fine-tuning remediation efforts on-the-spot. *In-situ* analysis is not appropriate for wet sediment samples. In this case, sediments must be dried and can then be measured either bagged or in sample cups.

For *ex-situ* testing, the XL 700 series can test prepared, representative soil samples (dried, ground, sifted, homogenized) to generate analytical-grade data quality when required. Both the XLi and XLt 700 Series soil analyzers come with sample-preparation protocols.

The NITON instrument is factory calibrated. NITON's Compton normalization software automatically corrects for any differences in sample density and matrix so site specific calibration standards are never required. The unit also analyzes

---

for zinc, arsenic, and lead as these elements may cause interference at certain concentration levels. Total analysis time does not exceed 120 seconds (after sample preparation).

Sample preparation, for those samples not analyzed directly *in-situ*, may include the grinding and/or sieving of dried samples using either mortar and pestle or electric grinder. Wet samples, at a minimum, are filtered to remove standing water then dried. Although EPA Method 6200 specifies that mercury samples should not be oven-dried due to the potential volatilization loss of mercury, NITON uses oven-dried sample material without negative impact.

#### 1.2.4 Ohio Lumex Co. Technology Description

The RA-915+ Mercury Analyzer is a portable AA spectrometer with a 10-meter (m) multipath optical cell and Zeeman background correction (Ohio Lumex, 2001). Among its features is the direct detection of mercury without its preliminary accumulation on a gold trap. The instrument has a wide dynamic quantification measuring range (5 µg/kg to 100 mg/kg). The RA-915+ includes a built-in test cell for field performance verification. The unit can be used with the optional RP-91 for an ultra low mercury detection limit in water samples using the “cold vapor” technique. For direct mercury determination in complex matrices without sample pretreatment, including liquids, soils and sediments to be analyzed during this Demonstration, the instrument will be operated with the optional RP-91C accessory.

The operating principle of the RA-915+ is based on the effect of differential, Zeeman AA spectrometry combined with high-frequency modulation of polarized light. This combination eliminates interferences and provides the highest sensitivity. The RP-91C attachment is intended to decompose a sample and to reduce the mercury using the pyrolysis technique. The RP-91C attachment is a furnace heated to 800 degrees Celsius (°C) where mercury is converted from a bound state to the atomic state by thermal decomposition and reduced in a two-section furnace. In the first section of the furnace the “light” mercury compounds are preheated and burned. In the second section a catalytic afterburner decomposes “heavy” compounds. After the atomizer, the gas flow enters the analytical cell of the attachment. Ambient air is used as a carrier gas; no cylinders with compressed gasses are required. Zeeman correction eliminates interferences, thus, no gold amalgamation is required. The instrument is controlled and the data is acquired by software based on a Microsoft Windows® platform.

**Application and Specifications** - The RA-915+ is a portable spectrometer designed for interference-free analysis/monitoring of mercury content in ambient air, water, soil, natural and stack gases, chlorine alkali manufacturing, spill response, hazardous waste, foodstuff, and biological materials. The Ohio Lumex system is fully operational in the field and could be set up in a van, as well as a helicopter, marine vessel, or hand-carried for continuous measurements. It is suitable for field operation using a built-in battery for measurements of ambient air and industrial gases. The RP-91 and RP-91C attachments are used to convert the instrument into a liquid or solid sample analyzer, respectively.

According to the RA-915+ Analyzer manual, the base unit has dimensions of 47 cm by 22 cm by 11 cm and weighs 7.57 kg. The palm unit measures 13.5 cm by 8 cm by 2 cm and weighs 0.32 kg. Power supply can be a built-in 6 volt rechargeable battery, a power pack adapter, an external electric battery, or an optional rechargeable battery pack. The RP-91C system includes a pumping unit that has dimensions of 34 cm by 24 cm by 12 cm and a power supply unit measuring 14.5 cm by 15 cm by 8.5 cm. Site requirements cited in the manual include a temperature range of 5 to 40 °C, relative humidity of up to 98%, atmospheric pressures of 84 -106.7 kilopascals, along with requirements for sinusoidal vibration and magnetic field tension. Sensitivity of the instrument is not affected by up to a 95 percent background absorption caused by interfering components (dust, moisture, organic and inorganic gases).

**Operation** - The instrument calibration is performed by use of liquid or solid primary National Institute of Standards and Technology (NIST) traceable standards. The normal dynamic analytical range is from 5 µg/kg to 100 mg/kg of direct determination without dilution. No sample mineralization is needed, and no waste is generated. Sample throughput is up to 30 samples per hour without an auto sampler. Table 1-3 presents a summary of the analysis conditions provided by the vendor.

#### 1.2.5 MTI, Inc. Technology Description

The principle of analysis used by the MTI, Inc. PDV 5000 is anodic stripping voltammetry (ASV) (MTI, Inc., 2002). A negative potential is applied to the working electrode. When the electrode potential exceeds the ionization potential of the analyte metal ion in solution ( $M^{n+}$ ), it is reduced to the metal which plates onto the working electrode surface as follows:





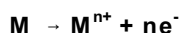
**Table 1-3.** Ohio Lumex RA-915+ Detection Limits for Various Matrices.

Sample Matrix	Detection Limit	Sample vol/weight	Atomization Techniques	# of Analyses/hr
Ambient air	2 ng/m <sup>3</sup>	20 L/min	without atomization	real-time, 1/sec
Natural and other gases	2 ng/m <sup>3</sup>	5-20 L/min	without atomization	real-time, 1/sec
Water	0.5 ng/L	20 mL	cold vapor	15
Oil, condensate	1 µg/kg	10 mg	pyrolysis	15
Solids, sediments	5 µg/kg	200 mg	pyrolysis	30
Urine	5 ng/L	1 mL	cold vapor	15
Tissues	1-5 µg/kg	20 mg	pyrolysis	15
Hair	20 µg/kg	10 mg	pyrolysis	15
Blood	0.5 µg/L	0.2 mL	cold vapor	15
Plants	2 µg/kg	50 mg	pyrolysis	15
Foodstuff	1-10 µg/kg	5-50 mg	pyrolysis	15

µg/kg - microgram per kilogram  
 L/min - Liters per minute  
 mg - Milligram  
 mL - Milliliter  
 ng/L - Nanogram per liter  
 ng/m<sup>3</sup> - nanogram per cubic meter  
 sec - Second

Where:  $M^{n+}$  = analyte metal ion in solution  
 $ne^-$  = number of electrons  
 M = metal plated onto the electrode

The longer the potential is applied, the more metal is reduced and plated onto the surface of the electrode (also known as the "deposition" or "accumulation" step), concentrating the metal. When sufficient metal has been plated onto the working electrode, the metal is stripped (oxidized) off the electrode by increasing, at a constant rate, a positive potential applied to the working electrode. For a given electrolyte solution and electrode, each metal has a specific potential at which the following oxidation reaction will occur:



The electrons released by this process form a current. This is measured and may be plotted as a function of applied potential to give a "voltammogram". The current at the oxidation or stripping potential for the analyte metal is seen as a peak. To calculate the sample concentration, the peak height or area is measured and compared to that of a known standard solution under the same conditions. As a metal is identified by the potential at which oxidation occurs, a number of metals may often be determined simultaneously, due to their differing oxidation potentials. The plating step makes it possible to detect very low concentrations of metal in the sample. The length of this step can be varied to suit the analyte concentration of the sample. For example, analysis of a 10 µg/kg solution of Pb may require a 3 to 5 minute accumulation step, while a solution in the mg/kg range would require less than 1 minute. Laboratory versions of the ASV device can measure ppt concentrations.

The MTI, Inc. PDV 5000 can be operated as a stand-alone instrument for screening, or attached to a laptop resulting in better limits of detection.

**Applications and Specifications** - As noted above, ASV can detect multiple metals in a single scan, but in the majority of cases, a specific metal is best analyzed using a specific electrolyte and electrode combination. This is essential for detection limits in the low µg/kg range. Where the detection range is in the mg/kg range, it is possible to analyze a larger range of metals per scan, but the reproducibility will be around 10% as opposed to the 3% typically seen when optimum conditions are used. The field conditions that may affect accuracy and precision include sample homogeneity, sample

---

handling errors, pipetting errors, unpredictable matrix effects, and sample and cell contamination. High silver concentrations can interfere with mercury determinations.

For solids, test kits can be used that include all required reagents. To “digest” the solids, a slightly modified Method 3050B is used from EPA’s Test Methods for Evaluating Solid Waste; Physical/Chemical Methods (SW-846).

The MTI, Inc. PDV 5000 weighs approximately 700 grams (g) and has dimensions of 10 cm by 18 cm by 4 cm. It can operate off a 110V AC source or direct current battery.

**Operation** - According to the vendor, it is realistic to expect the PDV 5000 to obtain data from the field that is within 20% of the true value. For this reason it is best to use the PDV 5000 to classify samples as “above a threshold concentration” or “below a threshold concentration.” For example, a lead limit of 20 µg/kg is allowed in drinking water. Therefore, the PDV 5000 should be calibrated with a 20 µg/kg lead standard and any result that is above 20 µg/kg, less 20% (i.e., 16 µg/kg), should be considered as potentially being above the 20 µg/kg limit.

The standard curve method compares the sample response with that of one or more known standards. Volts can allow calibration curves of between one and ten standards to be constructed and then compared with up to 15 samples. Generally, calibration is based on a single point comparison whereby the current generated by the standard is compared to the current generated by the sample. The response for a particular analyte will be proportional to its concentration in the analytical cell, so dilution by electrolyte or other reagents must be taken into consideration. For best results, the sample concentration in the cell should be close to the cell concentration of the standard with which it is being compared. Standard addition calibration involves analyzing a sample and then “spiking” the same sample solution with a small volume of standard before re-analyzing that solution. The same sample can be spiked and re-analyzed once or several times depending on the operator’s preference. The results from the sample and spiked sample runs are then plotted and a line of regression is fitted that is used to calculate the sample concentration.

## 1.3 Pre-Demonstration Activities

Pre-demonstration activities included development of a Pre-demonstration Plan dated September 2002, along with collection and homogenization of soils and sediments in late September 2002. There were six objectives for the Pre-demonstration:

- Establish concentration ranges for testing vendor analytical equipment during the Demonstration;
- Evaluate sample homogenization procedures;
- Determine mercury concentrations in homogenized soils and sediments;
- Select a reference method and qualify potential referee laboratories for the Demonstration;
- Collect and characterize soil and sediment samples which will be used in the Demonstration; and
- Provide soil and sediment matrices to the vendors for self-evaluation.

Figure 1-1 presents a flow diagram for the Pre-demonstration experimental design. Pre-demonstration activities and the results are discussed in the following subchapters. Site descriptions are provided in Subchapter 1.3.1, sampling activities are summarized in Subchapter 1.3.2, homogenization procedures are described in Subchapter 1.3.3, and Pre-Demonstration results are presented in Subchapter 1.3.4.

### 1.3.1 Site Descriptions

Soil and sediment samples were collected from four sites for use during the Demonstration. The following subchapters provide a brief description of each of those sites, including concentrations of mercury expected based on background data supplied by the sites.

#### 1.3.1.1 Carson River Mercury Site

The Carson River Mercury site includes mercury-contaminated soil at former gold and silver mining mill sites; mercury contamination in waterways adjacent to the mill sites; and mercury contamination in sediment, fish, and wildlife over more than a 50-mile length of the Carson River. Mercury is present at Carson River as either elemental mercury and/or inorganic mercury sulfides with less than 1%, if any, methyl mercury. This site provided both soil and sediment samples across the range of contaminant concentrations desired for the Demonstration. The point of contact (POC) is Wayne Praskins of EPA Region 9.

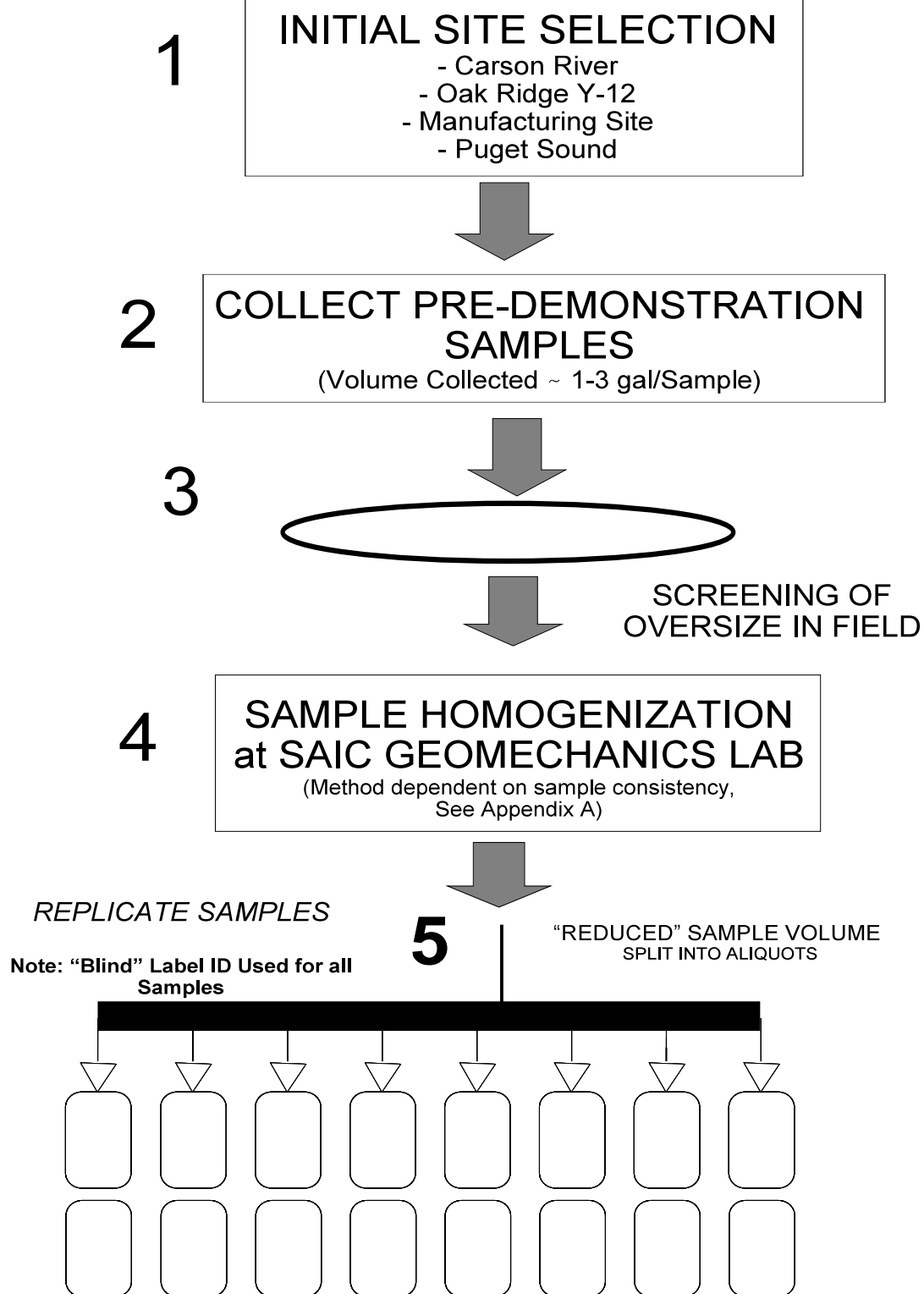


Figure 1-1. Experimental Design Flow Diagram.

**Site Location and History** - The site begins near Carson City, Nevada and extends downstream to the Lahontan Valley and Carson Desert. Contamination at the site is a legacy of the Comstock mining era of the late 1800s, when mercury was imported to the area for processing gold and silver ore. Ore mined from the Comstock Lode was transported to mill sites, where it was crushed and mixed with mercury to amalgamate the precious metals. The mills were located in Virginia City, Silver City, Gold Hill, Dayton, Six Mile Canyon, Gold Canyon, and adjacent to the Carson River between New Empire and Dayton. During the mining era, an estimated 7,500 tons of mercury were discharged into the Carson River drainage, primarily in the form of mercury-contaminated tailings (i.e., waste rock).

**Characterization** - Today, the mercury is in the sediments and adjacent flood plain of the Carson River and in the sediments of Lahontan Reservoir, Carson Lake, Stillwater Wildlife Refuge, and Indian Lakes. In addition, tailings with elevated mercury levels are still present at and around the historic mill sites, particularly in Six Mile Canyon. Historical mercury contamination data are presented in Table 1-4.

**Table 1-4.** Mercury in Tailings Piles - Six Mile Canyon Area of Carson River Site<sup>1</sup>

PARAMETER (Mercury)	TAILINGS PILE (TP) AREA								
	TP003	TP004	TP005	TP006	TP007	TP008	TP009	TP017	TP018
No. of Samples	6	16	6	6	22	11	5	10	5
Maximum Value (mg/kg)	1,039	904	937	691	4,672	350	700	1,300	1,606
Minimum Value (mg/kg) <sup>2</sup>	4	4	8	4	4	4	4	4	4
<b>Mean (mg/kg)</b>	<b>729</b>	<b>331</b>	<b>269</b>	<b>191</b>	<b>916</b>	<b>139</b>	<b>336</b>	<b>587</b>	<b>478</b>

<sup>1</sup> Source: EPA Region 9. *Revised Draft - Human Health Risk Assessment and RI Report, Carson River Mercury Site* (1994).

<sup>2</sup> The method detection limit (MDL) was 8 mg/kg, therefore levels below the MDL are reported as ½ the MDL (4 mg/kg)

#### 1.3.1.2 Y-12 National Security Complex

The Y-12 National Security Complex site is located at the U.S. Department of Energy's (DOE) Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. Mercury contamination is present in the soil at the Y-12 facility in many areas and also occurs in the sediments of the Upper East Fork of Poplar Creek (UEFPC). Both soil and sediment samples were collected from this site. The POCs are Elizabeth Phillips of DOE at ORNL and Janice Hensley of Bechtel Jacobs.

**Site Location and History** - The Y-12 Site is an active manufacturing and developmental engineering facility that occupies approximately 800 acres on the northeast corner of the DOE Oak Ridge Reservation adjacent to the city of Oak Ridge, Tennessee. Built in 1943 by the U.S. Army Corps of Engineers as part of the World War II Manhattan Project, the original mission of the installation was electromagnetic separation of uranium isotopes and weapon components manufacturing as part of the national effort to produce the atomic bomb. Between 1950 and 1963, large quantities of elemental mercury were used at Y-12 during lithium isotope separation pilot studies and subsequent production processes in support of thermonuclear weapons programs.

**Characterization** - Soils in the Y-12 facility are contaminated with mercury in many areas. One of the areas of known high levels of mercury in soils is in the vicinity of the "Old Mercury Recovery Building." At this location mercury was recovered by first "roasting" and then vaporizing. Mercury contamination also occurs in the sediments of the UEFPC. Recent investigations show that bank soils containing mercury along this reach of stream were eroding and contributing to mercury loading; stabilization of the bank soils along this reach of the creek was recently completed. Additional information on soil and sediment mercury concentrations, based upon historical data are presented in Tables 1-5 and 1-6.

#### 1.3.1.3 Confidential Manufacturing Site

A confidential manufacturing site contains elemental mercury, mercury amalgams, and mercury oxide in shallow sediments (less than 0.3 meters deep) and deeper soils (3.65 to 9.14 meters below surface). This site provided soil with concentrations across the desired contaminant range. The POC is Jim Rawe of SAIC.

**Table 1-5.** Y-12 Site Mercury Concentrations in Surface and Subsurface Soil at Building 8110.

Boring/Station ID	Depth Interval (feet bls)	Concentration (mg/kg)
Surface interval	0-5	144
Subsurface interval	5-10	48
Surface interval	---	---
Subsurface interval	4-6	303
Surface interval	0-1	100
Subsurface interval	1-3	25
Surface interval	0-0.3	30
Subsurface interval	3.0-4.0	1,436
Surface interval	0-1.5	21
Subsurface interval	10.5-11.0	1,040
Surface interval	---	---
Subsurface interval	6.0-6.3	44
Surface interval	---	---
Subsurface interval	5.0-6.0	135
Surface interval	0-2	134
Subsurface interval	2.0-4.0	199
Surface interval	2.0-4.0	39
Subsurface interval	5.0-5.8	84
Surface interval	---	---
Subsurface interval	4.0-6.0	20

<sup>1</sup> Source: Rothchild et al., 1984. Note: a dashed line indicated no sample collected/no data.  
bls - below land surface

**Table 1-6.** Mercury Concentrations (mg/kg) in Sediments - Upper East Fork of Poplar Creek at Y-12<sup>1</sup>

Parameter	STATION ID					
	LR-1	UEFPC-1	UEFPC-2	UEFPC-3	UEFPC-4	UEFPC-5
Elemental Mercury	8.32	6.37	5.26	30.1	29.7	28.5
Methylmercury	0.0632	0.00326	0.0514	0.0225	0.019	0.0142
Mercuric sulfide	7.82	2.45	6.18	1.46	3.41	4.08
Total mercury	140	14.1	125	38.7	51	38.7

<sup>1</sup> Source: DOE, 1998

**Site Location and History** - A confidential east coast manufacturing site was selected for participation in this Demonstration. The site had three operations that resulted in mercury contamination. The first operation involved amalgamation of zinc with mercury. The second process was the manufacturing of zinc oxide. The final operation was the reclamation of silver and gold from mercury-bearing materials in a retort furnace. Operations led to the dispersal of elemental mercury, mercury compounds such as chlorides and oxides, and zinc-mercury amalgams.

**Characterization** - Mercury values range from as low as 0.05 mg/kg to over 5,000 mg/kg with average values of approximately 100 mg/kg. Mercury can be found in soils at depths ranging from surface levels to approximately 9.14 m

below ground surface. Additional details about the historical distribution and concentration of mercury at this site are provided in Table 1-7.

**Table 1-7.** Mercury in Subsurface Soils at the Confidential Manufacturing Site.<sup>1</sup>

DEPTH INTERVAL (feet bls)	SAMPLE LOCATIONS/ (Concentrations in mg/kg)								
	A	B	C	D	E	F	G	H	I
12-13	< 0.56	8.7	68.2	1,910	1.3	21.8	418	11.7	< 0.06
14-15	< 0.56	43	7.6	114	3	339	557	8	17.1
16-17	< 0.55	117	0.8	1.5	4.9	244	494	14.9	1.3
18-19	< 0.59	0.16	0.62	0.11	19.5	2,260	1,549	9.3	9.9
20-21	< 0.53	61.2	0.13	116	28.8	342	349	5.3	2,300
22-23	< 0.62	0.4	0.34	10.1	0.66	2.1	4,060	81.5	580
24-25	< 0.59	5.4	0.066	3.7	3.7	180	30.4	3.7	---
26-27	< 0.66	2.2	< 0.047	2.6	0.15	0.091	7.1	16.3	---
28-29	< 0.18	1	0.67	1.7	21.4	2.4	8.5	42.8	---
30-31	< 0.5	0.092	< 0.059	0.89	< 0.059	43.9	3.2	42.8	---

<sup>1</sup> Source: From Confidential Monitoring Site, 2000 (Received from on-site representative). A dashed line indicates no result available for that interval.

#### 1.3.1.4 Puget Sound

The Puget Sound site consists of offshore sediments contaminated with mercury, polynuclear aromatic hydrocarbons, and phenolic compounds. The particular area of the site used for this Pre-demonstration (and Demonstration) activity consists of the Georgia Pacific, Inc. Log Pond in Bellingham Bay, Washington. SAIC is currently performing a SITE remedial technology evaluation in the Puget Sound. As part of ongoing work at that site, SAIC collected additional sediment for use during this MMT project. This site will be used to provide sediment in several concentration ranges. Joe Evans of SAIC is the primary POC for the Puget Sound site.

**Site Location and History** - The Georgia Pacific Log Pond is located within the Whatcom Waterway in Bellingham Bay, a well-established heavy industrial land use area with a maritime shoreline designation. Log Pond sediments measure approximately 1.52 to 1.82 m thick, and contain various contaminants including mercury, phenols, PAHs, polychlorinated biphenyls and wood debris. The area was capped in late 2000 and early 2001 with an average of seven feet of clean capping material as part of a Model Toxics Control Act interim cleanup action. The total thickness ranges from approximately 0.15 m along the site perimeter to 3 m within the interior of the project area. The restoration project produced 2.7 acres of shallow sub-tidal and 2.9 acres of low intertidal habitat, all of which had previously exceeded the Sediment Management Standards cleanup criteria (Anchor, 2001).

**Characterization** - Total PAHs range from 50 to 1200 mg/kg, and detected phenolic compounds (phenol, 4-methylphenol, and 2,4-dimethylphenol) range from 350 to 670 µg/kg. Mercury concentrations range from 0.16 to 400 mg/kg (dry wt.). The majority (98%) of the mercury detected in nearshore ground waters and sediments of the Log Pond is believed to be comprise of complexed divalent (Hg++) forms such as mercuric sulfide (Bothner, et al., 1980, ENSR, 1994, cited in Anchor, 2000). Zinc is also present in 18 of 27 samples at concentrations greater than 200 mg/kg. Additional information about the distribution and concentration of mercury collected as part of a pre-demonstration effort conducted in May, 2002 is presented in Table 1-8.

**Table 1-8.** Mercury in Selected Test Plot Core Locations - Puget Sound (Sampled in May 2002).

Horizon Sampled <sup>1</sup>	Core Sample ID	Core Depth Interval (meters)	Mercury Level (mg/kg-dry wt.)
Cap Sediments (top)	PD-T3-00.0-1.3-S	0.0 - 0.39	0.28
Cap Sediments (top)	PD-T5-0-2.3-S	0 - 0.70	3.87
"Contaminated Layer" (middle)	PD-T1-1.2-10.0	0.36 - 3.04	192
"Contaminated Layer" (middle)	PD-T2-0.8-6.8	0.02 - 2.07	98.3
"Contaminated Layer" (middle)	PD-T3-1.3-7.6	0.39 - 2.31	112
"Contaminated Layer" (middle)	PD-T4-1.1-6.25-A	0.33 - 1.90	118
"Contaminated Layer" (middle)	PD-T5-2.3-6.8	0.70 - 2.07	46.4
"Contaminated Layer" (middle)	PD-T6B-3.5-7.0	1.06 - 2.13	74.7
Native Sediments (bottom)	PD-T3-7.6-9.7-N	2.31 - 2.95	0.16
Native Sediments (bottom)	PD-T6B-7.0-9.1	2.13 - 2.77	0.46

<sup>1</sup> Three horizons were sampled. Cap sediments are 0.8-2.3 feet thick medium sand. "Contaminated layer" sediments are 1.37 - 2.68 meters thick clayey or sandy silt containing wood debris. Bottom native sediments are moderately stiff, silty, medium-to-fine sands with scattered shell and plant (twig) pieces.

### 1.3.2 Site Sampling Activities

Sampling activities for each of the four sites are summarized in the following subchapters. At each site, the soil and/or sediment was collected, homogenized by hand in the field, and sub-sampled for quick-turn around analysis. These sub-samples were sent to analytical laboratories to determine the general range of mercury concentrations at each of the four sites. In addition, at each site, soil and/or sediment samples were shipped to SAIC's GeoMechanics Laboratory for additional sample homogenization (as described in Subchapter 1.3.3 and Appendix A) and sub-sampling for use during the Pre-demonstration. For each sample point, the geographical positioning system coordinates or the latitude and longitude position was collected and recorded.

#### 1.3.2.1 Carson River Mercury Site

Sixteen near-surface soil samples were collected between 2.54 cm and 7.62 cm below ground surface. Two sediment samples were collected at the water-to-sediment interface. All eighteen samples were collected on September 23, 2002 with a hand shovel. Samples were collected in Six Mile Canyon and along the Carson River.

The sampling sites were selected based upon historical data from the site. Specific sampling locations in the Six Mile Canyon were selected based upon local terrain and visible soil conditions (e.g., color and particle size). The specific sites were selected to obtain soil samples with as much variety in mercury concentration as possible. These sites included hills, run-off pathways, and dry river bed areas. Sampling locations along the Carson River were selected based upon historical mine locations, local terrain, and river flow.

When collecting the soil samples, approximately 2.54 cm of surface soil was scraped to the side. The sample was then collected with a shovel, screened through a 6.3 millimeter (mm) (0.25-inch) sieve to remove larger material, and collected in 4.54 liter (L) sealable bags identified with a permanent marker. The sediment samples were collected with a shovel, screened through a 6.3 mm sieve to remove larger material, and collected in 4.54 L sealable bags identified with a permanent marker. Each of the 4.54 L sealable bags was placed into a second 4.54 L sealable bag, and the sample label was placed onto the outside bag. The sediment samples were then placed into 11.36 L buckets, lidded, and labeled with a sample label.

#### 1.3.2.2 Y-12 National Security Complex

Two matrices were sampled at Y-12 in Oak Ridge, TN; 1) creek sediment and 2) soil. A total of 10 sediment samples were collected; one sediment sample was collected from the Lower East Fork of Poplar Creek (LEFPC) and 9 sediment samples

---

were collected from the UEFPC. A total of 6 soil samples were collected from the Building 8110 area. The sampling procedures used are summarized below.

**Creek Sediments** - Creek sediments were collected on September 24-25, 2002 from the East Fork of Poplar Creek. Sediment samples were collected from various locations in a downstream to upstream sequence (i.e., the downstream LEFPC sample was collected first and the most upstream point of the UEFPC was sampled last). The sediment samples from Poplar Creek were collected using the following procedure:

- A commercially available clam-shell sonar dredge attached to a rope was slowly lowered to the creek bottom surface, where it was pushed into the sediment by foot. Several drops (usually 7 or more) of the sampler were made to collect enough material for screening. On some occasions, a shovel was used to remove overlying "hardpan" gravel to expose finer sediments at depth. Also, one sample consisted of creek bank sediments, which was collected using a stainless steel trowel.
- The collected sediment material was then poured onto a 6.3 mm sieve to remove material larger than 6.3 mm in diameter. Sieved samples were then placed in 13.63 L sealable plastic buckets. The sediment samples in these buckets were homogenized as well as possible with a plastic ladle.

**Soil** - Soil samples were collected from pre-selected boring locations on September 25, 2002 and sent for quick laboratory analysis in order to verify the presence of mercury prior to homogenization for the demonstration. All samples were collected in the immediate vicinity of Building 8110 using a commercially available bucket auger. Oversize material was hand picked from the excavated soil because the soil was too wet to be passed through a sieve. The screened soil was transferred to an aluminum pan, homogenized by hand, and sub-sampled to a 20 milliliter (mL) vial. The remaining soil was transferred to 4.54 L plastic containers.

#### *1.3.2.3 Confidential Manufacturing Facility*

Eleven subsurface soils were collected on September 24. All samples were collected with a Geoprobe® unit using plastic sleeves. Samples were collected in the former Plant # 2 area.

Drilling locations were determined based on historical data provided by the site. The intention was to gather soil samples across a range of concentrations. Because the surface soils were relatively clean fill, the sampling device was pushed to a depth of 3.65 m using a blank rod. Samples were then collected at pre-selected depths ranging from 3.65 to 8.53 m below the surface. Individual cores were 1.21 m long. The plastic sleeve for each 1.21 m core was marked with a permanent marker; the depth interval and the bottom of each core was marked. The filled plastic tubes were transferred to a staging table where appropriate depth intervals were selected for mixing. Selected tubes were cut into 0.6 m intervals, which were emptied into a plastic container for pre-mixing soils. When feasible, soils were initially screened to remove materials larger than 6.3 mm in diameter. In many cases, soils were too wet and clayey to allow screening; in these cases, the soil was broken into pieces by hand and using a wooden spatula, oversize materials were removed. These soils (screened or hand-sorted) were then mixed until the soil appeared visually uniform in color and texture. The mixed soil was then placed into a 4.54 L sample container for each chosen sample interval. This process was then repeated for each subsequent sample interval.

#### *1.3.2.4 Puget Sound*

Sediment samples collected on August 20 and 21 from the Georgia-Pacific Log Pond in Puget Sound were obtained beneath approximately 3.04 to 6.09 m of water using a vibra-coring system capable of capturing cores to one foot below the proposed dredging prism. The vibra-corer consisted of a core barrel attached to a power head. Aluminum core tubes, equipped with a stainless steel "eggshell" core catcher to retain material, were inserted in the core barrel. The vibra-core was lowered into position on the bottom and advanced to the appropriate sampling depth. Once sampling was completed, the vibra-core was retrieved and the core liner removed from the core barrel. The core sample was examined at each end to verify that sufficient sediment was retained for the particular sample. The condition and quantity of material within the core was then inspected to determine acceptability.

To verify whether an acceptable core sample was collected the following criteria had to be met:

- target penetration depth (i.e., into native material) was achieved;
- sediment recovery of at least 65% of the penetration depth must be achieved to deem the core acceptable; and
- sample appears undisturbed and intact without any evidence of obstruction or blocking within the core tube or core catcher.



---

The percent sediment recovery was determined by dividing the length of material recovered by the depth of core penetration below the mud line. If the sample was deemed acceptable, overlying water was siphoned from the top of the core tube, and each end of the tube capped and sealed with duct tape. Following core collection, representative samples were collected from each core section representing a different vertical horizon. Sediment was collected from the center of the core that had not been smeared by, or in contact with, the core tube. The volumes removed were placed in a decontaminated stainless steel bowl or pan, and mixed until homogenous in texture and color (approximately 2 minutes). After all sediment for a vertical horizon composite was collected and homogenized, representative aliquots were placed in the appropriate pre-cleaned sample containers for analysis. Samples of both the sediment and the underlying native material were collected in a similar manner. Distinct layers of sediment and native material were easily recognizable within each core. Once the samples were collected and homogenized in the field, they were sent to the SAIC GeoMechanics Laboratory for additional homogenization and sub-sampling. At that point, sub-samples were sent from the SAIC GeoMechanics Laboratory to one of the pre-selected analytical laboratories for a quick-turnaround analysis.

### 1.3.3 Soil and Sediment Homogenization

One of the objectives of the Pre-demonstration activities was to plan, implement, and evaluate the procedure by which the samples collected from the various sites and locations were homogenized and prepared for distribution to the parties involved in the Pre-demonstration. To ensure comparability between vendor results and the referee laboratory results, it is necessary to have a homogenous matrix, such that, all sub-samples have consistent mercury concentrations. It is not necessary, however, that the homogenized sample accurately reflects the actual concentration of mercury at a given location. The Pre-demonstration activities included the analysis of samples selected to adequately test the comparability of multiple sub-samples.

During the Pre-demonstration, eight homogenized samples were prepared - two from each of the four sites from which samples were collected. Three of the samples were prepared using the “slurry” homogenization procedure and the other five were prepared using the “dry” homogenization protocol (see Appendix A). Each homogenized batch had enough sample material to fill vials for distribution to the vendors (one sample each) and the candidate laboratories (each sample was sent as blind triplicates to each of the three labs used during the Pre-demonstration). As discussed in the following subchapter, results from the sample aliquots (sub-samples) collected from each of the homogenized batches indicated that the dry and slurry protocols were suitable for the purposes of the Demonstration, with an average relative standard deviation (RSD) of 13% for all 24 triplicates analyzed (8 samples in triplicate by each of the three labs).

### 1.3.4 Pre-Demonstration Results

As noted earlier, there were six objectives associated with Pre-demonstration activities (SAIC, 2002). The results supporting the achievement of each of these objectives are discussed below.

**Pre-Demonstration Objective No. 1 - Establish Concentration Ranges for Testing Vendor Analytical Equipment During the Demonstration:** Based upon the results of the homogenized soil and sediment samples analyzed by the candidate laboratories, the following concentration ranges were established for samples to be analyzed during the Demonstration:

- Low Concentration Range = ~ 1 µg/kg to ~ 100 µg/kg
- Mid Concentration Range = ~ 100 µg/kg to ~ 10 mg/kg
- High Concentration Range = ~ 10 mg/kg to ~ 1,000 mg/kg

These concentration ranges reflect the target ranges of each of the vendor technologies, the concentrations expected based on the samples collected from each of the site locations, and the need to present samples that will challenge both the field and laboratory methods on both the high and low end of the method limitations.

**Pre-Demonstration Objective No. 2 - Evaluate Sample Homogenization Procedures:** Based upon the results of triplicate analyses performed by the candidate laboratories, it was determined that the homogenization procedure was effective and adequate for sample preparation during the Demonstration. The average RSD for all field sample triplicates averaged between 11.8 and 14.9% at each of the three candidate laboratories, thereby meeting established criteria for the Pre-demonstration Plan. Similarly, SRM samples were analyzed in triplicate at each of the laboratories with average RSDs for these samples ranging from 6.1 to 13.3 percent.

The RSD results were used to further evaluate the homogenization procedure by assessing if each homogenized sample triplicate set had an RSD of <25%. A single sample set at two of the candidate laboratories had an RSD that slightly

exceeded this value; one sample triplicate at one of the labs had an RSD of 27.4% and one triplicate at another lab had an RSD of 30.5%. In both cases the remaining two laboratories had RSDs between 12.0% and 17.5%, within acceptable limits. The individual sample RSDs indicate that additional replicates should be performed during the Demonstration in order to reduce average variability in samples that are more difficult to homogenize. These Pre-demonstration results were also used to statistically determine the number of replicates needed during the Demonstration as discussed in detail in Chapter 3.

**Pre-Demonstration Objective No.3 - Determine Mercury Concentrations in Homogenized Soils and Sediments:**

Based upon the results of the triplicate analyses performed by the candidate laboratories, the mercury concentrations in the homogenized soils and sediments collected at the four selected field sites were determined as presented in Table 1-9. The sample concentrations from all sites ranged from approximately 0.18 to 993 mg/kg mercury.

**Table 1-9 . Pre-Demonstration Analytical Results from Candidate Laboratories**

Field Site/ Sample ID	Mercury Concentrations (mg/kg)			Percent Solids
	Minimum	Maximum	Average	Average
<b>Puget Sound</b>				
MFA-P-P-1-XXX	0.25	0.445	0.33	99.1
MFA-P-P-2-XXX	140	260	220	33.67
<b>Carson River</b>				
MFA-P-C-3-XXX	120	180	160	97.03
MFA-P-C-4-XXX	0.18	0.43	0.31	99.17
<b>Manufacturing Facility</b>				
MFA-P-M-5-XXX	26	50	40	98.07
MFA-P-M-6-XXX	420	993	675	99.2
<b>Oak Ridge Y-12 Plant</b>				
MFA-P-Y-7-XXX	7.7	13	9.7	65.97
MFA-P-Y-8-XXX	120	210	163	61.7
<b>SRM</b>				
MFA-P-S-9-XXX	0.056	0.092	0.079	97.6
MFA-P-S-10-XXX	62	99	78	99.1

**Pre-Demonstration Objective No. 4 - Select a Reference Method and Qualify Potential Referee Laboratories for the Demonstration:** Based on the dynamic range of the method, types of mercury included in the analysis, and the fact that the method was a widely-used protocol, SW-846 Method 7471B (analysis of mercury in solid samples by cold-vapor, AA spectrometry) was selected as the reference method. This conclusion was also supported by information obtained from the technology vendors, as well as the expected contaminant types and soil/sediment mercury concentrations expected in the test matrices.

Nine laboratories were sent a Statement of Work (SOW) for the analysis of mercury during the Pre-demonstration. Seven laboratories responded to the SOW with appropriate bids. (Two laboratories chose not to bid.) Three of the seven laboratories were selected as candidate laboratories based upon technical merit, experience, and pricing. The three candidate laboratories were sent ten samples in triplicate for a total of 30 analyses. Eight of the samples were the homogenized field samples and two were SRM samples. (See information presented in the previous subchapter.) Each of the laboratories reported results that were within the 95 percent Prediction Interval (PI). (Measurements should fall within the PI range 19 of 20 times.)

---

The referee laboratory, to be used for the Demonstration, was selected from one of the three candidate laboratories based upon the laboratory's interest in continuing into the Demonstration, the laboratory reported SRM results, the laboratory method detection and quantitation limit, the precision of the laboratory calibration curve, and cost. The data packages provided by the laboratories were reviewed and a pre-award audit was performed in order to determine final laboratory selection. This is explained in detail in Chapter 5.

**Pre-Demonstration Objective No. 5 - Collect and Characterize Soil and Sediment Samples That Will be Used in the Demonstration:** Soil and sediment samples were collected from four different sites: Puget Sound, Washington; Carson River Area, Nevada; Oak Ridge, Tennessee; and a Manufacturing Facility on the East Coast. These samples were characterized as non-homogenous grab samples to determine mercury concentration ranges for subsequent homogenous samples to be created and used during the Demonstration.

**Pre-Demonstration Objective No. 6 - Provide Soil and Sediment Matrices to the Vendors for Self-Evaluation:** Vendors were sent homogenized field samples and SRMs for purposes of a self evaluation. Eight vendors participated in the Pre-Demonstration. Each of the vendors was sent two homogenized samples from each of the four sampling sites. (Two of the homogenized samples were sent to the vendors in triplicate.) The vendors were also sent the SRM samples; however, the concentration of one of the SRMs was below the detection limit for several of the vendors. These vendors were, therefore, sent a duplicate of one of the homogenized samples. This resulted in each of the vendors receiving 14 samples. Laboratory results were then sent to the vendors after analysis in order to enable them to perform a self-evaluation by comparing their results to the laboratory results. Immediately following the Pre-demonstration, two of the vendors chose to drop out of the Demonstration. An additional vendor chose to drop out about one month prior to the demonstration thereby leaving 5 vendors participating.

**Lessons Learned:** In addition to planned objectives, there were several lessons learned as a result of Pre-Demonstration activities. These included issues related to the slurry sample preparation and custody seals.

**Slurry Samples:** Several of the sediment samples had standing water upon collection. These samples were shipped to the SAIC GeoMechanics Laboratory with standing water, and the homogenized sub-samples were sent to the vendors with standing water. The standing water presented a problem with several of the vendors. First, the bottles were sufficiently full as to prevent mixing of the samples without causing some spillage. Second, the method of collecting aliquots from the samples with standing water was not consistent between all vendors and laboratories. Therefore, the slurry samples prepared for the Demonstration will have the standing water removed by the SAIC GeoMechanics Laboratory.

The procedure used by the referee laboratory to collect aliquots from the sample jars is included as Appendix B of this QAPP.

**Custody Seals:** Each sample bottle shipped to the laboratories and vendors had a custody seal on the lid. Some of the sample codes on the labels were damaged by the custody seals. Therefore, during the Demonstration, a method of ensuring the custody of samples, without applying seals directly to each bottle, will be employed. The method will likely require placing the bottles into a secondary container and placing the custody seal onto that container.

## **1.4 Project Objectives**

In accordance with *QAPP Requirements for Applied Research Projects (EPA, 1998)*, the technical project objectives of this Demonstration are categorized as primary and secondary. Critical data support primary objectives, and non-critical data support secondary objectives.

### **1.4.1 Primary Objectives**

The primary objectives for the Demonstration of the individual field measurement devices are summarized below and described in more detail in Subchapter 3.2.1:

- Primary Objective # 1.** *Determine the sensitivity of each field instrument with respect to the Method Detection Limit (MDL) and Practical Quantitation Limits (PQL) generated by each vendor.*
- Primary Objective # 2.** *Determine the potential analytical accuracy associated with the field measurement technologies.*
- Primary Objective # 3.** *Evaluate the precision of the field measurement technologies.*
- Primary Objective # 4.** *Measure the amount of time required for performing five functions related to mercury measurements: 1) mobilization and setup; 2) initial calibration; 3) daily calibration; 4) demobilization; and 5) sample analysis.*

---

**Primary Objective # 5.** *Estimate the costs associated with mercury measurements for the following four categories: 1) capital; 2) labor; 3) supplies; and 4) investigation-derived waste (IDW).*

#### **1.4.2 Secondary Objectives**

The secondary objectives for the Demonstration of the individual field measurement devices are summarized below and described in more detail in Subchapter 3.3:

- |                                 |  |
|---------------------------------|--|
| <b>Secondary Objective # 1.</b> | <i>Document the ease of use, as well as the skills and training required to properly operate the device.</i> |
| <b>Secondary Objective # 2.</b> | <i>Document potential health and safety concerns associated with operating the device.</i>                   |
| <b>Secondary Objective # 3.</b> | <i>Document the portability of the device.</i>   |
| <b>Secondary Objective # 4.</b> | <i>Evaluate the durability of the device based on its materials of construction and engineering design.</i>  |
| <b>Secondary Objective # 5.</b> | <i>Document the availability of the device and spare parts.</i>  |

---

## **Chapter 2**

### **Project Organization**

#### **2.1 General Responsibilities**

This chapter identifies the participants in the Field Analysis of Mercury in Soil and Sediment Demonstration and delineates the responsibilities of each participant. The organizational structure of this project is described below and illustrated in Figure 2-1.

##### **2.1.1 EPA**

The EPA NERL TOM, Dr. Stephen Billets, is responsible for all aspects of the Demonstration, including budget, scheduling, technical performance, data quality and quality assurance, overall health and safety, hazardous waste disposal, and report preparation. He is the primary EPA POC with the analytical vendors whose equipment is being evaluated during the Demonstration. He is also the primary EPA POC with each of the sites from which soils and sediments to be used during the Demonstration were collected. Finally, he is responsible for managing the efforts of the contractor, SAIC, in this effort.

George Brilis is the EPA NERL Quality Assurance (QA) Manager with responsibility for overseeing project data quality. He will independently evaluate the quality of all data gathered during this project and review of the Field Demonstration's QAPP and Innovative Technology Verification Reports (ITVR).

Ann Vega is the EPA National Risk Management Research Laboratory / Land Remediation and Pollution Control Division QA Manager responsible for QA oversight of the SITE Program. She will also be responsible for QA review and endorsement of the Field Demonstration's QAPP and ITVR.

##### **2.1.2 DOE**

Elizabeth Phillips is the DOE POC for the Demonstration, which is planned to take place at the DOE's ORNL in Oak Ridge, Tennessee. Ms. Phillips is providing assistance to Dr. Billets and Mr. Nicklas on a variety of Demonstration logistical issues, including site access, site facilities for the Demonstration participants, and hazardous waste staging on site.

##### **2.1.3 Tennessee Department of Environment and Conservation**

Dale Rector is the Tennessee Department of Environment and Conservation (TDEC), Department of Energy Oversight Division POC for the Demonstration. Mr. Rector is providing assistance to Dr. Billets and Mr. Nicklas on a variety of Demonstration logistical issues, including visitor access to the Demonstration.

##### **2.1.4 SAIC**

SAIC is the prime contractor for this Technical Directive and is responsible for implementing the Pre-demonstration and Demonstration phases of this project. SAIC will provide the necessary staff, equipment, and fixed facilities to perform all aspects of the Pre-demonstration and Demonstration. John Nicklas is SAIC's TOM; as such, he is responsible for all facets of this project, including budgeting, scheduling, subcontracting sampling and analytical services, coordinating with and providing oversight of vendors, coordinating with site contacts to obtain samples, and overseeing staff technical performance, health and safety, and report preparation. Mr. Nicklas will be supported by the following project staff:

---

JimRawe, Joe Tillman, John King, Mike Bolen, Allen Motley, and Andy Matuson. They are responsible for overseeing vendor activities during the MMT Demonstration, collecting and interpreting data, and preparing draft and final reports.

Joe Evans, SAIC's QA Manager for the contract, will oversee overall data quality by reviewing the Demonstration Plan, overseeing selection of the referee laboratory, performing field and laboratory assessments and audits, and reviewing draft and final reports. He will establish data quality objectives for the project and review analytical data to evaluate whether these objectives were met. He will provide project QA oversight and assist in report preparation, including a discussion of project data quality. He is independent of SAIC "line management," as noted in Figure 2-1.

Fernando Padilla is responsible for the health and safety of SAIC personnel. He will develop a health and safety plan to ensure personnel safety during all aspects of the Demonstration. He will establish, as necessary, site-specific health and safety monitoring parameters and appropriate safety limits.

Sara Hartwell, Rita Schmon-Stasik, Maurice Owens, and Herb Skovronek will serve as technical advisors. Ms. Hartwell will assist in the selection of appropriate analytical methods. Ms. Schmon-Stasik will assist in establishing data quality objectives, author chapters of the Demonstration Plan, assist with method and laboratory selection, and provide general technical assistance to the SAIC TOM. Mr. Owens will identify the statistical requirements and perform the statistical evaluation for the Demonstration. Dr. Skovronek will provide and coordinate peer review for the project.

Nancy Patti and Mark Pruitt will provide the necessary facilities and direct soil and sediment homogenization, along with sample splitting and aliquoting. Ms. Patti developed the sample preparation (homogenization, splitting, and aliquoting) procedure included in this plan. She will ultimately prepare and distribute the soil and sediment samples for analyses by the vendors and the analytical laboratories.

Finally, Mr. W. Kevin Jago of the SAIC, Oak Ridge office will serve as a local liaison between SAIC and DOE and as a POC for Demonstration sample receipt.

#### **2.1.5 Referee Laboratory**

The referee laboratory is Analytical Laboratory Services, Inc. (ALSI). ALSI is responsible for analyzing and reporting data for all demonstration samples, plus any additional quality control samples required by this plan. Mr. Ray Martrano is the laboratory manager and is responsible for all phases of ALSI's involvement in this project.

#### **2.1.6 Vendors**

A total of five vendors are participating in this Demonstration. Table 2-1 lists these five vendors. The table also identifies the type of instrument to be utilized, and summarizes the purpose and application of the instruments.

Vendors will be responsible for reviewing and endorsing this plan prior to the Demonstration. They will be responsible for supplying all necessary information regarding their respective technologies. The vendors will also be responsible for performing the type and number of analyses specified in this plan, including quality control samples, and promptly reporting those results to SAIC.

### **2.2 Contact Information**

Table 2-2 lists the Demonstration project participants and corresponding contact information for each.

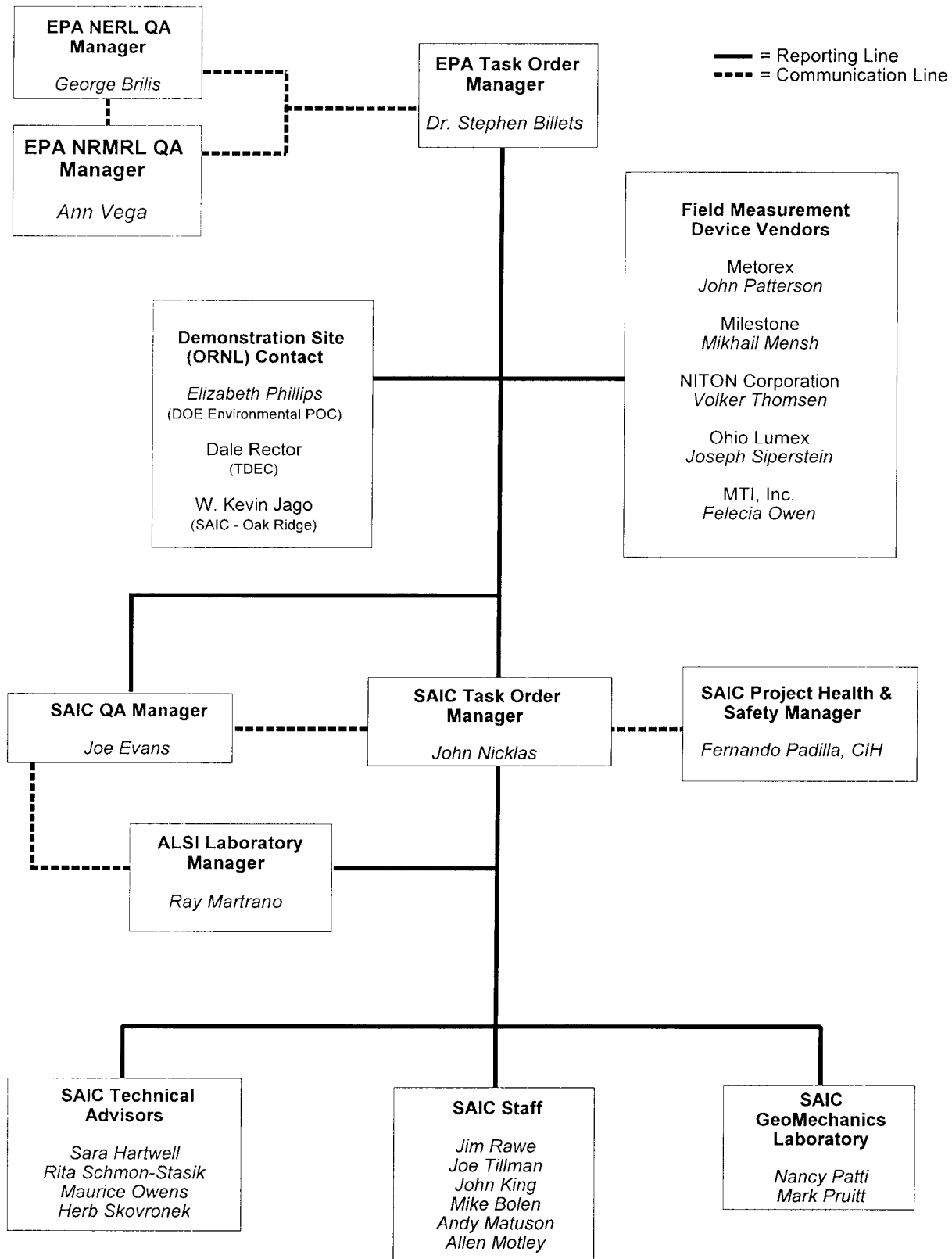


Figure 2-1. Organizational Chart

**Table 2-1.** Vendors Selected for the Mercury Field Analysis Demonstration.

<b>Company</b>	<b>Technical Name</b>	<b>Principle of Operation</b>	<b>Design Application/ Description</b>	<b>Applicable Media</b>
Metorex	X-Ray Fluorescence	Energy Dispersive X-Ray Fluorescence	Energy Dispersive X-Ray Fluorescence technology.	Sediment and soil samples
Milestone Inc.	Direct Mercury Analyzer (DMA-80)	Method 7473 - Thermal Decomposition, Amalgamation, Atomic Absorption	Designed for matrix independent analysis of a broad range of solid and liquid samples.	Solid and liquid samples (matrix independent)
NITON LLC	XL-700 Series Multi-Element Analyzer	X-Ray Fluorescence	Portable, multi-element testing for on-site metal contamination.	Soil, sediment, air filter, and thin-film samples
Ohio Lumex Co.	Portable Mercury Analyzer Lumex RA 915	Atomic Absorption Spectrometry, Thermal Decomposition Attachment RP 91C	Direct, fast, and precise measurements of mercury.	Air, liquid, soil, and sediment samples
MTI, Inc.	Portable Digital Voltammeter 500	Anodic Stripping Voltammetry	Designed for on-site analysis.	Sediment and soil samples



**Table 2-2.** Demonstration Contact List.

Name	Organization/Role	Address	Phone/Fax	E-mail
<b>EPA</b>				
Steve Billets	EPA-NERL/ESD TOM	P.O. Box 93478 Las Vegas, NV 89193-3478	P - 702-798-2232	billets.stephen@epa.gov
George Brilis	EPA-NERL/ ESD QA Manager	P.O. Box 93478 Las Vegas, NV 89193-3478	P - 702-798-3128	brilis.george@epa.gov
Ann Vega	EPA-NRMRL/ LRPCD QA Manager	26 W. Martin Luther King Dr. Cincinnati, OH 45268	P - 513-569-7635	vega.ann@epa.gov
<b>DOE</b>				
Elizabeth Phillips	DOE Environmental POC	Oak Ridge Operations Office Oak Ridge, TN 37831	P - 865-241-6172	phillipsec@oro.doe.gov
Roger Jenkins	UT-Battelle/ORNL	One Bethel Valley Rd. Oak Ridge, TN 37831	P - 865-574-4871	jenkinsra@ornl.gov
<b>TDEC</b>				
Dale Rector	TDEC POC	761 Emery Valley Road Oak Ridge, TN 37830	P - 865-481-0995	dale.rector@state.tn.us
<b>SAIC</b>				
John Nicklas	SAIC TOM	950 Energy Dr. Idaho Falls, ID 83401	P - 208-528-2110 F - 208-528-2197	john.h.nicklas@saic.com
Mike Bolen	SAIC Observer	411 Hackensack Ave., 3 <sup>rd</sup> Floor Hackensack, NJ 07601	P - 201-498-7335 F - 201-489-1592	michael.m.bolen@saic.com
Joe Evans	SAIC QA Manager	950 Energy Dr. Idaho Falls, ID 83401	P - 208-528-2168 F - 208-528-2197	joseph.d.evans@saic.com
Sara Hartwell	SAIC Technical Advisor	11251 Roger Bacon Dr. MS R-1-7 Reston, VA 20190	P - 703-318-4662 F - 703-318-4682	sara.w.hartwell@saic.com
W. Kevin Jago	SAIC Oak Ridge Support	151 Lafayette Dr. Oak Ridge, TN 37831	P - 615-481-4600	jagow@saic.com
John King	SAIC Observer	411 Hackensack Ave., 3 <sup>rd</sup> Floor Hackensack, NJ 07601	P - 201-498-7333 F - 201-489-1592	john.j.king@saic.com
Andy Matuson	SAIC Observer	411 Hackensack Ave., 3 <sup>rd</sup> Floor Hackensack, NJ 07601	P - 201-498-7343 F - 201-489-1592	andrew.f.matuson@saic.com
Allen Motley	SAIC ORNL Support	151 Lafayette Drive Oak Ridge, TN 37831	P - 865-481-4607 F - 865-481-4757	c.allen.motley@saic.com
Maurice Owens	SAIC Statistician	11251 Roger Bacon Dr. Mail Stop R-2-2 Reston, VA 20190	P - 703-318-4513 F - 703-709-1041	maurice.e.owens.iii@saic.com
Fernando Padilla	SAIC Project H&S Manager	11251 Roger Bacon Dr. MS R1-5 Reston, VA 20190	P - 703-318-4573 F - 703-736-0915	fernando.d.padilla@saic.com
Nancy Patti	SAIC GeoMechanics Lab Manager	595 E. Brooks Ave., Suite 301 North Las Vegas, NV 89030	P - 702-739-7376 F - 702-739-7479	nancy.c.patti@saic.com
Mark Pruitt	SAIC GeoMechanics Lab Technician	3960 Howard Hughes Pkwy. Ste 200, Las Vegas, NV 89109	P - 702-739-7376 F - 702-739-7479	NA

**Table 2-2 (Cont'd).** Demonstration Contact List.

<b>SAIC (Cont'd)</b>				
Rita Schmon - Stasik	SAIC Chemist	411 Hackensack Ave., 3 <sup>rd</sup> Floor Hackensack, NJ 07601	P - 201-498-8426 F - 201-489-1592	rita.m.schmon-stasik@saic.com
Herb Skovronek	SAIC Peer Review Coordinator	411 Hackensack Ave., 3 <sup>rd</sup> Floor Hackensack, NJ 07601	P - 201-498-7345 F - 201-489-1592	herbert.s.skovronek@saic.com
Joe Tillman	SAIC Observer	2260 Park Ave., Suite 402 Cincinnati, OH 45206	P - 513-569-5869 F - 513-569-5864	joseph.w.tillman@saic.com
<b>REFEREE LABORATORY</b>				
Ray Martrano	ALSI Manager	34 Dogwood Lane Middletown, PA 17057	P - 717-944-5541 F - 717-944-1430	rmartrano@analyticalab.com
<b>VENDORS</b>				
Mikhail Mensh	Milestone	160B Shelton Road Monroe, CT 06468	P - 203-261-6175 F - 203-261-6592	support@milestonesci.com
Felecia Owen	MTI, Inc.	1609 Ebb Drive Wilmington, NC 28409	P - 910-392-5714 F - 910-392-4320	fowen@owenscientific.com
John I.H. Patterson	Metorex, Inc.	Princeton Crossroads Corp. Center 250 Phillips Blvd., Ste. 250 Ewing, NJ 08618	P - 609-406-9000 F - 609-530-9055	john.patterson@metorexusa.com
Joseph Siperstein	Ohio Lumex Co.	9263 Ravenna Road, Unit A-3 Twinsburg, OH 44087	C - 330-405-0837 P - 888-876-2611 F - 330-405-0847	siperst@yahoo.com
Volker Thomsen	NITON Corporation	900 Middlesex Turnpike, Bldg. 8 Billerica, MA 01821	P - 800-875-1578 F - 978-670-7430	vthomsen@niton.com

---

## Chapter 3

### Experimental Approach

This Demonstration consists of the independent evaluation of five different field technologies for the determination of mercury in soil and sediment. Environmental samples from various locations, comprising different matrices and containing varying mercury concentrations, will be analyzed by each field technology vendor, as well as a referee laboratory performing the reference method selected. Specially prepared spiked samples using  $\text{HgCl}_2$  will be included as an additional reference material. Spikes will be prepared from environmental matrices and concentrations determined in replicate by the referee laboratory for comparison to vendor results. Certified SRMs will also be analyzed to further assess performance. This section describes the experimental approach for evaluating the field mercury measurement technologies. It details the preparation and selection of the environmental samples and the SRMs, as well as the test design for the Demonstration (Subchapter 3.1). Subchapter 3.2 presents the project objectives along with the methodology and statistical approach for evaluating each primary objective. Subchapter 3.3 presents the secondary objectives along with the evaluation mechanism.

#### 3.1 Experimental Design

The evaluation of the five technology vendors will be conducted at the ORNL site over a 4-day period, during which it is expected that each vendor will analyze 150 to 200 samples. All technologies will be independently evaluated as per the technical project objectives discussed in detail below. The mechanism for evaluating the field technologies centers around obtaining homogeneous environmental, SRM, and spiked samples with challenging levels of mercury concentrations, to be analyzed by each of the vendors. All samples will be provided to the vendors and the referee laboratory according to a blind code that provides only basic information as to the matrix of the sample (based on the site from which it was collected).

It is important to the equitable evaluation of all technologies, that the matrix analyzed be the same for all vendors and the laboratory; therefore the Pre-demonstration included extensive study to design and confirm the suitability of a procedure for preparing well-mixed, homogeneous samples from the soils and sediments collected from various locations. The results of the study were discussed in Subchapter 1.3. This homogenization protocol, presented in detail in Appendix A, will be implemented for all samples prepared for the Demonstration.

##### 3.1.1 Field (Environmental) Sample Selection and Preparation

Test samples were collected and prepared during the Pre-demonstration with the ultimate goal of producing a set of consistent test soils and sediments to be equally distributed among all participating vendors and the referee laboratory for analysis during the Demonstration. Samples were collected from different locations at four sites:

- Carson River Mercury Site (near Virginia City, NV)
- Y-12 National Security Complex (in Oak Ridge, TN)
- Manufacturing Facility (Eastern U.S.)
- Puget Sound (Bellingham, WA)

The collected matrices, soils and sediment, varied in 1) soil consistency and soil type and 2) mercury contamination levels. Table 3-1 shows the number of distinct test samples that were collected from each of the four field sites.

**Table 3-1.** Test Samples Collected from Each of the Four Field Sites.

Field Site	No. Of Samples / Matrices Collected	Areas For Collecting Sample Material		Volume Required
Carson River	18 - Soil or Sediment	•	Tailings Piles (Six mile Canyon)	≥ 4.54 L each
		•	River Bank Sediments	
Oak Ridge (Y-12)	10 Sediment 6 Soil	•	Poplar Creek Sediments	~ 13.63 L each for sediment;
		•	Old Mercury Recovery Bldg. Soils	≥ 4.54 L each for soil
Manufacturing Site	11 Soil	•	Subsurface Soils	≥ 4.54 L each
Puget Sound	4 Sediment	•	High Level Mercury (below cap)	~ 13.63 L each
		•	Low Level Mercury (native material)	≥ 4.54 L each

From these samples, those with mercury concentrations falling within three broad ranges were selected and will be prepared for distribution to the vendors. Samples will be homogenized using the same protocol as was used during the Pre-demonstration, with the removal of standing water from the slurry samples. Based on information provided about the technologies, the ranges include low-level concentrations (1-100 µg/kg), mid-level (100 µg/kg - 10 mg/kg) and high-level mercury contamination (10 - 1000 mg/kg). Table 3-2 summarizes the contaminant range each vendor is expected to analyze and indicates the approximate concentration of mercury in the majority of the samples each vendor will receive.

**Table 3-2.** Field Sample Contaminant Ranges for Vendor Technologies.

Vendor Technology	Contaminant Range of the Majority of the Samples to be Analyzed		
	Low (1-100 ug/kg)	Medium (100 µg/kg-10 mg/kg)	High (10-1000 mg/kg)
Metorex			X
Milestone	X	X	
NITON			X
Ohio Lumex	X	X	
MTI, Inc.		X	X

Each vendor will receive 150 - 200 samples, in replicates of up to seven. Field samples will be provided to each vendor from a variety of sites, such that, a majority of the samples have concentrations within the range of the vendor's technology. Some samples will have expected concentrations at or below the estimated level of detection for each of the vendor instruments. These samples are designed to evaluate the reported MDL and PQL, and also to assess the prevalence of false positives. Field samples distributed to each vendor will include sediments and soils prepared by both the slurry and dry homogenization procedures. Samples will be submitted to the vendor and the referee laboratory using a "blind code"; the site of collection will be identified but no other information regarding expected concentration or replicate status will necessarily be provided. This blind code will be known only by the SAIC TOM, SAIC QA Manager, and the SAIC GeoMechanics Laboratory Manager. Selected field samples will also be spiked with aqueous HgCl<sub>2</sub> to generate samples with additional concentrations.

### 3.1.2 SRM Sample Selection

Certified SRMs will be analyzed by both the vendors and the referee laboratory. These samples are homogenized matrices which have a known amount of mercury. Concentrations are certified values, as provided by the supplier, based on independent confirmation via multiple analysis of multiple lots and/or multiple analyses by different laboratories (i.e., round robin testing). These analytical results are then used to determine a "true" value, as well as a statistically derived interval (a 95% confidence interval) that provides a range within which the true value is expected to fall.

The SRMs selected are designed to encompass the same contaminant ranges indicated previously: low-, medium- and high-level mercury concentrations. In addition, SRMs of varying matrices will be included in the Demonstration to

---

challenge the vendor technologies as well as the referee laboratory. The referee laboratory will analyze all SRMs. All SRM samples will be submitted using a "blind code"; the site of collection will be identified but no other information regarding expected concentration or replicate status will necessarily be provided. SRMs will be intermingled with site location samples, labeled in the same manner as field samples.

### **3.1.3 Spiked Samples**

Spike samples will be prepared by the SAIC GeoMechanics Laboratory. Aqueous  $\text{HgCl}_2$  will be used in order to evenly distribute the contaminant in a slurry matrix. Spikes will be prepared using environmental samples from one or more of the selected sites. Additional information will be gained by preparing spikes at concentrations not previously obtainable. Similar to sample results, the laboratory results will be considered the "true" value and vendor results will be compared to the reference laboratory values. The SAIC GeoMechanics Laboratory ability to prepare spikes will be tested prior to the demonstration and evaluated in order to determine expected variability and accuracy of the spiked sample. This will be included in a special report, supplemental to the demonstration.

### **3.1.4 Vendor Testing**

Upon arrival at the ORNL site, vendors will set up their measurement devices, at the direction and oversight of SAIC, and prepare to begin testing the Demonstration samples. At the start of the Demonstration, vendors will be provided with a cooler of samples: each sample identified with a blind code. Samples will be identified with respect to the site from which they were collected, since in any field application the location and general type of the samples would be known. It will not be obvious what samples are replicates, nor will SRM samples be distinguished from field samples. Each vendor will be responsible for analyzing all samples provided, performing any dilutions or reanalyses needed, calibrating the instrument if applicable, performing any maintenance necessary, and reporting all results. Samples will be provided to each vendor in accordance with procedures outlined in Chapter 4.

### **3.1.5 Independent Laboratory Confirmation**

All samples, field, SRMs, and spikes will be analyzed at the referee laboratory at the same replicate frequency. Therefore, the laboratory will analyze significantly more samples than any one individual vendor. At the same time the field analyses begin, sample coolers will be shipped from the SAIC GeoMechanics Laboratory to the referee laboratory. The samples will all be identified in the same way, and all samples will be labeled according to the "blind code." All sample analysis at the referee lab will be in accordance with SW-846 Method 7471B. The referee laboratory's standard operating procedure (SOP) is included in Appendix B.

### **3.1.6 Schedule**

Table 3-3 presents the tentative schedule for field Demonstration activities.

## **3.2 Primary Project Objectives**

This section details the project objectives and the method of measuring or evaluating each of those objectives. In accordance with *QAPP Requirements for Applied Research Projects* (EPA, 1998), the technical project objectives of this Demonstration are categorized as primary and secondary. Critical data support primary objectives, and non-critical data support secondary objectives. Section 3.2.1 discusses in detail the five primary objectives that were introduced in Section 1.4.1. Section 3.2.2 describes how these objectives will be evaluated and the statistical approach to be used.

### **3.2.1 Statement of Primary Objectives**

#### *3.2.1.1 Primary Objective #1: Sensitivity*

Sensitivity is the ability of a method or instrument to discriminate between small differences in analyte concentration. (EPA, 2002). It can be discussed in terms of MDLs or instrument detection limits as well as PQLs. Detection limit (DL) involves the ability of the instrument and/or method to confidently determine the difference between a sample that does contain the

**Table 3-3.** Projected Field Measurement Demonstration Schedule.

Activity	Date
Final Demonstration Plan to EPA	December 20, 2002
Comments due from EPA on final Demonstration Plan	January 3, 2003
Demonstration Plan approved/endorsed by EPA	February 11, 2003
SAIC arrives at ORNL site to prepare sample bottles for distribution	May 1, 2003
Vendors arrive on site to begin set-up	May 5, 2003
Samples arrive at referee laboratory	May 2, 2003
Vendors receive first batch of samples; field measurements begin	May 5, 2003
Field testing concludes, vendors demobilize and leave site	May 9, 2003
First of five ITVRs submitted to EPA	June 30, 2003
Fifth ITVR submitted	September 1, 2003
EPA approval of final ITVR	September 30, 2003
SAIC submits Demonstration Summary Report	October 27, 2003

analyte (mercury) of interest at a low concentration and a sample that does not. The DL is generally considered to be the minimum true concentration of an analyte producing a non-zero signal that can be distinguished from the signals generated when no concentration of the analyte is present, with an adequate degree of certainty. For this project, a primary project objective will be to assess the sensitivity of each field technology with respect to the MDL and PQL generated by each vendor.

Table 3-4 presents the expected MDLs for each measurement device based on data provided by the developers. These are estimates but will be used to determine the standards needed in order to verify actual MDLs during the demonstration. The reference method MDL will be verified by the referee laboratory. The PQL of the referee laboratory is the lowest concentration calibration standard. This low standard is 10 µg/kg based upon Pre-demonstration results. SAIC will document exactly which calibration options are used by each vendor during the demonstration. The actual concentration of the lowest calibration standard for any of the vendors is estimated around 10 µg/kg but may be lower. In the event that the vendor is able to measure lower concentrations for samples or SRMs below 10 µg/kg, the selected referee laboratory (ALSI) has confirmed that it too can calibrate it's instrument using a lower calibration curve to achieve quantitation limits that are up to 100 times lower than the 10 µg/kg standard noted above. This was verified as part of the Pre-demonstration audit. In the event that this becomes necessary, re-analysis of these low concentration samples will be performed by ALSI using it's lower calibration curve.

**Table 3-4.** Estimated Sensitivities for Each Field Measurement Device.

Vendor / Referee Laboratory	Expected , units
Metorex	10 mg/kg
Milestone Inc.	8 µg/kg
NITON Corporation	20 mg/kg
Ohio Lumex Co.	10 µg/kg
MTI, Inc.	100 µg/kg
Referee Laboratory (ALSI) Method SW-846 7471B:	10 µg/kg

---

#### 3.2.1.2 Primary Objective #2: Accuracy

The second primary objective of this Demonstration is to determine the potential analytical accuracy associated with the field measurement technologies. For the purposes of this project, accuracy will be assessed by field measurements made by the vendors and compared to the measurements made by the referee laboratory. In addition, accuracy will be assessed by comparison to the certified result for the SRM and by spike samples prepared by the SAIC GeoMechanics laboratory. Each of these assessments will be discussed separately in the final report. SRMs provide very tight statistical comparisons but do not provide all associated matrices nor all ranges of concentrations. The spike samples prepared by the SAIC GeoMechanics Laboratory, using previously collected environmental samples as well as including these same previously collected samples without spikes, will ensure a more complete comparison. Concentration ranges for each vendor are based upon information provided by the vendor and appropriate samples will be included to test different concentrations (low, medium, and high) within the vendors predicted range of operation.

#### 3.2.1.3 Primary Objective #3: Precision

The experimental design for this Demonstration includes a mechanism to evaluate the precision of the field measurement technologies. Each homogenized sample prepared from the soils and sediments collected previously will be analyzed as (blind) replicate samples by each technology vendor as well as the referee laboratory. These replicate sample results will be used to calculate an RSD for each method, including the reference method. Average field method RSD values will be compared to the reference method for an assessment of precision.

#### 3.2.1.4 Primary Objective #4: Time per Analysis

The amount of time required for performing the analysis will be measured and reported in five categories: mobilization and set-up, initial calibration, daily calibration, demobilization, and sample analyses. Mobilization and set-up are the time it takes to unpack and prepare the instrument for operation. Initial calibration is the time it takes to perform the vendor recommended on-site calibrations. Daily calibration is the vendor-recommended calibrations performed on subsequent field days, but this may be the same as the initial calibration, a reduced calibration, or none. Demobilization is the time it takes to tear down the instrument and package it for shipment. Sample analysis includes the preparation, measurement, and calculation of demonstration samples and necessary quality control (QC) samples performed by the vendor.

#### 3.2.1.5 Primary Objective #5: Cost

To estimate the cost associated with mercury measurements, the following four cost categories will be considered: 1) capital; 2) labor; 3) supplies; and 4) IDW. The calculated costs will not be compared among the vendors, nor will they be compared with the reference laboratory.

### 3.2.2 Statistical Approach and Evaluation of Primary Objectives

The following paragraphs discuss how each of the primary objectives will be evaluated for this Demonstration. Primary objectives have been previously stated and are the criteria by which the individual field technologies will be evaluated. Specifically these include sensitivity, precision, accuracy, time per analysis, and cost. Sensitivity, precision, and accuracy all require additional explanation in terms of the experimental design and the descriptive statistics that will be used as the tools for evaluation. The purpose of this section is to describe the approach and subsequent evaluation of these objectives. It should be noted, however, that while possible statistical tests that will be used for data interpretation have been presented, exact statistical tests will be determined at the end of the Demonstration based upon actual results.

#### 3.2.2.1 Sensitivity

Two separate and distinct sensitivity parameters are included for evaluation. MDL is the more common sensitivity evaluation. The purpose of this measurement is to determine the level at which an individual field instrument will be able to detect a minimum concentration that is statistically different from instrument background or noise. Guidance for the definition of the MDL is provided in EPA G-5i (EPA, 2002). The evaluation of MDL requires seven different measurements of a low concentration standard or sample. Following procedures established in 40 CFR Part 136 for water matrices, the Demonstration MDL definition will be as follows:

$$MDL = t_{(n-1, 0.99)} s$$

where:

$t_{(n-1, 0.99)}$  = 99<sup>th</sup> percentile of the t-distribution with (n-1) degrees of freedom  
n = number of measurements  
s = standard deviation of replicate measurements

The PQL is another important measure of sensitivity. This is defined in EPA G-5i as the lowest level at which the instrument is capable of producing a result that has significance in terms of precision and bias. It is usually considered the lowest standard on the instrument calibration curve. It is often 5 to 10 times higher than the MDL, depending upon the analyte, the instrument being used, and the method for analysis. The PQL measurement is often much more meaningful than the MDL because it defines a specific concentration with an associated level of accuracy.

The PQL will be defined by each vendor calibration curve. Once the vendor has determined the level of its low calibration standard (this method will be discussed in the final report), the evaluation will include a determination of the percent difference (%D) between the calculated value and true value. [The true value in this case is the value defined by the reference laboratory for samples or spikes, or the certified value provided by the supplier in the case of standard reference materials (SRMs).] For example, if the low point of the calibration curve (the concentration which defines the PQL) is thought to be 1 mg/kg, then a %D will be calculated by using the reported value of the low standard versus its true value. Therefore, if the reported value is 1.15 mg/kg and the true value is 1 mg/kg, then the %D would be 15%. The equation for the %D calculation is included below:

$$\%D = \frac{|C_{\text{true}} - C_{\text{calculated}}|}{C_{\text{true}}} \times 100$$

where

$C_{\text{true}}$  = true concentration as determined from the calibration curve  
 $C_{\text{calculated}}$  = calculated test sample concentration

The % D will be reported for each individual vendor. The associated PQL for the reference method, along with the %D for the referee laboratory, will be reported for purposes of comparison. There is no statistical comparison between these two values but only a descriptive comparison for purposes of this evaluation. (The %D requirement for the referee laboratory has been previously defined as 10% or less. The expected reference method PQL is approximately 10 µg/kg.)

### 3.2.2.2 Accuracy

Accuracy is the instrument measurement compared to a standard or true value. For purposes of this Demonstration, three separate standards will be used. The primary standard will be SRMs. These will be obtained from reputable suppliers with reported concentrations and associated 95% confidence intervals. All SRMs will be analyzed by the referee laboratory, and selected SRMs will be analyzed by each vendor based upon instrument capabilities and concentrations of SRMs that can be obtained. Therefore, not all vendors will analyze all SRMs. SRMs will cover an appropriate range for each vendor. Replicate SRMs will be analyzed by each vendor and by the laboratory.

The second accuracy determination will be a comparison of vendor results for field samples to the referee laboratory results. These will be used to ensure that "real-world" samples are tested for each vendor. The referee laboratory result will be considered the standard for comparison to each vendor.

The third measure of accuracy will be spiked field samples. These will be analyzed by the vendors and the laboratory in replicate in order to provide additional measurement comparisons to a known or laboratory defined "true" value. Spikes will be prepared to cover additional concentrations not available from SRMs or environmental samples. The accuracy comparison is explained in more detail later in this discussion.

The intention of the following discussion is to provide examples of how accuracy evaluations will be performed. There will likely be several ways to perform accuracy comparisons. Statistical evaluations will be determined once the data has been reviewed with the project statistician. In consultation with the project manager and QA manager the project statistician will determine several possible means of evaluation based upon reported data or results.



---

The purpose for SRM analysis by the referee laboratory is to provide a check on laboratory accuracy. During the Pre-demonstration, the referee laboratory was chosen, in part, based upon the analysis of SRMs. This was done in order to assure that a competent laboratory would be used for the Demonstration. Because of the need to provide confidence in laboratory analysis during the Demonstration, the referee laboratory will analyze SRMs as an on-going check on laboratory bias.

The Pre-demonstration laboratory evaluation was conducted to help ensure that laboratory SRM data would fall within expected ranges. It is possible that during the Demonstration the laboratory may fail to fall within the expected concentration ranges for a particular SRM. In the event that this occurs, laboratory corrective action will include a check of their calibration and calibration criteria for that particular run. If this is found to fall outside pre-specified ranges then the laboratory will be asked to recalibrate and rerun the appropriate SRM. The second set of data will then likely confirm that the laboratory is within compliance.

If, however, this is not the case and laboratory calibration criteria are satisfied, then SAIC will have the laboratory perform two more sets of analysis for the SRM in question. Therefore there will be a total of three separate sets of data for the SRM in question. Based upon these three sets of data it will be determined either that the initial SRM set of results is in error or that perhaps the SRM concentration reported by the respective manufacturer is in error. (This could occur as a result of the sample preparation process.) With this information SAIC and the EPA Project Manager will make a decision as to whether this SRM should be used for evaluation or whether the laboratory result should be used instead of the manufacturer reported result.

Evaluation of vendor and laboratory analysis of SRMs will be performed in several different fashions. Accuracy will be reported by noting the average concentration of the analyzed sample by the vendor and laboratory compared to the 95% two-tailed confidence interval for the SRM. (95% confidence intervals around the true value are provided by the SRM supplier.) This will be reported for individual sample concentrations and average concentrations of replicate measurements made at the same concentration.

Two-tailed confidence intervals are computed as follows:

$$\bar{x} \pm t_{(n-1, 0.975)} \cdot s / \sqrt{n}$$

where:

- $t_{(n-1, 0.975)}$  = 97.5th percentile of the t-distribution with (n-1) degrees of the freedom
- $n$  = number of measurements
- $s$  = sample standard deviation of replicate measurements

The number of SRM results for the vendor's analytical instrumentation and the referee laboratory that are within the associated 95% confidence interval will be evaluated. For example, the referee laboratory may be within this confidence interval 95% of the time (i.e., 5% or more of the time, values may fall outside this interval simply because of statistical uncertainty). The vendor results may only be within this window 50% of the time, depending upon actual instrument conditions. If vendor results are outside this window more than 10% of the time, for example, then it might be assumed that instrument bias for that particular vendor may be an issue, but this is not strong evidence for such a prediction considering the statistical uncertainty associated with the 95% confidence interval. If a vendor is outside this window 30% of the time or even 50% of the time as noted above, then this is stronger evidence of vendor bias and therefore the vendor result may be off-set from the true value and accuracy may be considered as questionable.

Another measure of accuracy that may be determined for SRMs might be a frequency distribution that would show the percentage of measurements within, for example, a 30% window of a reported concentration, within a 50% window, and outside a 50% window of a reported concentration. This could be reported as average concentrations of replicate results from the vendor for a particular concentration and matrix compared to the same collected sample from the laboratory. These are descriptive statistics and are used to better describe comparisons, but are not intended as inferential tests.

In addition, sample results from environmental and spiked samples for the vendor compared to the referee laboratory will be used as another accuracy check. Vendor sample results for a given field sample will be compared to the 90% confidence interval for the replicates analyzed by the laboratory for the same field sample. Average comparisons for a

---

specific matrix or concentration will be made in order to provide additional information on that matrix or concentration. Comparison to laboratory values will be similar to the comparisons noted above for SRMs. Comparisons will be made using average concentrations in order to eliminate measurement variability.

Accuracy is a combined measure of bias plus precision or variability. Replicate analyses at a specified concentration can be used to determine average concentrations and a 90% confidence interval. A 90% confidence interval will be used for replicate measurements made by the referee laboratory on environmental samples compared to vendor results. Using the Student's t-test, a comparison between vendor results and SRMs can be performed to determine if sample populations are significantly different. This will also be performed for referee laboratory results for the collected samples compared to vendor results for these same samples.

If sample populations overlap, then results will not be considered as significantly different. If sample populations do not overlap, then sample results will be considered as significantly different at a 0.1 level of significance. Because this test does not separate precision from bias, if a vendor's computed confidence interval was extremely wide due to a highly variable result (indication of poor precision), the two confidence intervals may overlap and, therefore, there may be no significant difference between the two results. This test could then give the false impression that vendor results were "better" because populations would not be significantly different. Therefore, this result would need to be reported in such a fashion stating that vendor results are overlapping the 90% confidence interval because of poor precision. If such a case were to occur, it may be best not to report the result of this test. For this reason, precise statistical determinations on how to interpret results cannot be made at this time.

### 3.2.2.3 Precision

Precision is usually thought of as repeatability of a specific measurement. Precision is often reported as RSD. RSD is computed from a specified number of replicates. The more replications of a measurement the more confidence associated with a reported RSD. Replication of a measurement may be as few as 3 separate measurements to 30 or more measurements of the same sample, depending upon the degree of confidence desired in the specified result. In addition, the precision of an analytical instrument may vary depending upon the matrix being measured, the concentration of the analyte, and whether the measurement is made for an SRM or a field sample. The purpose of this evaluation is to determine the field instrument's capability to precisely measure analyte concentrations under real-life conditions. Instrument repeatability will, therefore, be measured using collected samples from each of four different sites.

As noted previously, precision - or an instrument's capability to replicate a measurement - may be dependent upon matrix and concentration. Samples from four different sites have been obtained for evaluating each vendor's instrument. Within each site there may be two separate matrices, soil and sediment. (Not all sites have both soil and sediment matrices, nor are there all concentrations for each matrix.) Concentrations for purposes of this demonstration have been determined only as low, medium, or high. Ranges of test samples (environmental, SRMs, and spikes) have been selected to cover the appropriate analytical ranges of each vendor's instrumentation. Because the vendors have different working ranges, not all vendors will analyze the same samples. Specific concentrations of test samples are not included in the QAPP because of the necessity to ensure that this evaluation remains unbiased and that no vendor has an advantage in performing the analyses by knowing in advance approximate sample concentrations. Not all vendors are capable of measuring similar concentrations. Some instruments are better at measuring low concentrations and others are geared toward higher concentration samples or have other attributes such as cost or ease of use that define their specialty. Each vendor will be tested with samples from different sites, different matrices when possible (as noted above depending upon available concentrations), and different concentrations (high, medium, and low) using a variety of samples. Sample concentrations for an individual instrument will be chosen based upon vendor attributes in terms of expected low, medium, and high concentrations that the particular instrument is capable of measuring.

The referee laboratory will measure replicates of all samples. This will be used for purposes of precision comparisons to the individual vendor. RSD for the vendor and the laboratory will be calculated individually in the following manner:

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

---

Where:

S = standard deviation of replicate results

$\bar{x}$  = mean value of replicate results

A descriptive determination for differences between a vendor RSD and referee laboratory RSD will be determined. (Note that no attempt will be made to compare different vendors. The purpose of this Demonstration is to evaluate each vendor's instrumentation compared to standard laboratory procedures.) In addition, an overall average RSD will be calculated for all measurements made by the vendor and the laboratory. RSD comparisons are descriptive between the vendor and laboratory and will be compared accordingly.

Other statistical comparisons may be used depending upon actual Demonstration results. The statistics noted above assume normality. If results are determined to be log-normal, alternate statistical determinations will be considered. In addition, replicate measurements for SRMs will also be performed, therefore, RSDs for these measurements may be useful but will not be the primary measurement for determination of precision.

#### 3.2.2.4 Time Per Analysis

The time per analysis will be determined by dividing the total amount of time required to analyze the 150 to 200 samples by the number of analyses. In the numerator, sample analysis will include preparation, measurement, and calculation of Demonstration samples and necessary QC samples performed by the vendor. In the denominator, the total number of analyses will include only Demonstration samples, not QC analyses or re-analyses of samples.

Downtime that is required or occurs between each sample as a part of operation and handling will be considered a part of the sample analysis time. Downtime that occurs due to instrument breakage or unexpected maintenance will not be counted in the assessment, but will be noted in the final report as an additional time. Any downtime caused by instrument saturation or memory effect will be addressed based upon its frequency and impact on the analysis.

Any unique time measurements will be addressed in the final report. For example, if soil samples are analyzed directly, and sediment samples require 2 hours of drying time before the analyses starts, then the statement will be made that soil samples can be analyzed in X hours, and that sediment samples require 2 hours of drying before analyses can be started.

Recorded times will be rounded to the nearest 15-minute interval. It should also be noted that the number of developer personnel used will be noted and factored into the cost calculations in Section 3.2.5. No comparison will be made among various vendors, or between a vendor and the applicable referee laboratory.

#### 3.2.2.5 Cost

A summary of the costs that will be estimated for each measurement device is provided below:

- The capital cost will be estimated based on published price lists for purchasing, renting, or leasing each field measurement device. If the device is purchased, the capital cost will include no salvage value for the device after work is completed.
- The labor cost will be estimated for each field measurement device based on the number of people required to analyze samples during the Demonstration. The labor rate will be based on a standard hourly rate for a technician or other appropriate operator. During the Demonstration, the skill level required will be confirmed based on input from each vendor regarding the operation of its device to produce mercury concentration results, and based on observations made by SAIC. The labor costs will be based on: 1) the actual number of hours required to complete all analyses, quality assurance, and reporting; and 2) the assumption that a technician who has worked for a portion of a day would be paid for an entire 8-hour day.
- The cost of supplies will be estimated for each device based on any supplies required to analyze the field and SRM samples during the Demonstration. Supplies will include items not included in the capital category, such as, a balance, extraction solvent, glassware, pipettes, spatulas, agitators, and similar materials. SAIC will note the type and quantity of all supplies brought to the field and will document all supplies used during the Demonstration.

- 
- If a vendor typically provides all supplies to a user, the vendor's costs will be used to estimate the cost of supplies. If the supplies required to analyze field samples are covered by the purchase cost, this cost will not be broken out separately as part of the cost of supplies. However, the costs of any additional supplies required for analysis of field and SRM samples will be included in the cost of supplies. If a vendor provides supplies as part of a refill kit, the cost for the number of kits required to analyze all of the Demonstration samples will be included in the cost of supplies. If a vendor creates refill kits specific to a user's needs, the associated cost of supplies will be based on the cost of the refill kits that the developer uses during the Demonstration. Unless a vendor allows a user to return unused portions of a refill kit, the cost of supplies will be estimated under the assumption that no salvage value is associated with unused refill kit supplies. If unused supplies can be returned to a vendor, the quantities of unused supplies will be noted during the Demonstration, and the appropriate credit will be applied to the cost of supplies minus any restocking charge.
  - If a vendor typically does not provide all required supplies to a user, SAIC will estimate the cost of supplies using independent vendor quotes. SAIC will note the identification numbers and manufacturers of supplies used by the developer during the Demonstration and will attempt to obtain pricing information for these supplies. If the costs of the supplies are not available, SAIC will use the prices of comparable supplies to estimate the cost of supplies. If unused supplies can be returned to a vendor or manufacturer, the quantities of unused supplies will be noted during the Demonstration and the appropriate credit will be applied to the cost of supplies minus any restocking charge.
  - All maintenance and repair costs during the demonstration will be documented or provided by each vendor. Equipment costs will be estimated based on this information and standard cost analysis guidelines for the SITE Program.
  - The IDW disposal cost will be estimated for each device. Each vendor will be provided with one or more 90.91 L laboratory pack containers for disposal of hazardous wastes, as required. IDW generated may include decontamination fluids and equipment, spent solvents and/or acids, unused chemicals that cannot be returned to the vendor or an independent supplier, mercury-contaminated soil and sediment samples, and soil and sediment extracts. Contaminated personal protective equipment (PPE) normally used in the laboratory will also be placed into a separate container. The disposal costs for these laboratory packs will be included in the overall analytical costs for each vendor.
  - The cost per analysis will be estimated for the field measurement devices based on the number of analyses performed. However, as the number of samples analyzed increases, the initial capital costs and certain other costs would be distributed across a greater number of samples. Therefore, the unit costs would decrease. For this reason, two costs will be reported. The initial capital costs and the operating costs per analyses will be reported. A comparison to the referee laboratory's method costs will not be made. A generic cost comparison to data gathered from several different laboratories will be made to better provide a standard of comparison. Additional explanation regarding this cost comparison will be made in the final report.

### 3.3 Secondary Objectives

Secondary objectives will be evaluated based on observations made by SAIC during the Demonstration. Because of the number of vendors involved, SAIC's three technology observers will be required to make simultaneous observations of one or two vendors each during the Demonstration. (There will be a total of five vendors therefore one observer will only oversee one vendor and the other two observers will each oversee two vendors.) Four procedures will be implemented to ensure that these subjective observations made by the observers are as consistent as possible. First, forms have been developed for each of the five secondary objectives. These forms will assist in standardizing the observations. Secondly, the observers will meet each day before the evaluation begins, at significant break periods, and after each day of work to discuss and compare observations regarding each device. Thirdly, a fourth SAIC observer will be assigned to independently evaluate only the secondary objectives; this will ensure that a consistent approach is applied in evaluating these objectives. Finally, the SAIC TOM and QA Manager will circulate among the evaluation staff during the Demonstration to ensure that a consistent approach is being followed by all personnel. The individual approaches for addressing these five secondary objectives are discussed in the following subsections. It should be noted that the tables included in this section are provided to show what observations or measurements will be made for each objective. However, during the Demonstration, these tables will be combined into a single table to minimize redundancy and to present observation categories in a sequential fashion, making the job of the observer easier. Therefore the forms presented in this section are not intended as the final forms to be used but are only examples.

### 3.3.1 Secondary Objective #1: Ease of Use

The skills and training required for proper device operation will be noted; these will include any degrees or specialized training required by the operators. This information will be gathered by interviews of the operators. The number of operators required will also be noted. The ease of use will also be evaluated by subjective observations on the ease of use of the equipment and major peripherals required to measure mercury concentrations in soils and sediments. If available, the operating procedure will be evaluated to determine if it is easy to use and understandable. It should be noted that if the equipment is only provided with a trained operator, this objective will not apply to that vendor unit. Table 3-5 summarizes the observations that will be made in support of this objective.

**Table 3-5.** Example Ease of Use Form.

Vendor Name:	_____	Date:	_____
Equipment Name/Type:	_____	Observer Signature:	_____
Model No.:	_____		
Number of Operators	_____	Operator Names	_____
			_____
			_____
Degrees/Training:	_____		
	_____		
	_____		
Standard Operating Procedure Available:	_____	Used?	_____
(Yes or no)	_____	Easy to Use?	_____
Comments:	_____		
	_____		

### 3.3.2 Secondary Objective #2: Health and Safety Concerns

Health and safety concerns associated with device operation will be noted during the Demonstration. Criterion will include hazardous materials used, the frequency and likelihood of potential exposures, and any direct exposures observed during the Demonstration. In addition, any potential for exposure to mercury during sample digestion and analysis will be evaluated based upon equipment design. Basic electrical and mechanical hazards will also be noted, as well as any other health and safety concerns. Equipment certifications, such as Underwriters Laboratory, will be documented. Table 3-6 summarizes the observations that will be made in support of the evaluation of this objective.

**Table 3-6.** Example Health and Safety Concerns Form.

Vendor Name:	_____	Date:	_____
Equipment Name/ Type:	_____	Observer Signature:	_____
Model No.:	_____	Serial No.:	_____
Certifications (e.g., UL):	_____ _____ _____		
Chemical Used:	_____	Exposure:	_____
	_____		_____
	_____		_____
Potential Mercury Exposure:	_____ _____		
Mechanical Hazards:	_____ _____ _____		
Comments on Health and Safety Concerns:	_____ _____ _____		

### 3.3.3 Secondary Objective #3: Portability of the Device

The portability of each device will be evaluated by observing transport, measuring setup and tear down time, determining the size and weight of the unit and peripherals, and evaluating the ease with which the instrument is repackaged for movement to another location. The use of battery power or the need for an AC outlet will also be noted. Table 3-7 lists the criteria that will be used to evaluate instrument portability.

### 3.3.4 Secondary Objective #4: Instrument Durability

The durability of each device will be assessed by noting the materials and quality of construction and major peripherals. All device failures, routine maintenance, repairs, and downtime will be documented during the Demonstration. No specific tests will be performed to evaluate durability; rather, subjective observations will be made using Table 3-8 as guidance.

**Table 3-7.** Example Portability of the Device Form.

Vendor Name:	_____	Date:	_____
Equipment Name/Type:	_____	Observer Signature:	_____
Model No.:	_____		
Weight:	_____	Dimensions:	_____
Time - Setup:	_____	- Tear Down:	_____
Power Source:	_____		
Comments on Portability:	_____		
	_____		
	_____		
	_____		

**Table 3-8.** Example Instrument Durability Form.

Vendor Name:	_____	Date:	_____
Equipment Name/Type:	_____	Observer Signature:	_____
Model No.:	_____		
Materials of Construction:	_____	Quality of Construction:	_____
	_____		_____
	_____		_____
	_____		_____
Downtime (duration of each event):	_____	Reason (each event):	_____
	_____		_____
	_____		_____
Maintenance (List activity):	_____	Reason:	_____
	_____		_____
Repairs (Identify):	_____	Reason:	_____
	_____		_____
	_____		_____

### 3.3.5 Secondary Objective #5: Availability of Vendor Instruments and Supplies

The availability of each device will be evaluated by determining whether additional units and spare parts are readily available from the vendor or retail stores. The developer's office (or a web page) and/or a retail store will be contacted to identify current supplies of the tested measurement device and spare parts. This portion of the evaluation will be performed after the field Demonstration, in conjunction with the cost estimate. In addition, if replacement parts or spare devices are required during the Demonstration, their availability and delivery time will be noted.



---

## Chapter 4

### Demonstration Activities

#### 4.1 Preparation of Test Material

This chapter details the sample preparation, containerization, preservation, custody, shipping, and archiving procedures that will be used for all samples prepared for the Demonstration. This includes homogenized field samples and spiked samples prepared at the SAIC GeoMechanics Laboratory and SRM samples purchased from commercial providers. Each of the sample types is discussed separately in the following subchapters.

##### 4.1.1 Homogenized Field Samples and Spikes

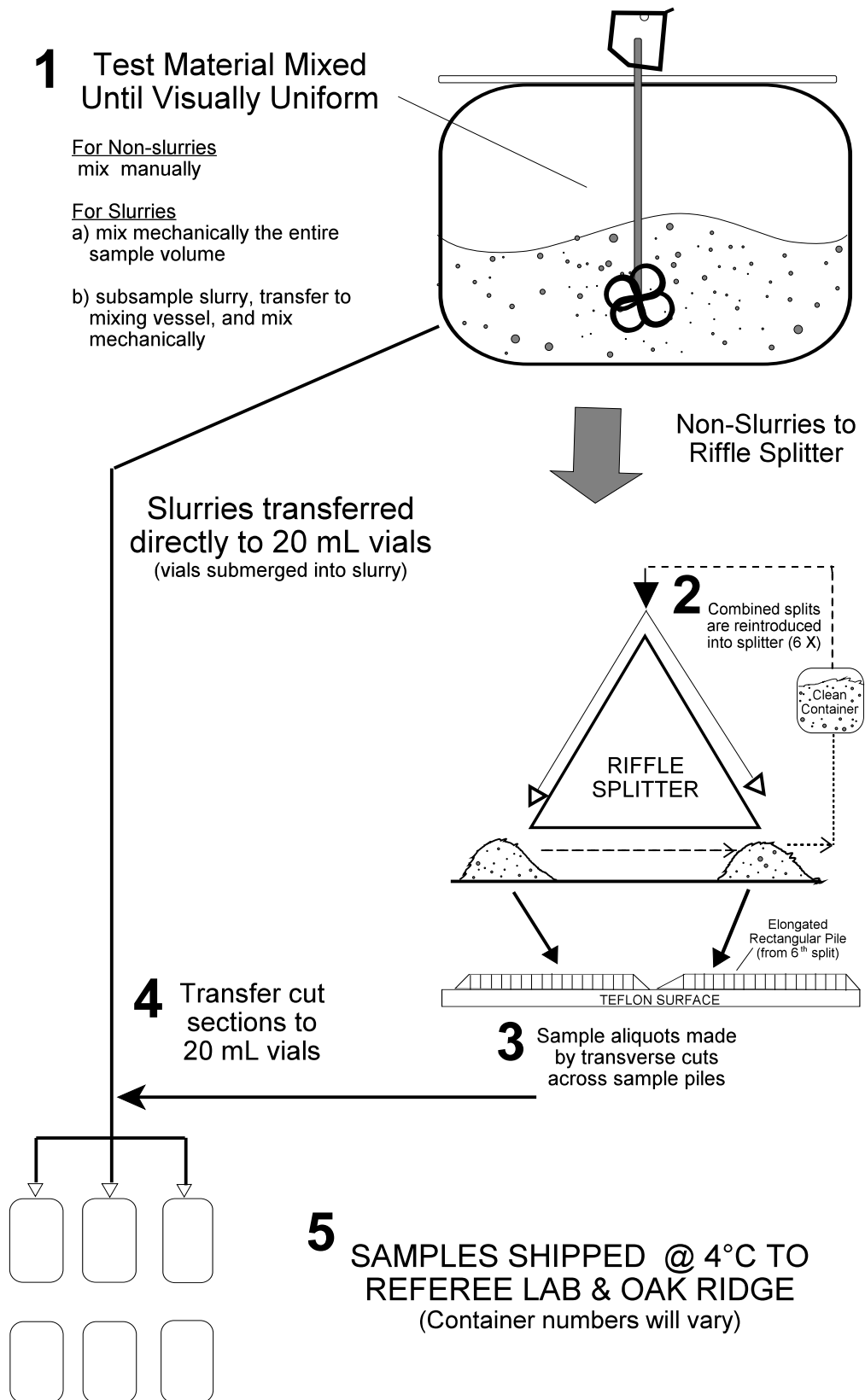
Homogenized field samples that are to be used for the Demonstration will be prepared at the SAIC GeoMechanics Laboratory in Las Vegas, Nevada. (This was the same laboratory used during the Pre-Demonstration.) Currently, there are more than 50 separate field samples being stored in plastic containers at the SAIC GeoMechanics Laboratory. The field samples were collected from four different field sites during the Pre-demonstration portion of this project (refer to Subchapter 1.3).

The field samples collected during the Pre-demonstration sampling events comprise a variety of matrices, ranging from material having a high clay content to material composed mostly of gravelly, coarse sand. The field samples also differ with respect to moisture content, since several were collected as wet sediments. The specific sample homogenization procedure to be used by the SAIC GeoMechanics Laboratory will largely depend on the moisture content and physical consistency of the sample. A sample homogenization procedure has been developed by the SAIC GeoMechanics Laboratory, which are: 1) non-slurry type sample homogenization and 2) slurry type sample homogenization. This SOP is detailed in Appendix A. (This homogenization procedure was tested during the Pre-demonstration and found to be satisfactory based upon the results of replicate samples.)

Figure 4-1 summarizes the homogenization steps, beginning with sample mixing. It should be noted that prior to the mixing process (i.e., Step 1 in Figure 4-1), all field samples being processed will be inspected to ensure that oversized material has been removed and that there are no clumps that would hinder homogenization. Non-slurry type samples will be air-dried in accordance with the procedures in Appendix A so that they can be passed multiple times through a riffle splitter. Due to their high moisture content, they are not easily air-dried and cannot be passed through a riffle splitter while wet. Slurries will not be air dried and will bypass the riffle splitting step. The homogenization steps for each type of matrix are briefly summarized as follows.

##### Preparing Slurry Matrices

If the sample matrix is a slurry (i.e., wet sediments), the mixing steps will be thorough enough that the sample containers can be filled directly from the mixing vessel. There will be two separate mixing steps of the slurry-type samples. Slurries will initially be mixed mechanically within the sample container (i.e., bucket) in which the sample was shipped to the SAIC GeoMechanics Laboratory. A sub-sample of this pre-mixed sample may be transferred to a second mixing vessel. A mechanical drill equipped with a paint mixing attachment will be used to mix the sub-sample. As shown in Figure 4-1, slurry type samples will bypass the sample riffle splitting step. To ensure all contain the same material, the entire set of containers to be filled will be submerged into the slurry as a group (see Appendix A for details). The filled vials will settle for a minimum of two days and the standing water will be removed using a Pasteur pipette or another appropriate device.



**Figure 4-1.** Test Sample Preparation at the SAIC GeoMechanics Laboratory.

---

#### Preparing "Non-Slurry" Matrices

If the sample matrix is a soil, or sediment having no excess moisture content, the material will be subjected to both a mixing step (Step 1) and the sample riffle splitting step (Step 2). Prior to these steps the material will be air-dried and sub-sampled to reduce the volume of material to a size that is easier to handle.

As shown in Figure 4-1 (Step 1), the non-slurry sub-sample will be manually hand-stirred with a spoon or similar equipment until the material is visually uniform. Immediately following manual mixing, the sub-sample will be mixed and split six times to homogenize it (Step 2). After the 6th and final split, the sample material will be leveled to form a flattened, elongated rectangle and cut into traversed sections to fill the containers (Steps 3 and 4). After homogenization, the filled 20-ml sample vials will be prepared for shipment (Step 5). Details of the entire homogenization procedure are presented in Appendix A.

#### Preparing "Spiked" Samples

Spiked samples will be prepared in a similar fashion to slurry samples. If soils are used for spike preparation, then water will be added to make the soil a slurry. If sediment slurries are used for spikes water may or may not be added depending on the consistency of the sediment. Based upon pre-demonstration studies (separate spiking report) a desired consistency similar to cake batter is needed in order to sufficiently mix the aqueous  $\text{HgCl}_2$  into the sample. Once mixed, the sample is air dried and then oven dried for 24 hours to ensure a consistent matrix is achieved. These samples are subsequently aliquoted and shipped to the respective vendors and laboratory for analysis. A separate spiking report is being prepared as a supplement to the QAPP describing pre-demonstration spiking studies.

##### *4.1.1.1 Sample Volumes, Containers, Preservation, and Holding Time*

A subset from the Pre-demonstration field collected samples will be selected for use in the Demonstration based on their mercury concentration range and sample type (i.e., sediment vs. soil). Several of these samples will also be spiked using  $\text{HgCl}_2$  in an aqueous solution with the soil being spiked in the form of a slurry. The SAIC GeoMechanics Laboratory will prepare individual batches of field sample material to fill sample containers for a participating vendor. Due to the variability of vendor instrument measurement ranges for mercury detection, not all vendors will receive samples from the same field material. The majority of the total vials prepared from each field sample will comprise vials for the five vendors to test during the Demonstration. A set of vials from each field sample will be shipped to the referee laboratory for mercury analysis. Another set of vials will be archived at the SAIC GeoMechanics Laboratory as reserve samples. To properly record and track which field samples have been homogenized and aliquoted, how many vials of each field sample have been prepared, and where each set of vials was shipped (or archived), the SAIC GeoMechanics Laboratory will prepare a sample homogenization form. An example of this form is shown as Figure 4-2.

Because of the critical nature of providing blind samples for the vendors, the details describing sample concentration and replicate samples are not included in the QAPP. It should be noted, however, that the EPA Project Manager was the first to provide information in terms of the number of samples needed, the expectation associated with concentration range, and the split between standard reference materials (SRMs), field samples, and spikes. With this information the SAIC Project Manager has prepared a chart that outlines samples and sample concentrations. Because the concentration ranges for each vendor are different, not all the same samples will be sent to every vendor. The goal in deciding which samples to prepare was to ensure there would be adequate coverage of the concentration ranges for each of the vendors and that there would be sufficient numbers of samples to ensure a statistical comparison. The project statistician was also consulted concerning number of replicates needed at respective concentrations and this information was included in the decision making process for determination of sample concentrations, types of samples used, and number of samples to be prepared.

This entire process of choosing appropriate samples and concentrations was determined by the SAIC Project Manager, the QA Manager, and Assistant Project Manager. Final decisions regarding types, numbers, and sample concentrations will be made by the EPA Project Manager once it was internally decided upon within SAIC by the personnel noted above. This information will then be communicated to the SAIC GeoMechanics Laboratory Supervisor for preparation of field samples and spikes. SRMs will also be ordered, and once they arrive will be prepared by the SAIC Project Manager and QA Manager at the Idaho Falls Laboratory Facility (STAR Center). Preparation will include aliquoting each SRM into separate sample vials which are identical in size and color as the samples prepared by the SAIC GeoMechanics laboratory. This will ensure that SRMs appear no different from other samples and by preparing these SRMs at the STAR Center

## Project: Field Analysis of Mercury in Soils and Sediments

### Sample Homogenization Record Sheet

Sample Location (site name):

Page \_\_\_ of \_\_\_

As-Received Sample Names Used:

Type of Homogenization Procedure Used:

Date Lot was Made:

Assigned Lot Number:

Number of Vials Prepared:

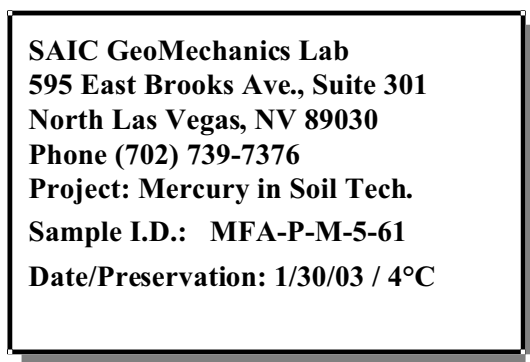
Name of Technician:

<i><b>Sample Received By</b></i>	<i><b>Sample Numbers Sent</b></i>

Figure 4-2. Example Sample Homogenization Form.

SAIC will ensure that there is no cross contamination from actual samples or spikes which are prepared in Las Vegas. The form in Figure 4-2 will serve as a record of sample preparation and copies will be kept by the SAIC GeoMechanics Laboratory, the SAIC Project Manager, and SAIC QA Manager, as appropriate.

Once all containers from a field sample are filled, each container will be labeled and cooled to 4°C. The sample labeling will consist of an internal code developed by SAIC. This "blind" code may be used throughout the entire Demonstration, or changed if deemed necessary. The only individuals that will need to know the key coding of the homogenized samples to the specific field collected samples will be the SAIC TOM, the SAIC GeoMechanics Laboratory Manager, and the SAIC QA Manager. The label used for the 20-ml vials will contain important sample information (i.e., sample analyses will not be designated on the label, but will be designated on the Chain-of-Custody (COC) form that will accompany samples shipped to the referee laboratory). An example label is provided as Figure 4-3.



**Figure 4-3.** Example Sample Label.

Mercury analyses will be performed both by the vendors in the field and by the referee laboratory. Minimum sample size requirements vary from 0.1 g or less (Milestone, 2002 & Ohio Lumex, 2002) to 8-10 grams (XRF technologies). Only the referee laboratory will be analyzing separate sample aliquots for the additional parameters of arsenic, lead, selenium, silver, copper, zinc, oil & grease, and total organic carbon (TOC). Since the mercury method (SW-846 7471B) being used by the referee laboratory uses 1 g for analysis, the sample size being collected and sent to all participants (20 ml vials) will be sufficient for all analyses. Table 4-1 summarizes the minimum sample volume, container type, preservation, and holding time requirements for the field samples prepared at the SAIC GeoMechanics Laboratory.

**Table 4-1.** Sample Volume, Containers, Preservation, and Holding Time Requirements

Parameter	Minimum Sample Size <sup>1</sup>	Container	Preservation	Holding Time
Mercury	10 g	Glass 20-ml vial	Cool to 4° C	28 days
Oil & Grease	5 g	Glass 20-ml vial	Cool to 4° C	28 days
TOC	5 g	Glass 20-ml vial	Cool to 4° C	28 days
Ag, As, Cu, Pb, Se, Zn	5 g	Glass 20-ml vial	Cool to 4° C	6 months

<sup>1</sup> Minimum sample size required for laboratory is less than 1 gram for mercury; other parameters require separate aliquot for laboratory analysis only.

Ag, As, Cu, Pb, Se, and Zn - Silver, Arsenic, Copper, Lead, Selenium and Zinc

C - Celsius

g - gram

ml - milliliter

TOC - Total Organic Carbon

---

#### 4.1.1.2 Sample Custody, Shipment, and Archiving

Preparation of the 20-ml sample vials for shipment will be performed in the following manner:

- Label bottles with prepared blind coded labels,
- Log the "blind coded" sample ID with the actual field sample ID,
- Secure labels with clear tape,
- Place sample containers in foam or other compartmentalized vial holders. If foam is not available, bubble-wrap or wrap with other appropriate material to prepare the vials for shipping,
- Add other sample protection material, as needed. Place vial holders or bubble-wrapped vials in freezer bags,
- Place vials in cooler with bagged wet ice to maintain sample temperature at 4°C during shipment to the referee laboratory and to the Oak Ridge office, and
- Place an original signed COC form inside the cooler (retain a copy) and apply custody seals to cooler. Sample custody seals will also be wrapped around each plastic bag inside each cooler containing the foam vial holders. Each custody seal will be attached in such a manner as to be able to detect unauthorized tampering with samples after preparation and prior to analysis. The SAIC GeoMechanics Laboratory Manager or the designated alternate will put his/her initials and the date on each seal.

An example COC form is provided as Figure 4-4. All information on the COC form should be filled out.

Prior to the Demonstration, the appropriate number of samples will be shipped to two destinations: 1) Oak Ridge, TN and 2) the referee laboratory (ALSI). The SAIC Oak Ridge office will serve as the designated shipping receipt location for Demonstration samples. The sample shipment arriving in Oak Ridge will be retained at all times in custody with SAIC at the Oak Ridge office until arrival of the Demonstration field crew. The coolers will be re-iced at this location, as needed, and the internal temperature of each cooler monitored and recorded on the appropriate COC form. Once the Demonstration crew arrives, the coolers will be retrieved from the SAIC office. The custody seals on the plastic bags inside the cooler will only be broken by SAIC personnel. Samples designated for analysis at the referee laboratory will be shipped by an overnight courier from the SAIC GeoMechanics Laboratory. The shipping addresses and contacts for the SAIC Oak Ridge office and the referee laboratory (ALSI) are provided in Table 4-2.

#### 4.1.2 SRM Samples

SRM samples containing mercury (only critical contaminant) at different concentrations will be purchased for the Demonstration to supplement the field sample concentration ranges. SRMs will be purchased as solid matrices (e.g., soil or sediment) that contain mercury and will be accompanied by certificates of analysis. At a minimum, as discussed earlier in subchapter 3.1.2, low level (1-100 µg/kg Hg), mid-level (100 µg/kg - 10 mg/kg), and high level (10 - 1000 mg/kg) SRMs will be distributed to the vendors in accordance with the concentration ranges suitable to their technologies.

In order to reduce the risk of sample cross-contamination at the SAIC GeoMechanics Laboratory, the SRMs will be shipped by one or more providers to the SAIC Idaho Falls office. SAIC will transfer the SRM material from the provider containers to 20-ml glass vials. Temporary labels will be fixed to the vials. Once all SRM vials are labeled, they will be sent to the SAIC GeoMechanics Laboratory in Las Vegas, where the SRM vials will be re-labeled with a "blind code" that will render them indistinguishable from each other and from the field samples. The vials will be cooled to 4°C and shipped to the SAIC Oak Ridge Office and the referee laboratory intermingled with the field samples.

For each separate concentration, replicate SRM vials will be prepared for each of the five vendors to test during the Demonstration. Replicate vials of each prepared SRM sample will be shipped to the referee laboratory for mercury analysis, and at least one replicate vial of each SRM will be archived at the SAIC GeoMechanics Laboratory as a reserve. To properly record and track which SRMs have been prepared (i.e., aliquoted to 20-ml vials), and where each set of vials were shipped (or archived), the SAIC GeoMechanics Laboratory will use the same or a similar form as shown in Figure 4-2.

#### 4.1.2.1 Sample Volumes, Containers, Preservation, and Holding Times

The minimum sample volume, container, preservation, and holding time requirements for SRM samples, that will be shipped from the SAIC GeoMechanics Laboratory to SAIC - Oak Ridge and the referee laboratory, are described in Table 4-1. The sampling date will be identified as the day the first samples are shipped from the SAIC GeoMechanics Laboratory.



**Table 4-2.** Shipping Addresses and Contacts for Demonstration Samples.

OAK RIDGE	REFEREE LABORATORY
Science Applications International Corp.	Analytical Laboratory Services, Inc.
151 Lafayette Drive	34 Dogwood Lane
Oak Ridge, TN 37831	Middletown, PA 17057
Attention: Kevin Jago / Allen Motley	Attention: Ray Martrano
Phone: (865) 481-4614 / Fax: (865) 481-4607	Phone: (717) 944-5541 / Fax: (717) 944-1430

#### *4.1.2.2 Sample Custody, Shipment, and Archiving*

Handling and shipment of SRM samples will use coded labels that will mask sample sources. The SRM samples will be shipped directly from one or more commercial suppliers to the SAIC Idaho Falls Office at the following address:

Science Applications International Corp.  
950 Energy Drive  
Idaho Falls, ID 83401  
Attention: John Nicklas / Joe Evans  
Phone / Fax: (208) 528-2110 / (208) 528-2168

All acquired SRMs will be packaged in containers much larger than vials. Therefore, at the SAIC Idaho Falls office, SRM samples will be aliquoted into 20-ml glass vials that are consistent with homogenized field samples. The prepared vials will be shipped at 4°C to the SAIC GeoMechanics Laboratory in Las Vegas at the following address:

SAIC GeoMechanics Laboratory  
595 East Brooks Ave., Suite 301  
North Las Vegas, NV 89030  
Attention: Nancy Patti  
Phone: (702) 739-7376

At the SAIC GeoMechanics Laboratory, the SRM samples will be incorporated into the same "blind coding" system used for the homogenized field samples so that they are indistinguishable from field samples. This process may be done several days prior to the Demonstration; the SRM vials will be kept at 4°C. SRM samples will be shipped directly from the SAIC GeoMechanics Laboratory per procedures in Subchapter 4.1.1.2.

## **4.2 Field Analysis by Vendors**

This chapter defines the procedures that will be applied by the complete Demonstration team during the field analysis of samples by vendors at the ORNL facility. This chapter details the procedures for distribution of samples to vendors by SAIC, record keeping by SAIC and the vendor, and EPA's and SAIC's handling of wastes generated during the Demonstration.

Field analyses will be performed by five vendors at the ORNL facility. Each vendor will receive sediment, soil, and SRM samples for analysis. Demonstration samples will cover a range of mercury concentrations; this range will vary for each vendor.

### **4.2.1 Distribution of Samples**

During the Demonstration, all field samples, and SRMs utilized to fill in missing concentration ranges will be collectively termed "Demonstration samples." All Demonstration samples will be handled as "blind samples." For the Demonstration,



---

the only individuals who will know the key coding of the Demonstration samples will be the SAIC TOM, the SAIC GeoMechanics Laboratory Manager, and the SAIC QA Manager. The samples will be shipped from the SAIC GeoMechanics Laboratory to the SAIC office in Oak Ridge. Samples will be shipped in containers that will be placed in a cooler, cooled with ice to 4°C, and shipped to SAIC's Oak Ridge office using a COC form and custody seals.

Once received at the SAIC office, sample vials will be distributed into separate coolers for each vendor. SRM samples will be intermixed. Separate coolers will be dedicated to each vendor and labeled with the vendor's name. The SAIC TOM will oversee distribution of samples and placement in vendor coolers (coolers will be provided by SAIC). The coolers will be iced and maintained at 4°C for the duration of the Demonstration.

An SAIC technology observer (see subchapter 4.3.1.2) will distribute sample sets (by geographic location) to the vendors. Each observer will be responsible for supplying samples to either one or two vendors. At the beginning of each day of the Demonstration, each observer will transfer a sample cooler and COC form to each of the two vendors. The vendors will inspect the samples and sign the applicable COC form documenting the transfer of custody. At the end of the day, all samples will be returned to SAIC under control of the COC forms. Any samples that are not analyzed during the first day will be returned to the vendor for analysis at the beginning of Day 2. Once analysis of the first sample location is completed by the vendor, SAIC will provide a cooler containing samples from the second location. Samples will be provided at the time they are requested by the vendor. Once again, the sample transfer will be documented using a COC form.

This process will be repeated for each sample location. Until that time, SAIC will maintain custody of all remaining sample sets. SAIC will maintain custody of samples that have already been analyzed and will follow the waste handling procedures in Chapter 4.2.2 to dispose of these wastes.

#### **4.2.2 Handling of Waste Material**

SAIC will make every attempt to minimize the volume of IDW generated during the Demonstration. The Demonstration will take place at DOE-ORNL, a large quantity generator. DOE-ORNL has in place a "Waste Management Plan", and ORNL personnel will provide a staging area for storage and disposal of Demonstration wastes. EPA will ultimately be responsible for proper disposal of all wastes generated during the Demonstration, assisted by SAIC. It is anticipated that the overwhelming majority of IDW generated will consist of PPE, mostly disposable gloves. Other significant solids generated may include excess sample material, paper towels or wipes, and disposable plastic and glassware. Those items not coming into direct contact with contaminated sample material will be discarded into a garbage can or dumpster. Liquid wastes that may be generated during the Demonstration include spent or excess chemicals (e.g., reagents) from the test instruments and decontamination water. All IDW generated will be managed and disposed of in accordance with site-specific IDW management practices defined by DOE-ORNL.

Any decontamination water will be placed in an on-site drum for non-hazardous liquid waste; DOE-ORNL or SAIC will provide this drum. Spent chemicals from the field instrumentation will be staged in appropriate containers provided by ORNL. Alternatively, the vendors may retain their spent chemicals. In either case, SAIC will measure the volume of waste generated for estimating disposal costs. Vendors will be responsible for unused, excess chemicals.

After the Demonstration, any hazardous waste will be staged by ORNL pending actions by EPA to remove the waste to an off-site, state-approved hazardous waste facility. SAIC will assist EPA in labeling and handling wastes while on the site. ORNL will "green tag," transport, and stage the waste materials on the site. EPA, with assistance from SAIC, will have ultimate responsibility for off-site shipment and disposal of all hazardous wastes.

### **4.3 Field Observations**

This chapter details the activities that will be performed during the field Demonstration. It identifies the responsibilities during the field Demonstration and defines record keeping requirements.

#### **4.3.1 Roles and Responsibilities**

Chapter 2 defines overall responsibilities for this Demonstration project. This chapter defines the specific roles and responsibilities of the vendors and SAIC during the field Demonstration portion of the project.

##### *4.3.1.1 Vendor Responsibilities*

The vendors are individually responsible for shipping their respective instruments to the Demonstration location. The vendors are responsible for tracking and, as necessary, expediting equipment shipments to ensure that there are no

---

schedule delays. Equipment set up on the site will occur on Monday of the Demonstration week under the oversight of SAIC. No equipment set up is to begin until SAIC notifies the vendors. Vendors are responsible for ensuring that equipment is shipped to the proper location, arrives on time, and is operable.

Vendors are also responsible for operating, maintaining, and repairing their equipment during the Demonstration, as well as reporting analytical results to SAIC (see section 7.2). Vendors will participate in a kickoff meeting on the morning of the first day to coordinate all field Demonstration activities. During this meeting, project logistics, scheduling, and responsibilities will be reviewed. An SAIC observer will be assigned to each vendor; this person will coordinate with the vendor representative to accomplish project objectives. In addition, the vendor will be responsible for the following activities (note the referenced chapter for the applicable project objective):

- Promptly report analytical results, including replicates and QC, to SAIC (Subchapter 3.2.1.1 to 3.2.1.3)
- Supply information to SAIC on the cost of the instrument, supplies, and parts used during the Demonstration (Subchapter 3.2.1.5)
- Estimate before the Demonstration the waste volume that will be generated, and report wastes generated during the Demonstration (Subchapter 3.2.1.5)
- Provide in advance of the Demonstration all SOPs for the instrument (Subchapter 3.3.1)
- Provide information on operator qualifications and training (Subchapter 3.1.1.5 and 3.3.1)
- Supply in advance of the demonstration a list of all chemicals used and corresponding Material Safety Data Sheets (MSDSs) (Subchapter 3.3.2)
- Provide equipment specifications, including dimensions, weight, electrical requirements, and other information related to equipment design (Subchapter 3.3.2 through 3.3.4)
- Report all downtime during the Demonstration and the reason for the downtime. Report also any repairs along with parts and supplies used (Subchapter 3.2.1.5, 3.3.4, and 3.3.5)

#### *4.3.1.2 SAIC Responsibilities*

SAIC will assign one observer per one or two technologies (i.e., XRF, AA, etc.) (each of three SAIC observers will be dedicated to two vendors except one observer who will be responsible only for the fifth vendor). A fourth observer will be responsible for monitoring all vendor technologies during the Demonstration in order to ensure consistency in the approach for the secondary objectives, which are subjective.

The dedicated SAIC observers will be responsible for assisting their assigned vendors in finding its Demonstration location and other logistical issues. However, the vendors will ultimately be responsible for all such logistical issues. The SAIC observer will be responsible for the following activities (note the referenced chapter for the applicable project objective):

- Notify the vendor when timing of sample analysis begins (Subchapter 3.2.1.4)
- Time equipment setup, sample analyses, and equipment disassembly (Subchapter 3.2.1.4)
- Obtain recorded analytical results (including replicates and QC samples) provided by the vendor (Subchapter 3.2.1.1 through 3.2.1.3)
- Record and notify the vendor the number of sample analyses completed (Subchapter 3.2.1.4)
- Document the duration of instrument downtime, the reasons for the downtime, and the required instrument repairs (Sections 3.2.1.4 and 3.3.4)
- Document the number of vendor operators, and the quantity of supplies and parts used (Subchapter 3.2.1.5)
- Collect information on the cost of the instrument, supplies, parts, and labor, and estimate costs for use of the instrument (Subchapter 3.2.1.5)
- Evaluate the ease of use of the instrument (Subchapter 3.3.1)
- Document chemicals used, review MSDSs, and evaluate health and safety concerns of the instrument (Subchapter 3.3.2)
- Evaluate instrument portability (Subchapter 3.3.3)

- 
- Evaluate instrument durability (Subchapter 3.3.4)
  - Evaluate the availability of the instrument and supplies (Subchapter 3.3.5)

#### **4.3.2 Records**

Project records will include:

- Analytical results, including replicates and other QC samples provided by the vendor
- Calculations and results for MDLs and PQLs (sensitivity), percent difference from standards (accuracy), and RSDs (precision)
- Field logs documenting the time required for instrument setup, calibrations, analysis of samples, and instrument demobilization
- Field logs documenting the evaluation results for ease of use, portability, durability, and other secondary information
- Completed and signed COC forms used for each transfer of samples from one party to another
- All instrument evaluation information (including cost data) collected from vendors, vendor web pages, suppliers, and other sources as part of this Demonstration.

A detailed discussion of the records that will be maintained follows for each project objective.

##### *4.3.2.1 Primary Objectives*

###### *Primary Objective # 1: Evaluate Instrument Sensitivity*

SAIC observers will obtain PQL values from each vendor and maintain records of the analytical results and calculations used to determine MDLs and associated calibration curves to determine the PQL. SAIC will document exactly which calibration options are used by each vendor during the demonstration. PQL determination will be performed at least once during the Demonstration and perhaps more than once, depending upon individual vendor calibration requirements. The MDL analysis will be performed during the Demonstration through the analysis of blind samples; corresponding records will be maintained.

###### *Primary Objective # 2: Evaluate Instrument Accuracy*

SAIC observers will receive records of blind replicate analyses performed by each vendor to calculate instrument accuracy. Records will include the time of the analysis, the sample number, the numerical result, and the units of measurement. Calculations of instrument accuracy will be maintained as part of the project record.

###### *Primary Objective # 3: Evaluate Instrument Precision*

SAIC observers will receive records of blind replicate analyses performed by each vendor to calculate instrument precision. Records will include the time of the analysis, the sample number, the numerical result, and the units of measurement. Precision calculations will also be maintained as part of the project record.

###### *Primary Objective # 4: Evaluate Instrument Throughput*

SAIC will maintain the following records to evaluate instrument throughput:

- Time required for instrument set up and demobilization.
- Calibration time.
- Total number and types of samples analyzed by each vendor.
- Start and completion time for each set of sample analyses (daily except in the case of significant downtime due to personnel breaks/lunch).
- Duration and reasons for any equipment downtime.

###### *Primary Objective # 5: Estimate Cost to Use Vendor Instruments*

---

SAIC will maintain records used to estimate the cost of using vendor instruments. Examples will include:

- Rental or purchase price of instruments, if applicable.
- Vendor quoted price per sample.
- Capital cost based on published data.

#### *4.3.2.2 Secondary Objectives*

SAIC observers will maintain records on the name, type, model, and serial number of the vendor analytical equipment. In addition, the observers will document the date of all observations and record their names. The recordkeeping requirements for each secondary objective are discussed below:

##### *Secondary Objective # 1: Ease of Use*

SAIC observers will maintain records of the number of operators and the qualifications and training of each (supplied by each vendor). A copy of any SOPs will be kept as part of the project record, including observations on the ease of the use of the SOP and equipment.

##### *Secondary Objective # 2: Health and Safety Concerns*

SAIC observers will maintain records of equipment certifications and notes on potential mechanical, electrical, and chemical hazards based on Demonstration activities.

##### *Secondary Objective # 3: Portability*

SAIC observers will keep records of the weight, dimensions, power source requirements, setup and tear down time, any other observations related to equipment portability.

##### *Secondary Objective # 4: Durability*

SAIC observers will maintain information on the materials of construction, quality of construction, downtime during Demonstration (including duration and reason), routine maintenance performed or required, and any repairs that were performed during the Demonstration (including parts required and reason for repair).

##### *Secondary Objective # 5: Availability of Vendor Instruments and Supplies*

SAIC observers will maintain records used to evaluate the availability of equipment and supplies. Records will include field notes, results of web searches, phone records, and any other information utilized to evaluate this objective.

---

## **Chapter 5**

### **Referee Laboratory Testing and Measurement Protocols**

The referee laboratory will analyze all samples that are analyzed by the vendor technologies in the field under the conditions prescribed by the reference method selected. The following subchapters provide information on the selection of the referee laboratory and reference method as well as details on the performance of the reference method in accordance with EPA protocols. Other parameters to be analyzed by the referee laboratory are also discussed briefly.

#### **5.1 Referee Laboratory Selection**

During the planning of the Pre-demonstration phase, nine laboratories were sent a statement of work SOW for the analysis of mercury to be performed as part of the Pre-demonstration. Seven laboratories responded to the SOW with appropriate bids. (Two laboratories chose not to bid.) Three of the seven laboratories were selected as candidate laboratories based upon technical merit, experience, and pricing. These laboratories received and analyzed blind samples and SRMs during Pre-demonstration activities, as discussed in Chapter 1. The referee laboratory to be used for the Demonstration was selected from these three candidate laboratories. Final selection of the referee laboratory was based upon the laboratory's interest in continuing into the Demonstration, the laboratory-reported SRM results, the laboratory MDL for the reference method selected (SW-846 Method 7471B), the precision of the laboratory calibration curve, other technical considerations, the laboratory's ability to support the demonstration, and cost.

A preliminary audit was performed at two of the laboratories in order to make a final decision on a referee laboratory for the Demonstration. (One of the three candidate laboratories was eliminated from selection prior to performing a pre-audit. Upon discussion with this laboratory it was determined that they would not be able to meet requirements for the quantitation limit for the Demonstration. Their lower calibration standard was approximately 50 µg/kg and the vendor comparison requirements were well below this value.) To ensure a complete and fair comparison the same auditor assessed both laboratories. Mr. Joe Evans, the SAIC QA Manager, performed these audits.

Results of the SRM samples were compared for the two laboratories. Each laboratory analyzed each sample (there were two SRMs) in triplicate. Both laboratories were within the 95% prediction interval for each SRM. In addition, the average result from the two SRMs was compared to the 95% confidence interval for the SRM.

Calibration curves from each laboratory were reviewed carefully. This included calibration curves from the analyses previously performed and calibration curves for other laboratory clients. The QC requirement was that the correlation coefficient be 0.995 or greater and that the lowest point on the calibration curve be within 10% of the predicted value. Both laboratories were able to achieve these two requirements for all curves reviewed and for a lower standard of 10 µg/kg, which was the lower standard required for the Demonstration based upon information received from each of the vendors. In addition, MDLs based upon an analysis of 7 standards were reviewed. Both laboratories could achieve an MDL that was below 1 µg/kg.

It should be noted that vendor claims in terms of sensitivity are driving how low this lower quantitation standard should be. These claims are somewhat vague, and the actual quantitation limit each vendor can achieve is uncertain. Some vendors claim to be able to go as low as 1 µg/kg, but it is uncertain if this is actually a PQL or a DL. Therefore, it may be necessary that the laboratory actually be able to achieve even a lower PQL than 10 µg/kg. This will be discussed in more detail in the conclusion part of this chapter.

---

The analytical method used by both laboratories was based upon SW-846 Method 7471B. SOPs from both laboratories were reviewed. Each SOP followed the reference method. In addition, interferences were discussed. There was some concern that organic interferences may be present in the samples previously analyzed by the laboratories. Because these same matrices were expected to be part of the Demonstration, there was some concern associated with interferences and how these interferences would be eliminated. This is discussed in the Conclusion portion of this chapter.

Sample throughput was somewhat important in that the laboratories would receive all Demonstration samples at the same time and it is desirable that these samples be run at the same time as the field samples in order to eliminate any question or variable associated with loss of contaminant due to holding time. This meant that the laboratory would receive approximately 300 samples in the period of a few days for analysis. It was also desirable for the laboratory to produce a data report within a 21 day turnaround time for purposes of the Demonstration. Both laboratories indicated that this was achievable. Instrumentation was reviewed and examined at both laboratories. Each laboratory was using a Leeman instrument for analysis. One of the two laboratories had back-up instrumentation in case of problems. Both laboratories indicated that their Leeman mercury analyzer was relatively new and had not been a problem in the past.

Previous SITE program experience was another factor considered as part of these pre-audits. This is because the SITE program generally requires a very high level of QC, such that most laboratories are not familiar with the QC required unless having previously participated in the program. The other factor was that the SITE program generally requires analysis of relatively “dirty” samples and many laboratories are not used to analyzing such “dirty” samples. Both laboratories have been long-time participants in this program.

Other QC factors, such as analyses on other SRM samples not previously examined, laboratory control charts, and precision and accuracy results were examined during the audit. Each of these issues was closely examined. In addition, because of the desire to increase the representativeness of the samples for the Demonstration, each laboratory was asked if sample aliquots could be increased to 1 g (the method requirement noted 0.2 g). Based upon previous results, it was noted during the audit that both laboratories routinely increased sample size to 0.5 g. They indicated that increasing the sample size would not be a problem. Besides these QC factors other, less tangible QA elements were examined. This included analyst experience, management involvement in the demonstration, and internal laboratory QA Management. These elements were also factored into the final decision.

## **Conclusion**

There were very few factors that separated the quality of these two laboratories. Both were exemplary in performing mercury analysis. There were, however, some minor differences based upon this evaluation that were noted by the auditor. These were as follows:

- ALSI had back-up instrumentation available. Even though neither laboratory reported any problems with its primary instrument (the Leeman mercury analyzer), ALSI did have a back-up instrument in case there were problems with the primary instrument or in the event that the laboratory needed to perform other mercury analyses during the Demonstration time.
- As noted, the low standard requirement for the calibration curve was one of the QC requirements specified for this Demonstration in order to ensure that a lower quantitation could be achieved. This low standard was 10 µg/kg for both laboratories. ALSI, however, was able to show experience in being able to calibrate much lower than this, using a second calibration curve. In the event that vendors are able to analyze at concentrations as low as 1 µg/kg with precise and accurate determinations, ALSI will be able to perform analyses at lower concentrations as part of the Demonstration.
- Management practices and analyst experience were considered similar at both laboratories. ALSI has participated in a few more SITE demonstrations than the other laboratory, but this difference is not significant because both laboratories have proven themselves capable of handling the additional QC requirements for the SITE program. In addition, both laboratories have internal QA management procedures that provide the confidence needed to achieve SITE requirements.
- Interferences for the samples previously analyzed were discussed and data were reviewed. ALSI ran two separate runs for each sample. This included a run with stannous chloride and a run without stannous chloride. (Stannous chloride is the reagent used to release mercury into the vapor phase for analysis. Sometimes organics can cause interferences in the vapor phase. Therefore, a run with no stannous chloride would provide information on organic interferences.) The other laboratory did not routinely perform this analysis. Some samples were thought to contain organic interferences, based on previous sample results. The Pre-demonstration results were reviewed

---

and it was determined that no organic interferences were present. Therefore, while this was thought to be a possible discriminator between the two laboratories in terms of analytical method performance, it became moot for the samples included in this Demonstration.

The factors above were considered in the final evaluation. Because there were only minor differences in the technical factors, cost of analysis was used as the discriminating factor. (If there had been significant differences in laboratory quality, cost would not have been a factor). ALSI was significantly lower in cost than the other laboratory. Therefore, ALSI will be used as the referee laboratory for the Demonstration.

## **5.2 Reference Method**

The selection of the SW-846 Method 7471B as the reference method was based on several factors, predicated on information obtained from the technology vendors, as well as the expected contaminant types and soil/sediment mercury concentrations expected in the test matrices. There are several laboratory - based, promulgated methods for the analysis of total mercury. In addition, there are several performance-based methods for the determination of various mercury species. Based on the vendor technologies, it was determined that a reference method for total mercury would be needed. Table 5-1 summarizes the methods evaluated, as identified through a review of the EPA Test Method Index. The procedure used for the reference method selection is summarized below. In selecting which of the potential methods would be suitable as a reference method, consideration was given to the following questions:

- Is the method widely used and accepted? Is the method an EPA-recommended, or similar regulatory method? The selected reference method should be in sufficient use that it can be cited as an acceptable method for monitoring and/or permit compliance among regulatory authorities.
- Does the selected reference method provide QA/QC criteria that demonstrate acceptable performance characteristics over time?
- Is the method suitable for the types of mercury expected to be encountered? The reference method must be capable of determining, as total mercury, all forms of the chemical contaminant known or likely to be, present in the matrices.
- Will the method achieve the necessary detection limits to adequately evaluate the sensitivity of each vendor technology?
- Is the method suitable for the concentration range expected in the test matrices?

Methods evaluated for total mercury analysis included SW-846 Method 7471B, SW-7473, SW-7474, EPA Method 1631, EPA 6200, and EPA 245.7. These methods are in Table 5-1. Consideration was given to the dynamic range of the method, types of mercury included in the analysis, and whether the method was a widely-used protocol. Based on these considerations, it was determined that SW-846 Method 7471B (analysis of mercury in solid samples by cold-vapor, atomic absorption spectrometry) would be the best reference method. Method SW-7474, an atomic fluorescence spectrometry method using SW-3052 for microwave digestion of the solid, was also considered a likely technical candidate; however, the method is not as widely used or referenced, and it was determined that SW-7471B was the better choice for this reason. The following subchapters provide details on this method. Analytical methods for non-critical parameters are presented in Table 5-2.

### **5.2.1 Laboratory Protocols**

The critical parameter for this study is the analysis of mercury in soil and sediment samples. Samples to be analyzed by the laboratory include field samples, as well as SRM samples. Detailed laboratory procedures for subsampling, extraction, and analysis are provided in the SOPs included as Appendix B and are summarized briefly below.

**Table 5-1:** Methods for Total Mercury Analysis

Method	Analytical Technology	Mercury type(s) Analyzed	Approx. Conc. Range	Comments
SW-7471B	CVAAS	inorganic mercury and organo-mercury	10 - 2000 µg/kg	Widely used standard for total mercury determinations
SW-7473 (Uses Milestones DMA)	Thermal decomposition, amalgamation and AAS	inorganic mercury and organo-mercury	0.2 - 400+ µg/kg	Uses participating vendor's equipment
SW-7474 (Solids: prep 3052)	AFS	inorganic mercury and organo-mercury	1 µg/kg - mg/kg	Allows for total decomposition analysis; less widely used/referenced
EPA 1631	CVAFS	inorganic mercury and organo-mercury	0.5 - 100+ ng/L	Requires "trace" analysis procedures; written for waters; Appendix A of EPA 1631 written for sediment/soil samples
EPA 245.7	CVAFS	inorganic mercury and organo-mercury	0.5 - 200+ ng/L	Requires "trace" analysis procedures; written for waters will require dilutions of high-level mercury samples
EPA 6200	FPXRF	inorganic mercury	30 mg/kg	Considered only a screening protocol
TARGET RANGES: Based on vendor info	Not Applicable	inorganic mercury, possibly trace organo-mercury	10 µg/kg-1000+ mg/kg	

ng/L - Nanograms per liter

AAS = Atomic Absorption Spectrometry

AFS = Atomic Fluorescence Spectrometry

CVAAS = Cold Vapor Atomic Absorption Spectrometry

CVAFS = Cold Vapor Atomic Fluorescence Spectrometry

FPXRF = Field Portable X-Ray Fluorescence

**Table 5-2.** Analytical Methods for Non-Critical Parameters

Parameter	Method Reference	Method Type
Arsenic	SW-846 3050/6010	Acid digestion, ICP
Lead	SW-846 3050/6010	Acid digestion, ICP
Selenium	SW-846 3050/6010	Acid digestion, ICP
Silver	SW-846 3050/6010	Acid digestion, ICP
Copper	SW-846 3050/6010	Acid digestion, ICP
Zinc	SW-846 3050/6010	Acid digestion, ICP
Oil and Grease	EPA 1664	n-Hexane extraction, Gravimetric analysis
TOC	SW-846 9060	Carbonaceous analyzer



---

Samples will be analyzed for mercury using Method 7471B, a cold-vapor atomic absorption method, based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration. Potassium permanganate is added to eliminate possible interference from sulfide. As per the method, concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water. Copper has also been reported to interfere; however, the method states that copper concentrations as high as 10 mg/kg had no effect on recovery of mercury from spiked samples. Samples high in chlorides require additional permanganate (as much as 25 ml) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Therefore, free chlorine is removed by using an excess of hydroxylamine sulfate reagent (25 mL). Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

Prior to analysis, the contents of the sample container will be stirred and the sample mixed prior to removing an aliquot for the mercury analysis. An aliquot of soil/sediment (1 g) is placed in the bottom of a biological oxygen demand bottle, with reagent water and aqua regia added. The mixture is heated in a water bath at 95°C for 2 minutes. The solution is cooled and reagent water and potassium permanganate solution are added to the sample bottle. The bottle contents are thoroughly mixed and the bottle is placed in the water bath for 30 minutes at 95°C. After cooling, sodium chloride-hydroxylamine sulfate is added to reduce the excess permanganate. Stannous chloride is then added and the bottle attached to the analyzer; the sample is aerated and the absorbance recorded. A non-stannous chloride run is also included as an interference check when organic contamination is suspected. In the event of positive results of the non-stannous chloride run, the laboratory will report these results to SAIC so that a determination of organic interferences can be made.

#### **5.2.2 Laboratory Calibration Requirements**

The instrument will be calibrated for mercury detection in accordance with the method requirements using a five-point calibration curve that will include a standard concentration at the reporting detection limit. Standards are prepared in the same manner as the samples. Calibration curve requirements will be  $r^2 > 0.995$ , with continuing calibration verification standards run every 10 samples (using a mid-level calibration standard) and meeting a criterion of 90-110% recovery. In addition, a low standard check will be run after the five-point calibration curve to verify that the calculated concentration of the low standard is within 10% of the actual concentration. This will serve as a verification of the reported PQL. The calibration curve will be verified daily by the analysis of a second-source initial calibration verification standard, which will also meet criteria of 90-110% recovery. These calibration criteria are summarized in tabular form in Chapter 6.

### **5.3 Additional Analytical Parameters**

In addition to the critical parameter of mercury, the referee laboratory will also analyze arsenic, lead, selenium, silver copper, zinc, oil and grease, total solids, and total organic carbon (TOC) on selected samples according to the methods listed above.

---

## Chapter 6

### Referee Laboratory QA/QC Checks

For this SITE project, QA objectives associated with the reference method have been established to ensure that data generated by the laboratory are of adequate quality to achieve the project's technical objectives. It is critical for this Demonstration that the mercury values obtained by the referee laboratory, using the reference method, be accurate and precise. Concentrations for the certified SRM samples will be generated by both the laboratory and by each of the individual technology vendors, and will be compared to pre-established concentration ranges provided by the SRM supplier. The laboratory concentrations of mercury for the field soil and sediment samples will be the basis of comparison for the vendor results. Therefore, the following section discusses the QA/QC checks to be performed by the referee lab in compliance with SW-846 protocols for Method 7471B. Acceptance criteria for accuracy, precision, and completeness objectives are given, along with the expected detection limit of the critical measurements. Specific QC check procedures for critical measurements are discussed in Subchapter 6.2, including corrective actions to be taken in the event these QC checks do not meet criteria.

#### 6.1 QA Objectives

The critical measurement for this project is mercury in soil and sediment samples collected from the test locations, as well as in SRM samples. Table 6-1 summarizes QA objectives for this parameter, with the achievement of these objectives discussed below.

**Table 6-1: QA Objectives for Mercury Measurements by SW-846 Method 7471B**

Objective	Criteria
Accuracy (1)	80-120 % recovery
Precision (1)	RPD < 20%
Practical Quantitation Limit	0.01 mg/kg
Completeness	95 %
Representativeness (2)	RSD < 20%
Comparability	EPA-approved method

(1) Accuracy and precision assessed by the analysis of duplicate spikes

(2) Representativeness based on the results of multiple replicates of field samples

Precision for mercury will be assessed by the analysis of duplicate matrix spikes (MS/MSDs) performed on select project samples to determine the reproducibility of the measurements. The relative percent difference (RPD) between the spiked samples will be compared to the objectives given in Table 6-1.

Samples prepared as multiple replicates, as per Chapter 4, will be used to evaluate overall precision of the combined sampling, homogenization and analysis procedures. Precision will be assessed by calculating the RSD for the measurements. The analytical QA objectives will be applied to these samples as a guideline only; if the field replicates meet these objectives, then the combined precision is within the analytical expectations. If these guidelines are exceeded,

---

the nature of and reasons for any exceedance will be discussed in the final QA review of the data. Corrective action will not necessarily be possible or required.

Accuracy objectives for mercury are evaluated by the percent recovery of the MS/MSDs performed using project samples. In addition, accuracy of the analytical system will be verified by the analysis of second source standards. Laboratory control spikes (LCSs) will be analyzed with each batch of samples as a further assessment of analytical accuracy in the absence of matrix effects. These analyses are discussed further in Subchapter 6.2 and requirements for LCS results are specified in Table 6-2.

The SRM samples analyzed by the laboratory (as well as by the field measurement devices) will also provide an assessment of accuracy for each analytical technique (field and reference method) as discussed previously in Chapter 3. Results for these samples analyzed during the Demonstration will be compared to the concentration limits provided in the certification associated with the SRM.

Method detection limit for the reference method is determined in accordance with EPA 40 CFR Part 136, as a statistical calculation based on the analysis of 7 replicate low-level standards. Quantitation limit is defined as the PQL, determined by the lowest concentration standard meeting the specified calibration criteria (+/- 10 %D).

Comparability is based on the use of established EPA-approved methods for the analysis of the critical parameter. The determination of mercury is based on published methods, supplemented with well-documented procedures used in the laboratory to ensure reproducibility of the data. The selection of SW-846 Method 7471B as the reference method was discussed previously (See chapter 5)

Representativeness is achieved by collecting samples considered representative of the matrix at the time of collection. For the soil and sediment samples to be analyzed during the field Demonstration, this is achieved by the homogenization and sub-sampling procedures summarized in Chapter 4 and presented in detail in Appendix A.

Completeness refers to the amount of measurement data collected relative to that needed to assess the project's technical objectives. For this project, completeness objectives have been established at 95%, acknowledging the potential for loss of sample. Sample re-analysis is not expected to be a problem given the 28-day hold time for mercury.

## **6.2 QC Checks**

General QA objectives have been discussed in the preceding paragraphs. The following QC check procedures will be used to assess the critical parameters. These QC checks are summarized in Table 6-2, and discussed further below.

Calibration criteria were described in Subchapter 5.2.2. In addition to these requirements, mercury analysis will include the analysis of MS/MSD samples prepared using project samples. MS/MSD samples will be designated on the COC or will be performed at a frequency of 5% of the samples, whichever is more frequent. Samples will be spiked by the addition of approximately 5 times the native sample concentration, as estimated based on historical data or after screening of the primary sample. The sample, MS, and MSD will all be analyzed in the same batch, even if this requires re-analysis of the primary sample. If the initial spike preparation results in spiking levels that are inappropriately low relative to the native sample concentration and the MS/MSD do not meet criteria, the three samples (primary, MS, and MSD) will be re-digested and re-analyzed using an appropriate spike concentration. An LCS will be prepared and analyzed with each batch of samples prepared. If the results of both the LCS and the MS/MSD do not meet criteria, the entire analytical batch will be re-digested and re-analyzed. If one or the other fail, but not both, the laboratory QA Coordinator will contact the SAIC QA Manager to discuss and implement the appropriate corrective action.

QC Check	Frequency	Criteria	Corrective Action
Initial calibration – 5 pt (ICAL)	Initially and as required	R <sup>2</sup> > 0.995	Repeat calibration
Initial calibration verification (ICV) = 2 standard	After each ICAL and daily thereafter	90-110% recovery	Repeat analysis
Low level standard check	after ICAL	90-110% recovery	Re-calibrate (ICAL) Re-calibrate (ICAL)
Continuing calibration standard (CCV) using mid-level ICAL	Every 10 samples	90-110% recovery	Repeat analysis Re-calibrate (ICAL)
Calibration blank	Every 10 samples	Conc. < MDL (0.5 µg/l)	Repeat analysis, prepare fresh reagents
MS/MSD	5 % of samples	80-120% recovery, RPD < 20 %	Evaluate LCS Re-analyze MS/MSD Qualify data; notify SAIC
LCS (spiked blank)	With every MS/MSD	90-110% recovery	Evaluate MS/MSD results, if necessary, reanalyze batch

**Table 6-2.** QC Checks for Mercury Measurements by SW-846 Method 7471B

---

## **Chapter 7**

### **Data Reporting, Data Reduction, and Data Validation**

For data to be scientifically valid, legally defensible, and comparable, valid equations and procedures must be used to prepare those data. Evaluation of measurements is a systematic process of reviewing a body of data to provide assurance that the quality of the data is adequate for its intended use. The following subchapters describe the data reporting, data reduction, and data validation procedures to be used for laboratory data, for data generated by the vendors, and reports to be generated to discuss Demonstration evaluation results.

#### **7.1 Referee Laboratory**

##### **7.1.1 Data Reduction**

All data reduction will be completed as specified in SW-846 Method 7471B. Where data reduction is not computerized, calculation results will be recorded on the raw data printouts, on pre-printed bench sheets, or in permanently bound notebooks. The data reduction for some analyses may include analysts' interpretations of the raw data and manual calculations. When this is required, the analysts' observations and/or summary will be written in ink on the raw data sheets. Any corrections to data sheets will be made by lining out inaccurate information, initialing the line-out, and adding the revised information next to the line-out.

All mercury data will be reported on an as-received basis.

##### **7.1.2 Data Validation**

Data generated shall be reviewed by the Analytical Task Leader on a daily basis for completeness. Data will be reported in standard units, as described above. Data validation begins with the analyst and continues until the data are reported. The analyst will verify and sign the appropriate forms to verify the completeness and correctness of data acquisition and reduction. An independent reviewer will review this information to ensure close adherence to the specified analytical method protocols. All instrument systems must be in control, and QA objectives for precision, accuracy, completeness, and method detection limit must be met. In the event that data do not meet the project objectives, the sample shall be re-analyzed or re-extracted. If the sample still does not meet project requirements, the SAIC TOM and QA manager shall be notified immediately. The problems will be discussed and appropriate corrective actions shall immediately be implemented. If project objectives have been impacted, or changes were required in analytical procedures, these modifications will be clearly noted in the ITVR.

The principal criteria that will be used to validate the integrity of data during collection and reporting are as follows:

- Verification by the project analyst that all raw data generated for the project have been documented and stored. Storage locations must also be documented in the laboratory records
- Examination of the data by the laboratory manager or his or her designee to verify adequacy of documentation and agreement with method protocols
- Reporting of all associated blank, standard, and QC data, along with results for analysis of each batch of samples

- 
- Auditing by the analytical laboratory QA/QC manager of ten percent of the data generated.

Analytical outlier data are defined as those QC data lying outside of a specific QC objective window for precision or accuracy for a given analytical method. Should QC data be outside of such limits, the laboratory supervisor will investigate the potential causes of the problem. Corrective action (as discussed in Chapter 6) will be initiated as necessary and documented. Any outlier data will be flagged with a data qualifier in the laboratory report.

### **7.1.3 Data Storage Requirements**

The subcontracted referee laboratory (ALSI) will be responsible for storing on disc all raw data for 5 years. SAIC and/or its subcontractors will retain all hard copies of the analytical data for a period of 5 years. At the end of this 5 year period EPA will be contacted concerning the final fate of the above data.

### **7.1.4 Laboratory Reporting**

Laboratory reports will include tabulated results of all samples, along with a cross-reference of laboratory identification and field sample identification. The final report will also include method summaries, detailing any deviations from, or modifications to, the proposed methods. Data will be submitted in a report with sufficient detail such that independent validation of the data can occur. Raw data will include any calibration information, instrument printouts, lab bench sheets, sample preparation information, and other appropriate information. The completed report will be reviewed by the ALSI laboratory QA manager and be approved by the laboratory project manager (or their designees) prior to submittal to SAIC.

## **7.2 Vendor Reporting**

### **7.2.1 Field Reporting**

The format of the data record submitted to SAIC at the conclusion of the Demonstration is the choice of each vendor (i.e., table, text, etc.) but must include at a minimum the following information:

- SAIC sample identification code of each sample analyzed.
- Number of field analyses recorded for each sample.
- Sample volume (or mass) used for each analysis.
- Concentration of each sample analysis result.
- Statement as to whether the result is "as received" or dry weight.
- Manner in which the result was obtained (e.g., read digitally, print out, etc.).
- Any additional sample preparation conducted for any sample (e.g., dilutions, digestion procedures, etc.).
- Any QC samples and results that are required/recommended by the vendor and should be reported in the ITVR.

In addition, vendors are also expected to include "raw" data sufficient to validate the data provided. As applicable, this may include:

- Instrument calibration procedures (including calibration standards used).
- Instrument calibration records (i.e., calibration curves).
- Any suspected sample interferences (matrix or chemical).
- Any other observations/concerns regarding sample composition.
- Chain of custody records.
- Any general comments about the samples, containers, or information provided.

### **7.2.2 Data Reduction/Validation**

The steps taken to reduce data will be well-documented and provided in the report submitted by the vendors. The validation steps taken by the vendors are left to their discretion; data will need to be submitted at the conclusion of the Demonstration as "final" results. To the extent possible, SAIC will perform a validation of Vendor Data. Because it is primarily the Vendor's responsibility to provide data of adequate quality and because the exact process for Vendor analysis is "unknown," there are no formal validation processes for vendor data as there are for laboratory data. Obvious errors, however, will be pointed out to the Vendor and it will be left to the Vendor to re-verify or change any data supplied to SAIC. The final report will document validation steps taken by the vendor.

---

## 7.3 Final Technical Reports

SAIC will use the vendor field results and reference method data to prepare the ITVR for each vendor. These reports will present the results and evaluation of each vendor technology separately in separate documents. Results for the analysis of field samples and SRMs will be compared to the referee laboratory results and SRM certified limits. The vendors will not be compared to one another.

The ITVR will include a QA review and discussion as a separate and identifiable chapter. This review will include, at a minimum, the following information:

- A thorough discussion of the procedures used to define data quality and usability, and the results of these procedures. The discussion will focus on the data quality indicators such as precision, accuracy, completeness, comparability, and representativeness, and will include summary tables of the QC data obtained during the Demonstration. Results will be compared to the data quality objectives set forth in the Demonstration Plan to provide an assessment of the factors that contributed to the overall quality of the data.
- The results of any technical systems audits performed during the course of the project will be documented, including corrective actions initiated as a result of these audits and any possible impact on the associated data. If any internal audits were performed, these, too, will be reviewed.
- All changes to the original Demonstration Plan will be documented regardless of when they were made. The rationale for the changes will be discussed, along with any consequences of these changes.
- The identification and resolution of significant QA/QC problems will be discussed. Where it was possible to take corrective action, the action taken, and the result of that action will be documented. If it was not possible to take corrective action (for example, a sample bottle was broken in transit), this too, will be documented.
- A discussion of any special studies initiated as a result of QA/QC issues and/or corrective actions, including why the studies were undertaken, how they were performed, and how the results impacted the project data.
- A summary of any limitations on the use of the data will be provided including conclusions on how these constraints affect project objectives.

The QA chapter will provide validation of the measurements to be used in the evaluation of the technology. This section (and the final report) will be subject to review by the QA manager. All ITVRs will be reviewed by SAIC, EPA, and an Independent Peer Reviewer. This review will assess the assumptions made in evaluating the data and the conclusions drawn. The EPA TOM must approve the reports prior to release.

---

## **Chapter 8**

### **QA Assessments**

A quality assurance audit is an independent assessment of a measurement system. QA audits may be internal or external audits and performance or system audits. Internal laboratory audits are conducted by the project laboratory's QA/QC coordinator and may be functionally independent of the sampling and analytical teams. External audits are those conducted by an independent organization, such as EPA. For this SITE evaluation there will be a field internal systems audit conducted by the SAIC SITE QA manager during the field Demonstration event. In addition, the SAIC SITE QA Manager or his designee will perform a technical systems audit of the laboratory performing the homogenization procedure and the referee laboratory performing the mercury analysis. Performance and system audits are described below.

#### **8.1 Performance Audits**

Performance audits are intended to quantify performance of the total measurement system. These types of audits often include performance evaluation samples supplied by an independent regulatory agency. This type of audit is not envisioned for this project but as previously stated, SRMs are used for vendor and laboratory evaluation.

#### **8.2 Systems Audits**

In general, systems audits may be conducted on sampling, analytical, and other measurement and evaluation activities. These systems audits are performed by the SAIC SITE QA manager or his designee. These audits are designed to ensure systems are in place for satisfactory sampling, analysis, measurement, and evaluation of vendor technologies as designated in the Demonstration Plan. As appropriate, these audits will consist of any or all of the following items:

- Review of the organization and responsibilities to determine the functional operation of the quality assurance program
- Check on whether SOPs are available and implemented as written or as specified in the Demonstration Plan
- Assessment of traceability of samples and data including COC forms and custody seals
- Determination that the appropriate QC checks are being made and that appropriate documentation is maintained
- Determination of whether the specified equipment is available, calibrated, and in proper working condition
- Assurance that records, including notebooks, log sheets, bench sheets, and tracking forms are properly maintained
- Verification that the appropriate chain of command is followed in responding to variances and implementing corrective action.



---

### 8.2.1 Systems Audit - SAIC GeoMechanics Laboratory

During this Demonstration, the SAIC GeoMechanics Laboratory will be responsible for the homogenization and distribution of sample vials to be used during the field evaluation. The procedures to be used in performing these activities are presented in Chapter 4 and Appendix A. The SAIC QA manager will be on site during these activities to ensure that all protocols are being followed and proper documentation is maintained. The focus of the Technical Systems Audit (TSA) at the SAIC GeoMechanics Laboratory will include, but not be limited to, issues such as:

- Are homogenization procedures being accurately and consistently followed, including the selection of the procedure (slurry or non-slurry)?
- Are all sample preparation steps documented and recorded?
- Can all prepared sample vials be traced to their original sample identification?
- Is the "blind code" being used for sample identification?
- Can SRMs be traced to their original identification?
- Can the samples being sent to each vendor be accurately identified for comparison to laboratory results?

The results of this TSA will be reported to the EPA TOM by the SAIC QA manager.

### 8.2.2 Systems Audit - Referee Laboratory (ALSI)

The referee laboratory will be performing mercury analysis as the critical parameter for the Demonstration. The analyses will follow SW-846 Method 7471B (see Laboratory SOP, Appendix B) as discussed previously (Chapter 5 presented analytical requirements and Chapter 6 summarized QC checks). A pre-audit of the laboratory was performed as a condition of selection as the referee lab. The TSA for the Demonstration phase of the project will be conducted after samples have been received at the laboratory and shortly after analysis begins. The focus of the TSA at the referee laboratory will include, but not be limited to, issues such as:

- Are all preparation steps documented for all samples?
- Is standard preparation documented and are standards traceable?
- Are SOPs available for analytical, QA, and are reporting protocols being used?
- Is sample custody maintained and documented?
- Are sample analysis records kept and can sample results be traced back to the raw data?
- Are QC checks performed at the required frequency and are control limits met?
- Are analytical instrumentation calibration records evident (including spectrophotometers, balances, etc.)?
- Do the analysts appear familiar with the requirements of the Demonstration Plan?
- Are sample results correctly calculated and recorded?

### 8.2.3 Systems Audit - Vendor Technology Evaluation

The SAIC SITE Program QA manager will be present during the MMT Demonstration. He will conduct systems audits to ensure that the procedures defined in the Demonstration Plan are being properly implemented. Because each of three SAIC technology observers will simultaneously conduct measurements and evaluations of one or two vendors, and because some of these evaluations (especially the secondary objectives) will be subjective, it is critical that these measurements and evaluations be performed in a consistent fashion. Therefore, the SAIC QA manager will audit for consistency among these observers. These audits will be performed as early as possible in the Demonstration to ensure that all data are collected in the same fashion. In addition to the three technology observers, there will be a fourth observer whose role will be to evaluate the secondary objectives for all five vendors. His role will be to ensure consistency in these evaluations. He will work closely with the other three observers; their joint observations will be the basis for the evaluation of secondary objectives. The QA manager will audit to assure that the following procedures defined in this plan are followed:

- 
- Analytical results are promptly and consistently reported
  - MDLs and PQLs, along with applicable RPDs, are properly calculated and recorded
  - Replicate measurements are properly performed and recorded, and accuracy calculated based on the results from the referee laboratory
  - Replicate measurements are properly performed and recorded, and RSDs are properly calculated and recorded to document precision
  - The amount of time required for performing the analysis is consistently and properly measured and reported for five categories: mobilization and set-up, initial calibration, daily calibration, demobilization, and sample analyses
  - Information necessary to estimate the cost associated with mercury measurements is collected for the following four cost categories: 1) capital; 2) labor; 3) supplies; and 4) IDW. (Note: much of the information collection and all of the cost calculations will be performed subsequent to the field evaluation)
  - The skills and training required for proper device operation, including any degrees or specialized training received by the operators, are fully documented. The number of operators required and the evaluation of ease of use is also consistently performed and fully documented
  - Health and safety concerns associated with device operation, including hazardous materials used, the frequency and likelihood of potential exposures, and any direct exposures or hazards observed during the Demonstration are properly recorded
  - Information to evaluate the portability of each device, including ease of transport, setup and tear down time, size and weight of the unit and peripherals, need for a power source, and ease with which the instrument is re-packaged for movement to another location are noted in a consistent manner
  - Observation regarding the durability of each device, such as the materials and quality of construction and major peripherals, all device failures, routine maintenance, repairs, and downtime are documented according to procedures
  - The use of replacement parts or spare devices during the Demonstration, along with their availability and delivery time, are fully documented. After the field Demonstration, the developer's office (or web page) and/or retail store will be contacted to identify current supplies of the tested measurement device and spare parts.

### 8.3 Corrective Action

This subchapter defines the nature and timing of corrective actions that will be implemented in response to any findings during the systems audits (no performance audits are planned) performed for this project (Subchapter 8.3.1). In addition, Subchapter 8.3.2 describes corrective actions for data outside of control limits.

Corrective actions will be initiated immediately upon identification of any problems with the project that affect product quality. The initial responsibility for identifying the causes of laboratory problems lies with the analyst, who along with the laboratory QA manager or laboratory technical manager will work towards developing a solution. Field personnel who identify a problem with data collection activities will report the difficulty to the SAIC TOM or SAIC SITE QA manager. The root cause(s) of the problem will be determined, and its effect on the program will be identified. The SAIC TOM and QA manager, and appropriate laboratory personnel (e.g., laboratory QA manager) will develop a plausible corrective action. If necessary, the SAIC TOM will assist in developing corrective actions.

As data problems arise, the contractor team will investigate the problems and perform one or more of the following actions:

- If the problem occurs in the field, the SAIC observers will attempt to correct the problem. If the observers cannot correct the problem without loss of field data or samples, he/she will immediately contact the SAIC TOM or SAIC QA manager for additional instructions
- If the problem occurs in the laboratory, the laboratory supervisor will try to correct the problem. If the laboratory supervisor cannot correct the problem without loss of analytical data of known quality, he or she will immediately contact the laboratory project manager and/or their respective QA coordinator for additional instructions.

---

A corrective action memorandum will be prepared that documents the problem and then describes the proposed corrective action that will be implemented. All corrective actions will first be approved by SAIC in conjunction with the EPA. A copy of the memorandum will be sent to the SAIC SITE QA manager and the SAIC TOM. As required, a copy will be sent to the EPA TOM and to any other personnel who would be affected by the corrective action. The appropriate project manager or their designees will be responsible for implementing the corrective actions and for assessing the effectiveness in correcting the problem.

### **8.3.1 Corrective Action for Systems Audits**

As noted above, field and laboratory activities will be audited to ensure that required field and laboratory procedures are being followed. If deficiencies or problems are discovered during the audit, the SAIC QA manager or designee will prepare a corrective action memorandum to document the procedures to be implemented to correct the deficiency.

### **8.3.2 Corrective Action for Data Outside Control Limits**

If at any time the data fall outside previously designated limits, the following actions will be taken:

- If a laboratory person observes that instruments are not within calibration limits, the instruments will be immediately re-calibrated; samples will be re-analyzed once an acceptable calibration has been obtained
- If a field/laboratory person or engineering staff member observes data problems (for example, if results for specific QC analyses are outside the QC limits), he or she will immediately notify the appropriate QA manager or SAIC TOM. A determination will be made on the impact of the problem on the data quality and whether any corrective action should be taken
- If a field/laboratory person observes procedures not being done in accordance with the QAPP he or she will immediately notify the appropriate QA manager or SAIC TOM.

---

## Chapter 9

### References

Anchor Environmental. 2000. Engineering Design Report, Interim Remedial Action Log Pond Cleanup/ Habitat Restoration Whatcom Waterway Site, Bellingham, WA. Prepared for Georgia Pacific West, Inc. by Anchor Environmental, L.L.C., Seattle, WA. July 31, 2000.

Anchor Environmental. 2001. Year 1 Monitoring Report, Interim Remedial Action Log Pond Cleanup/ Habitat Restoration Project, Bellingham, WA. Prepared for Georgia Pacific West, Inc. by Anchor Environmental, L.L.C., Seattle, WA.

Bothner, M.H., R.A Jahnke, M.L Peterson, and R. Carpenter. 1980. Rate of Mercury Loss From Contaminated Estuarine Sediments. *Geochemical et Cosmochimica Acta*. 44:273-285

ChemRisk Inc. 1993. Oak Ridge Health Studies Phase I Report. DOE/OR/21981-T3-Vol.2-Part A.

Confidential Manufacturing Site 2002. Soil Boring Data from a Remedial Investigation Conducted in 2000.

Earth Technologies Inc. 1991. Resource Conservation and Recovery Act Facility Investigation for Group 2 Sites at the Oak Ridge Y-12 Plant, Tennessee Site Characterization Summary. Prepared for Martin Marietta Energy Systems, Oak Ridge Y-12 Plant.

ENSR. 1994. Georgia-Pacific Chlorine Plant RI/FS. Report prepared by ENSR, Inc. For Georgia-Pacific West, Inc. July, 1994

Foley, R.D., R.F. Carrier, and E.A. Zeighami. 1989. Results of the Outdoor Radiological and Chemical Surface Scoping Survey at the Y-12 Plant Site. Martin Marietta Energy Systems, Y/TS-600.

Metorex Inc. 2000. Responses to SAIC Field Activities Questionnaire, November 2002.

Milestone Inc. 2002. *The DMA-80 Direct Mercury Analyzer Manual*. Monroe, Connecticut.

Miller, Jerry R., P. Lechler, and M. Desilets. (No Date). The Role of Geomorphic Processes in the Transport and Fate of Mercury in the Carson River Basin, West-Central Nevada.

NITON LLC. 2002. Field Portable X-Ray Fluorescence Analyzer - Application: Field Analysis of Mercury in Soils and Sediment, USEPA SITE Program.

Ohio Lumex Co, Inc. 2001 Multifunctional Mercury Analyzer RA-915 Operation Manual. Cleveland, Ohio.

Ohio Lumex 2002 Responses to SAIC Field Activities Questionnaire, November 2002.

MTI, Inc., 2002. PDV 500 User Guide, Version 1.1.

---

MTI, Inc. 2002. Responses to SAIC Field Activities Questionnaire, November 2002.

Rothchild, E.R., R.R. Turner, S.H. Stow, M.A. Bogle, L.K. Hyder, O.M. Sealand, and H.J. Wyrick. 1984. Investigation of Subsurface Mercury at the Oak Ridge Y-12 Plant. Oak Ridge National Laboratory, ORNL/TM-9092.

SAIC. 2002. Draft Quality Assurance Project Plan for ECRT Puget Sound SITE Demonstration, August 2002.

SAIC. 2002. Draft Technical Memorandum Data Report for ECRT Puget Sound SITE Demonstration Pre-Demonstration Characterization of Sediments, July 2002.

SAIC. September 2002. Pre-Demonstration Plan for Field Analysis of Mercury in Soils and Sediment. Revision 0

U.S. Department of Energy (DOE) 1998. Report on the Remedial Investigation of the Upper East Fork of Poplar Creek Characterization Area at the Oak Ridge Y-12 Plant, Oak Ridge, Tennessee. DOE/OR/01-1641&D2.

U.S. Environmental Protection Agency. 1996. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846 CD ROM, which contains updates for 1986, 1992, 1994, and 1996. Washington DC.

U.S. Environmental Protection Agency. 1994. Region 9. December 1994. Human Health Risk Assessment and Remedial Investigation Report - Carson River Mercury Site (Revised Draft).

U.S. Environmental Protection Agency 1998. Unpublished. Quality Assurance Project Plan Requirements for Applied Research Projects, August 1998.

U.S. Environmental Protection Agency. 2002. Region 9 Internet Web Site. [www.epa.gov/region9/index.html](http://www.epa.gov/region9/index.html).

U.S. Environmental Protection Agency. 2002. Guidance on Data Quality Indicators. EPA G5i Washington D.C. July 2002.

Wilcox, J.W, Chairman. 1983. Mercury at Y-12: A Summary of the 1983 UCC-ND Task Force Study. Report Y/EX-23, November 1983.

## **Appendix A**

# **LABORATORY HOMOGENIZATION AND SUBSAMPLING OF FIELD COLLECTED GEOMATERIALS REVISION 1**

## **APPENDIX A**

### **LABORATORY HOMOGENIZATION AND SUBSAMPLING OF FIELD COLLECTED GEOMATERIALS REVISION 1**

#### **1. SCOPE AND APPLICATION**

The purpose of this laboratory procedure document is to describe the technique for the homogenization and splitting of geomaterials collected in the field and is intended for further distribution. Geomaterials received from field sites will be homogenized and aliquoted as described in this procedure.

#### **2. DISCUSSION AND CONSIDERATIONS**

Sampling, as discussed herein, is the process of collecting portions of a medium as something that is representative of a whole part. It is the intention that field-collected geomaterial from one source is to be homogenized and the subsequently aliquoted samples distributed. The final distributed samples will be representative of each other and the homogenized material from which they were cut -- not necessarily representative of the original field material. The inherent non-homogeneous nature of a field collected geomaterial dictates that any subsamples (aliquot) from this material must first be homogenized in a clearly defined way so that all produced subsamples (aliquots) represent each other and are interchangeable. A field geomaterial sample to subsample (aliquot) producing protocol is outlined in this procedure to obtain reliable, homogenized common samples for further intra laboratory/vendor investigation.

The goal of this procedure is to produce subsampled materials that meet these criteria.

The end resulting subsampled material may not (and need not be for this demonstration) necessarily be representative of the field site from which it came. It is clearly important to this project that the final distributed aliquoted subsamples are equal in their makeup (both texturally and chemically) and are produced from a common mother material. The common mother material may be initially handled in the field collection process and/or the processing laboratory prior to homogenization for ease in the homogenization and distribution process itself. For instance, large bits of debris may be removed from the arriving field geomaterial and not be included in any of the subsamples (aliquots) subsequently produced. Further, included vegetative cover, excess water, foreign inclusive materials, and overabundant biomass materials are all sometimes present in field-collected samples. This procedure allows for their removal prior to the final homogenization process. This makes the subsamples (aliquot) different from the original collection site, but allows them to be alike when further homogenized and prepared for distribution.

Prior to the actual field sampling, the true nature of the material will be unknown. As such, the reader will find two distinct preparation procedures that are presented to accommodate both "dry" and "wet" sample homogenization and aliquoting. It is left to the SAIC GeoMechanics Laboratory to evaluate the arriving field sample and discuss with the SAIC TOM the choice of preparation methods to use.

Instruction is offered on appropriate decontamination procedures for the general laboratory sampling and homogenizing equipment and is intended to prevent cross-contamination. To minimize the potential for cross contamination, the laboratory will use disposable equipment when practical. Sampling equipment such as scoops, bowls, spoons, etc. may be purchased, used, and readily disposed of, alleviating the need for decontamination.

#### **3. EQUIPMENT**

Geomaterial preparation equipment may include the following. The equipment described represents a general

guide to acceptable items that may be used while conducting this procedure. Useful items may be:

- Clean, contaminant free tarps, dropcloths, polyethylene sheeting, canvas.
- Various apparatus for grinding geomaterials such as mortar and pestle, motorized or manual grinders, blenders, stirring devices.
- Contaminant free pails, containers, storage boxes.
- Commercially available coolers.
- Stainless steel, plastic, or other appropriate homogenization buckets, tubs, bowls or pans
- Refrigerator.
- Scoops, spoons, spatulas, shoveling devices.
- Ice, blue ice.
- Labels.
- Chain of custody records and custody seals.
- Decontamination supplies/equipment .
- Personal protection equipment which may include latex (or other protective) gloves, respirators, safety glasses, aprons, steel toed boots.
- Riffle splitter.
- Teflon sheeting.
- Rectangular scoop.

#### **4. DECONTAMINATION**

The following steps will be followed to decontaminate any general laboratory equipment that has been in contact with a potentially contaminated media.

1. Scrub equipment with a non-phosphate detergent.
2. Rinse with tap water.
3. If the presence of oil and grease was observed and is present on the equipment, rinse with ethanol then rinse with tap water.
4. Rinse with a 1% HCl solution.
5. Rinse with deionized water.
6. Air dry when practical or use clean, disposable toweling to dry.

#### **5A. DRY PREPARATION PROCEDURE (NON-SLURRY MATRIX)**

1. Decontaminate any general laboratory equipment that has been in contact with a potentially contaminated media. Refer to Section 4 for instruction.
2. Lay out clean plastic sheeting (or any other appropriate dropcloth) over a surface large enough to allow the field sampled geomaterial to lay undisturbed while being air dried -- approximately one to two days. A large open container/tub is also acceptable to use.
3. Allow the field sampled geomaterial shipment container to equilibrate to room temperature and open the container.
4. Gather a representative field geosample by first emptying the entire representative field sample onto a large clean tarp or into a large open container/tub. Quarter the sample by making two roughly perpendicular top to bottom cuts through the sample forming four generally equal quarters. Take one or more quarters, depending upon the number of quarters required to obtain a portion that visually approximates >3 liters of material. Spread the material over the prepared dropcloth (container) allowing it to air dry.
5. Return the unused quarters to the shipment container, reseal, and store it.
6. Visually inspect the exposed field geosample for foreign and/or manmade materials and inconsistent natural fractions such as large cobbles, sticks, leaves, shells, etc., and dispose of these.



7. Allow the exposed geosample to air dry undisturbed for a period of approximately 2 days.
8. Break up the entire air-dried field geosample using any various convenient methods including hand crumbling, use of a mortar and pestle, roller, etc. which will help to facilitate eventual screening of the material.
9. Pass the entire fraction of the now air-dried laboratory sample through a No. 10 mesh screen (2 mm opening) onto a clean smooth surface.
10. Discard any portion of the air-dried laboratory sample not passing the No. 10 screen, setting aside that portion passing the No. 10 screen for further handling.
11. To reduce the sample size for ease of further handling, proceed by emptying the air-dried laboratory sieved sample out onto a clean, smooth surface and pile it into roughly a cone shape. Two top-to-bottom cuts will be made through the cone at roughly perpendicular angles to form four generally equal portions (quarters). Remove one quarter from the pile using a clean scoop and put into a clean container.
12. Visually ensure that there is sufficient material to fill the required amount of containers (approximately >0.75 liters). If there is insufficient sample amount, manually mix the remaining material left from the quartering procedure. Use the spatula and mix for 2 to 3 minutes until the sample appears to be uniform and repeat step 11. Add this additionally produced quarter to that originally prepared.
13. The representative laboratory sample should now be homogenized by using a variation of the riffle splitting method and begins by manually mixing the representative laboratory sample in the container with a spatula or spoon for 2 to 3 minutes or until the sample appears to be uniform.
14. Pour the representative laboratory sample from the mixing container through a riffle splitter.
15. Combine the resultant split halves back in the container.
16. Combine the halves and reintroduce them through the riffle splitter.
17. Repeat mixing and riffle splitting for a total of five times using the same container and spoon each time the resultant halves are combined (abridged from ASTM D6323-98 section 6.1.14.2).
18. Again, recombine the two halves taken from the riffle splitter in the container and pour through the riffle splitter a final sixth time. Keep both halves as produced in the two riffle pans.
19. Pour out one of the half portions of the riffled laboratory sample onto a clean smooth surface such as a Teflon sheet and shape into an elongated rectangular pile with a flattened top surface using a clean instrument such as a spatula or knife.
20. Visually ensure that the pile is wide enough to allow sampling which will produce one half the total samples required. The transverse cuts will be produced with a rectangular scoop; each pass should allow for enough volume to fill a 20 milliliter container at least 3/4 full.
21. Subsampling of the representative laboratory sample now commences. One complete top-to-bottom transverse cut is made across the pile and the scooped material is transferred into a clean, 20-milliliter container. Ensure that the container is filled approximately to at least 3/4 full by visual inspection. Cap the container and set aside.
22. Repeat transverse cuts until one half of the total amount of samples needed are produced (abridged from ASTM D6323-98 section 6.1.9.1).
23. Transfer the remaining material in the pile, after filling one half of the total amount of samples required, into a 4 oz (or other appropriately sized) jar. This same jar can be used for both halves. This jar will be held at the SAIC GeoMechanics laboratory until the SAIC TOM determines the sample no longer has value.
24. Repeat steps 19 through 23 using the remaining riffle split half.

25. Gather all containers of the capped and containerized subsplit samples and apply the appropriate unique premarked blind-coded labels.
26. Place in a refrigerator with temperature of approximately 4 degrees C to await shipment.
27. Forward the homogenized and subsampled material to the appropriate vendors and/or laboratories according to the Demonstration plan.

**5B. WET PREPARATION PROCEDURE (SLURRY MATRIX)**

1. Decontaminate any general laboratory equipment that has been in contact with a potentially contaminated media. Refer to Section 4 for instruction.
2. Allow the field sampled geomaterial shipment container to equilibrate to room temperature and open the container.
3. Visually inspect the exposed field geosample for foreign and/or manmade materials and inconsistent natural fractions such as large cobbles, sticks, leaves, shells, etc., and dispose of these.
4. Using a suitable hand-held drill motor with an attached clean paint stirring mixing rod, mix the entire shipment (in its original shipping container) at constant speed for a period of 2-4 minutes. Care should be taken to mix the entire field sample by moving the mixing rod throughout the whole volume of material during the entire mixing time. Do not allow the mixing to be stationary.
5. At the end of the preliminary mixing, gather a representative field geosample by immediately transferring approximately 2 liters of material to a clean container.
6. Reseal the shipment container containing the remaining original field geosample and store.
7. Using a constant speed, mix the 2 liters of slurry with a commercially available mixer, a handheld electric drill, or other appropriate instrument equipped with a stirring/mixing rod (e.g., paint stirring rod). Mix the slurry for approximately 3 minutes to homogenize it.
8. To subsample, use tongs or other convenient instrument to submerge the required number of 20-milliliter containers into the slurry at one time. (This may be accomplished by grouping the containers together and wrapping them with a rubberband to hold them as one unit and submerging the unit at one time into the slurry.)
9. Allow the containers to fill, pull the unit of bottles out of the slurry, wipe the sides of each vial, and immediately cap.
10. Gather all containers of the capped and containerized subsplit samples, remove excess slurry from the outside of the containers, and apply the appropriate unique pre-marked blind-coded labels.
11. Place in a refrigerator with temperature of approximately 4 degrees C and allow to settle for a minimum of 48 hours.
12. After settling, remove the containers from the refrigerator. Using a disposable, needle-nose Pasteur pipette or other appropriate device, remove the standing water from each container.
13. Return the containers to the refrigerator with temperature of approximately 4 degrees C to await shipping.
14. Forward the homogenized and subsampled material to the appropriate vendors and/or laboratories according to the governing plan.

## **6. REFERENCES**

American Society for Testing and Materials. 1998. "Standard Practice for Laboratory Subsampling of Media Related to Waste Management Activities", ASTM Designation: ASTM D6323-98.

Hawaii UST Technical Guidance Manual, Appendix 7-E , "Recommended Sampling and Analysis Procedures, Soil Sampling", 2000.

US EPA Environmental Response Team Standard Operating Procedures, SOP 2012, Soil Sampling, 2000.

American Society for Testing and Materials. 1987. "Standard Practice for Sampling Aggregates, ASTM Designation: D75-87.

"Sample Handling Strategies for Accurate Lead-In-Soil Measurements in the Field and Laboratory", Stephen Shefsky, NITON LLC, Billerica, MA, 1997.

## **Appendix B**

### **Analytical Laboratory Services, Inc.'s Standard Operating Procedures**

*Mercury by Cold-Vapor Atomic Absorption Using  
an Automated Continuous-Flow Vapor Generator*

*Subsampling Procedure for Nonvolatile Analysis or  
Preparation*

**Method:** 03-Hg  
**Revision:** 9  
**Date:** November 5, 2002  
**Page:** 1 of 19

**Document Title:** Mercury by Cold-Vapor Atomic Absorption Using  
an Automated Continuous-Flow Vapor Generator

**Document Control Number:**

**Organization Title:** ANALYTICAL LABORATORY SERVICES, INC.  
(ALSI)

**Address:** 34 Dogwood Lane  
Middletown, PA 17057

**Phone:** (717) 944-5541

**Approved by:**

\_\_\_\_\_  
Helen MacMinn,  
Quality Assurance Manager

\_\_\_\_\_  
Date

\_\_\_\_\_  
Ray Martrano,  
Laboratory Manager

\_\_\_\_\_  
Date

## TABLE OF CONTENTS

1	Scope and Application .....	3
2	Summary of Method .....	3
3	Interferences .....	4
4	Safety .....	4
5	Apparatus and Materials .....	5
6	Reagents .....	5
7	Instrument Calibration .....	6
8	Quality Control .....	7
9	Sample Collection, Preservation and Handling .....	9
10	Procedure .....	10
11	Calculations .....	11
12	Reporting Results .....	12
13	Waste Disposal .....	13
14	Pollution Prevention .....	13
	APPENDIX A .....	14
	SOP Concurrence Form .....	19

## **1 Scope and Application**

- 1.1 This document states the policies and procedures established in order to meet requirements of all certifications/accreditations currently held by the laboratory, including the most current NELAC standards.
- 1.2 This method is adapted from EPA Method 245.1, revision 3.0, May 1994; EPA Method 245.5, Mercury in Sediment, March 1983; SW-846 Method 7470B, Mercury in Liquid Waste, January 1998; and, Method 7471B, Mercury in Solid or Semisolid Waste, January 1998.
- 1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of cold vapor analysis. Each analyst must also be skilled in the interpretation of raw data, including quality control data.
- 1.4 This method measures total mercury (organic-inorganic) in drinking, surface, saline, and ground waters, domestic and industrial wastes, and mobility-procedure extracts. It also applies to soils, sediments, bottom deposits, and sludge-type materials.
- 1.5 In addition to inorganic forms of Mercury, organic materials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system.
- 1.6 All samples must be digested prior to analysis.
- 1.7 Method Detection Limits can be found in the metals department method detection limit book. The detection limits for a specific sample may differ from those listed due to the nature of interferences in a particular sample matrix.

## **2 Summary of Method**

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The samples/standards and reagents are pumped into the analyzer and mixed. Argon gas is introduced into the solution stream, which flows

to a mixing coil where the samples and reagents are thoroughly combined in the mixing coil. The gas and liquid stream is transferred to the gas/liquid separator where the gas and liquid phases are separated. The liquid waste is drained off and the gas is pumped to the absorption cell. The absorption cell is positioned in the light path of the mercury lamp. Absorbance (peak height) is measured as a function of mercury concentration and recorded as ppb of mercury.

### **3 Interferences**

- 3.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.
- 3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.
- 3.3 Sea waters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent (25 ml). Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.
- 3.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. All positive samples must be checked for false increases due to organics by analysis without the addition of stannous chloride.

### **4 Safety**

- 4.1 Operation of an atomic absorption spectrophotometer involves the use of argon gas and hazardous materials including corrosive fluids. Unskilled, improper, and careless use of equipment can create explosion hazards, fire hazards or other hazards, which can cause death, serious injury to personnel, or severe damage to equipment or property.
- 4.2 Caution shall be taken when handling all samples, standards, and QC material because of the acidic nature of the prepared samples as well as the possible mercury content in the samples.
- 4.3 Proper personal protective equipment must be used, including gloves, safety glasses, and lab coat.



- 4.4 The fume hood must be turned on during the analysis of mercury to vent the waste vapor.

## **5 Apparatus and Materials**

- 5.1 Leeman Labs PS200 Automated Mercury Analyzer - instrument with a double beam optical arrangement.
- 5.2 Blue sample pump tubing. Leeman Labs, cat. #309-00104-2.
- 5.3 Red reductant pump tubing. Leeman Labs, cat. #309-00033.
- 5.4 Yellow, blue, yellow pump tubing – used as drain tubing.
- 5.5 Mercury Hollow cathode lamp.
- 5.6 Finnpiptette with disposable tips. Baxter # P5055-51
- 5.7 Various Class A volumetric glassware
- 5.8 Various calibrated dispensers
- 5.9 40 ml VOA vials
- 5.10 25 ml graduated cylinder
- 5.11 Water Bath maintained at 95°C
- 5.12 8 ml polystyrene tubes, purchased from CPI.

## **6 Reagents**

- 6.1 Reagent water is water in which an interferant is not observed at the analyte of interest. For this purpose, ALSI uses a Filson Water Purification System, which provides analyte-free DI water greater than 16.0 megohm on demand. This water is used for preparation of all reagents, calibration standards, and as dilution water.
- 6.2 Liquid Argon - high purity grade, MG Industries or equivalent.
- 6.3 Stannous Chloride. Prepare by adding 100 g of stannous chloride crystal (VWR, cat. #JT3980-11 or equivalent) to a 1000 ml volumetric flask. Add 14.0 ml conc. H<sub>2</sub>SO<sub>4</sub>

**Method:** 03-Hg  
**Revision:** 9  
**Date:** November 5, 2002  
**Page:** 6 of 19

and stir until dissolved. Bring up to volume with reagent water.

- 6.4 Sulfuric Acid, conc. Baker Instra-analyzed grade or equivalent.
- 6.5 Sodium Chloride (NaCl.) Baker instra-analyzed grade. VWR, cat. #JT3625-15 or equivalent.
- 6.6 Hydroxylamine hydrochloride decolorizing reagent. To prepare, dissolve 120 g Hydroxylamine hydrochloride crystals (VWR, cat. #JT2196-1 or equivalent) and 120 g NaCl in reagent water in a 1000 ml volumetric flask. Bring up to volume using reagent water.

## **7 Instrument Calibration**

- 7.1 The instrument plots a standard calibration curve using five standards and a blank. The calibration standards, Blank, 0.2 µg/L, 1.0 µg/L, 2.0 µg/L, 4.0 µg/L, and 10.0 µg/L, are prepared. Starting with the blank and working toward the high standard, the standards are introduced into the mercury analyzer by the autosampler. Absorbance readings are recorded by the data system.
- 7.2 A calibration curve is drawn by plotting the absorbance readings on the y-axis and concentration readings on the x-axis. The software of the data system plots the curve. The calibration curve is used to calculate the concentration for the samples. The correlation coefficient must be 0.995 or greater.
- 7.3 A set of calibration standards is prepared along with every batch of mercury samples digested. It is these standards, which must be used to prepare the calibration curve for that batch of samples.
  - 7.3.1 This is especially important because Method 245.1 and Method 7470/7471 batches are prepared differently. Drinkingwater batch and groundwater/soil batch standards shall never be interchanged.
- 7.4 An Initial Calibration Verification (ICV) must be analyzed after every calibration to verify the instrument performance during analysis. The ICV is prepared from the second source standard. Analysis of the ICV immediately following calibration must verify that the instrument is within +/- 5% of calibration. Subsequent analysis of this standard is called the continuing calibration verification standard (CCV) and must be within ±10% of calibration. If outside of this range, determine and correct the problem. If necessary, recalibrate. Samples may not be analyzed until an acceptable ICV/CCV is analyzed.

- 7.5 Laboratory Control Sample (LCS). A same source standard as the calibration standards must be analyzed with each batch and after every calibration. It is prepared at 2.0 ppb from the same source as that of the calibration standards. The recovery must be within +/- 15% of the true value for the calibration. If outside of this range, determine and correct the problem and re-analyze. If necessary, recalibrate. Samples may not be analyzed until an acceptable LCS is analyzed.

## 8 Quality Control

- 8.1 All policies and procedures in the most current revision of the ALSI QA Plan shall be followed when performing this procedure.

### Quality Control Requirements

(Specific Project Requirements may override these requirements)

Parameter	Concentration	Frequency	Acceptance Criteria	Corrective Action
Calibration Blank (ICB/CCB)	NA	Prepared with each batch of samples. Analyzed after every ICV/CCV, at a minimum frequency of 10% and after calibration.	< MDL	Re-analyzed the blank. If still out of range, the problem must be solved by preparing a new blank, recalibration, or instrument maintenance. Samples following the last acceptable blank must be rerun.
Method Blank	NA	One digested with each batch of 20 or less samples. They are analyzed with that batch of samples.	<2.2 x MDL	Re-analyze the blank. The samples in the prep batch must be less than the reporting limit or greater than 10X the reagent blank value for the affected analyte. If not, the affected samples in that batch must be re-digested. If re-digestion is not possible, they will be reported with a qualifying comment.
Laboratory Control Sample (LCS) or Laboratory Fortified Blank (LFB)	Water: 2.0 ug/L Soil: 100 ug/kg	One digested with each batch of 20 or less samples. They are analyzed with that batch of samples.	85-115% R	Re-analyze the LCS. If the recovery is still outside the given range, the source of the problem must be identified and corrected before continuing analyses. If the

				problem cannot be identified, the samples in that batch must be re-digested. If re-digestion is not possible, report with a qualifying comment.
Matrix Spike (MS)*	Water: 5.0 ug/L Soil: 250 ug/kg	Frequency of 10% per matrix per batch	80-120% R	Re-analyze the MS. If still out of range analyze a post digestion spike (85-115%). If still out of range, a qualifying comment on the final lab report.
Matrix Spike Duplicate (MSD) or Duplicate (Dup)*	Water: 5.0 ug/L Soil: 250 ug/kg	Frequency of 10% (USACE samples - 100% frequency)	<20% RPD	Re-analyze the duplicate. If the sample is outside the range, redigest the sample. If still outside of acceptable limits, report with a comment on the lab report.
Initial/Continuing Calibration Verification Standard (ICV/CCV) (Second Source) IPC/QCS	4.0 ug/L	Immediately after calibration, after every ten samples, and after the last sample.	Immediately after calibration +/-5% R. Thereafter it must be within +/- 10% R.	Re-analyze the ICV. If still out of range, the problem must be identified and corrected before analyzing any samples. Any samples analyzed after the last acceptable ICV/CCV must be re-analyzed.

\* Samples selected for duplicate and matrix spike analysis shall be rotated among client samples so that various matrix problems may be noted and/or addressed. Poor performance in a duplicate or spike may indicate a problem with the sample composition and shall be reported to the client whose sample produced the poor recovery.

8.2 Sample concentrations must fall within the linear dynamic range to be reported. Any result greater than the calculated linear dynamic range must be diluted to fall within the calibration range. For drinking water, any sample with results greater than the highest standard will be diluted and reanalyzed until the concentrations are within the calibration range.

8.2.1 Linear Dynamic Range (LDR) - The upper limit of linearity must be determined. Analyze succeeding higher concentrations of the analyte until the percent recovery falls under 90%. The last concentration maintaining greater or equal to 90% recovery is considered the upper limit of linearity. Samples containing analytes greater than 90% of the upper limit of linearity must be diluted and reanalyzed for those analytes. The LDRs are verified annually or any time a change in operating conditions occurs that may change the LDR.

8.3 Method detection limits are determined annually using the procedure outlined in the ALSI Quality Assurance Plan. NOTE: If USACE samples are to be analyzed, an MDL check sample will be used to verify the MDL. The MDL check sample is at a concentration equal to 2 x the MDL. If a positive response is detected from the MDL check sample, another MDL study is not needed for that calendar year.

8.3.1 Practical Quantitation Limits (PQL) or reporting limits are determined by multiplying the MDL by 3-5 times, and adding an appropriate safety factor.

8.4 If the matrix spike fails criteria, a post digestion spike is performed. If the recovery of the post digestion spike is within 85-115%, the results will be reported. If outside of this range, comment on the final report.

## **9 Sample Collection, Preservation and Handling**

### **9.1 Sample Collection:**

9.1.1 Samples can be collected in plastic or glass bottles.

9.1.2 Aqueous samples requiring dissolved metals shall be filtered immediately on site before adding preservation for dissolved metals.

### **9.2 Sample Preservation:**

9.2.1 Preserve aqueous samples using HNO<sub>3</sub> to a pH <2. Sample preservation shall be performed immediately upon sample collection. If this is not possible, then samples would be preserved as soon as possible when received at the laboratory.

### **9.3 Sample Handling:**

9.3.1 All samples must be analyzed within 28 days of collection. All samples not analyzed within this time frame must be discarded and resampled for analysis.

9.3.2 All samples require digestion. Refer to the Sample Preparation SOP for procedures.

## **10 Procedure**

10.1 Turn on the fume hood and computer data system. Make sure that the Argon gas is at 50 psi.

- 10.2 If the computer program fails to load and the C prompt appears, type PS to load the software.
- 10.3 Type P for protocol and G to open a folder. Type in either 'waters' or 'soils' depending on the matrix being analyzed.
- 10.3.1 Name the folder by typing the date and 'W' for water or 'S' for soil. Press enter.
- 10.3.2 Press F1 to get back to the main menu.
- 10.4 Press F2 to open the macro. Type COLDSTRT and press enter. This will initiate heating of the lamp and will condition the pump tubing.
- 10.5 Change the pump tubing if there is evidence of wear such as flattening with red/red/red tubing. Remove and replace if needed. Securely clamp down the tubing.
- 10.5.1 Clean the drying cell with reagent water and dry. Fill the drying cell with Magnesium Perchlorate.
- 10.5.2 Fill the rinse bath with 10% HCl and place both probes into the rinse bath. Fill the Stannous Chloride bottle.
- 10.6 After approximately 2.5 hours, a flag will appear saying 'operation complete'. Place the Stannous Chloride probe into the stannous chloride bottle which is placed on a magnetic stirrer.
- 10.6.1 Press F1 to bring up the main menu. Press 'U' for utility and 'G' for Diagnostics. Use the arrow keys to move down to test optics. Press Enter. (The values need to be within 5% of each other.)
- 10.6.2 Press F1, for main menu. Press F2, for macro. Type APERTEST and Enter (to test aperture). The aperture shall be +/- 50 (~0). If not, adjust by slightly turning the lower screw with an allen wrench found inside the instrument.
- 10.7 Go back to the main menu. Add 1.5 mL of NaCl hydroxylamine hydrochloride to each vial and shake. Place calibration standards and QC's into appropriate positions in the tray.
- 10.7.1 Press F2 (macro) and type Cal 245/enter. The instrument will begin to automatically calibrate for approximately one hour. Once a flag appears saying Idle, hit F10 (stop) and F1 (main menu).
- 10.8 Type 'C' for calibration and 'L' for line calibration (The R factors need to be at least

- 0.995). Press 'A' for accept. Print screen by pressing F3. Go to the main menu.
- 10.9 Analyze check standard 1 (blank) by pressing F7 and then number 1. The blank shall be within +/- (MDL).
- 10.9.1 Check standard 2 (ICV) by pressing F7 and the #2. The initial QC shall be within 5% of the true value. The continuing CCV has to be within 10%.
- 10.10 Load the autosampler trays with the samples, while recording the sample ID in the logbook.
- 10.10.1 Go to the main menu and press 'A' for autosampler, 'R' for rack entry and make sure the instrument is programmed to check QC (4.0) every 10 samples (by typing C31 after every 10th sample) with a 10% acceptability.
- 10.10.2 Go back to the main menu and press 'S' for setup under Autosampler. Go under Station Rack 1 and type the first sample being analyzed and the last sample being analyzed.
- 10.11 Go to the main menu, hit F2, type autosam1. This will begin the analysis.
- 10.12 After analysis, any sample that has a result above the reporting limit (0.0005 mg/L for TWHG or 0.001 mg/L for SPLP's and SHG or 0.006 mg/L for TCLP's or 0.0002 mg/L for Hglow) must be rerun without stannous chloride to determine if an organic interference is present.
- 10.12.1 If the stannous chloride result is greater than the reporting limit, subtract the non-stannous chloride result to get the final mercury concentration.

## 11 Calculations

- 11.1 Samples results are documented directly from the readout of the instrument in ppb (from the calibration curve).
- 11.2 The results are converted to ppm and input into the LIM system.
- 11.3 Samples requiring dilution at the time of analysis to bring the result into calibration range are multiplied by the dilution factor used before inputting into the LIM system using the following equation:

$$A = \frac{Z(B)}{C}$$

where:

A= Concentration of mercury in the sample  
B= Final volume of the dilution (ml)  
Z= Concentration of mercury in the dilution  
C= Volume of sample aliquot used in the dilution

## 12 Reporting Results

- 12.1 Report water results in the computer as mg/L and soil results as mg/kg using three significant figures in the AMS LIMS. In the Horizon LIMS, do not round results. The LIMS will round off to 3 significant figures after all internal calculations have been completed.
- 12.2 All data produced will be reviewed and initialed by the supervisor or his designee to insure that data reported meets the required quality assurance and regulatory criteria.
- 12.3 Report results in the LIM system: All results are reported to three significant figures but limited to the number of decimal places in the reporting limit for the individual compound or analyte. For rounding off numbers to the appropriate level of precision, the laboratory will follow the following rules
  - 12.3.1 If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 1.443 is rounded off to 1.44.
  - 12.3.2 If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 1.446 is rounded off to 1.45.
  - 12.3.3 If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 1.435 is rounded off to 1.44, while 1.425 is rounded off to 1.42.



**Method:** 03-Hg  
**Revision:** 9  
**Date:** November 5, 2002  
**Page:** 13 of 19

- 12.4 When entering data into the Horizon LIMS, do not round off results. The LIMS will automatically round results off to 3 significant figures after all internal calculations are completed.
- 12.5 Any sample with a result less than the reporting limit is reported as ND (non-detectable) with the appropriate detection limit in the AMS LIMS. Report the actual result in the Horizon LIMS.

### **13 Waste Disposal**

Refer to ALSI SOP 19-Waste Disposal.

### **14 Pollution Prevention**

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. Management shall consider pollution prevention a high priority. Extended storage of unused chemicals increases the risk of accidents. The laboratory shall consider smaller quantity purchases which will result in fewer unused chemicals being stored and reduce the potential for exposure by employees. ALSI tracks chemicals when received by recording their receipt in a traceable logbook. Each chemical is then labeled according to required procedures and stored in assigned locations for proper laboratory use.

Method: 03-Hg  
Revision: 9  
Date: November 5, 2002  
Page: 14 of 19

## APPENDIX A

Protocol: waters			
Rev: 2.008	Time: 11:46:55	14 Aug 1998	
Folder: 081398w	Seq: 79	Print: On	
User:	Batch:	Id:	Cup: Gas: LPM
State: None	Exit: Off Autosampler: On		
F1: Main Menu			
PROTOCOL	Instrument	DATA OUTPUT	
Get	Operation	Open folder	
set Values		Specify report	
On/off, times, gains		folder Maintenance	
Limits			
Maintenance	Help		
	CALIBRATION	UTILITY	
	Standards	user Name	
	check standards	diagnostics	
	spike Quantities	edit Startup	
AUTOSAMPLER	Line calibration	Macros	
Setup	accepted Values	Exit	
Rack entry	Reset		
rack Maintenance			

Protocol: waters			
Rev: 2.008	Time: 11:52:52	14 Aug 1998	
Folder: 081398w	Seq: 79	Print: On	
User:	Batch:	Id:	Cup: Gas: LPM
State: None	Exit: Off Autosampler: On		
UTILITY: Diagnostics	Motor	Pos. Sen	Slp
Zero detector	Tip X	CT rev 0.000 Pcode rev 4.000 Memory 82112 Disk 147898176	
Aper test	Tip Y		
Lamp high	Tip Z		
Lamp low	Gas		
Acquire 5 U ref.			
Test optics			
Tip home			
Out to port			
In from port			
Run pcode from			
solenoids 15			
halt 0 0 0			
Enter to run test, Ins to select motors, Sensors on			

sure to you is not intended to

Method: 03-Hg  
Revision: 9  
Date: November 5, 2002  
Page: 15 of 19

## APPENDIX A

Protocol: waters					
Rev: 2.008		Time: 12:25:01		14 Aug 1998	
Folder: 081398w		Seq: 79		Print: On	
User:	Batch:	Id:	Cup:	Gas:	LPM
State: None	Xmit: Off Autosampler: On				

AUTOSAMPLER: Setup					
station rack	from cup	to cup	standards	station 1	station 2
1				1 16 31 46	1 16 31 46
2			S1 C1	2 17 32 47	2 17 32 47
			S2 C2	3 18 33 48	3 18 33 48
			S3 C3	4 19 34 49	4 19 34 49
Update cups: UI = S1	US = S2			5 20 35 50	5 20 35 50
				6 21 36 51	6 21 36 51
frequencies: UI	US			7 22 37 52	7 22 37 52
				8 23 38 53	8 23 38 53
check: C1 C2 C3 C4 C5 C6 C7				9 24 39 54	9 24 39 54
Halt: N 10 10 0 0 0 0 0				10 25 40 55	10 25 40 55
Name				11 26 41 56	11 26 41 56
Rinse time (0-999 seconds)	50			12 27 42 57	12 27 42 57
Cups per rack	60			13 28 43 58	13 28 43 58
		Extra	C7	14 29 44 59	14 29 44 59
Tip to cup (0=rinse)				15 30 45 60	15 30 45 60

Protocol: waters					
Rev: 2.008		Time: 12:29:36		14 Aug 1998	
Folder: 081398w		Seq: 79		Print: On	
User:	Batch:	Id:	Cup:	Gas:	LPM
State: None	Xmit: Off Autosampler: On				

AUTOSAMPLER: Rack entry Rack 1 Range 1 -60 Clear seq Undo eXit					
cup Id	Extended id	Weight	Volume	Macro	check Help
1 1		1.0000	1.0000		
2 2		1.0000	1.0000		
3 3		1.0000	1.0000		
4 4		1.0000	1.0000		
5 5		1.0000	1.0000		
6 6		1.0000	1.0000		
7 7		1.0000	1.0000		
8 8		1.0000	1.0000		
9 9		1.0000	1.0000		
10 10		1.0000	1.0000	C31	
11 11		1.0000	1.0000		
12 12		1.0000	1.0000		
13 13		1.0000	1.0000		
14 14		1.0000	1.0000		
15 15		1.0000	1.0000		

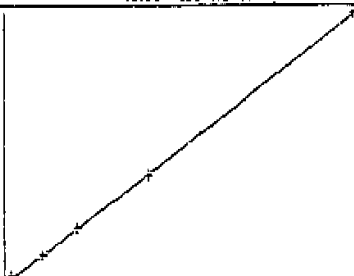
PgDn

Column entry, Ins to switch

Method: 03-Hg  
Revision: 9  
Date: November 5, 2002  
Page: 16 of 19

## APPENDIX A

Protocol: waters				
Rev: 2.000		Time: 12:33:06 14 Aug 1998		
Folder: 081398w		Seq: 79		Print: On
User:	Batch:	ID:	Cup:	Gas: LPM
State: None		Xmit: Off Autosampler: On		
CALIBRATION: Line Calibration				
Line: Hg	Conc.	Calc.	Dev.	Accepted
S1	.000	-.055	-.055	Quadratic
S2	.200	.157	-.043	StdLinear
S3	1.00	1.02	.021	C
S4	2.00	2.05	.046	Accept
S5	4.00	4.07	.072	n
S6	10.0	9.96	-.041	StdAdd
A	.0000000	r	.999901	
B	1.75458e-5	C	-5.54039e-2	



	Mean	zRSD	Relative Absorbance	
S1	24	1186.21	-11737	-181 230
S2	12124	2.6	11919	12407 11966
S3	61325	0.86	61767	61464 60744
S4	119756	0.76	120737	119588 118945
S5	235253	0.45	236463	234656 234648
S6	570782	0.34	573035	569490 569015

Protocol: waters									
Rev: 2.000		Time: 12:34:30 14 Aug 1998							
Folder: 081398w		Seq: 79		Print: On					
User:		Batch:		Id:		Cup:		Gas: LPM	
State: None		Xmit: Off Autosampler: On							
CALIBRATION: Standards									
Line	Units	UI	US	S1	S2	S3	S4	S5	S6
Hg		.00000	4.0000	.00000	.20000	1.0000	2.0000	4.0000	10.000
Column entry, Ins to switch									

Method: 03-Hg  
Revision: 9  
Date: November 5, 2002  
Page: 17 of 19

## APPENDIX A

Protocol: waters		Rev: 2.008	Time: 12:34:56	14 Aug 1998	
Folder: 081398w	Seq: 79	Print: On			
User:	Batch:	Id:	Cup:	Gas:	LPM
State: None			Xmit: Off Autosampler: On		
CALIBRATION: Check Standards					
C1=0 ±	C2 ± %	C3 ± %	C4 ± %	C5 ± %	C6 ± %
C7 ± %					
Hg	.07040	4.0000	5	4.0000	10
Column entry, Ins to switch					

Protocol: waters		Rev: 3.008	Time: 12:35:42	14 Aug 1998	
Folder: 081398w	Seq: 79	Print: On			
User:	Batch:	Id:	Cup:	Gas:	LPM
State: None			Xmit: Off Autosampler: On		
PROTOCOL: Set Values					
Number of integrations	2	(1 - 5)			
uptake time	45	(1 - 99 seconds)			
Weight	N				
Dilution	N				

sure to you is not intended to

Method: 03-Hg  
Revision: 9  
Date: November 5, 2002  
Page: 18 of 19

## APPENDIX A

Protocol: SYSTEST	
Rev: 2.008	Time: 12:36:55 14 Aug 1998
Folder: SYSTEST	Seq: 5
User:	Batch:
State: None	Id:
	Cup:
	Gas: LPM
	Xmit: Off Autosampler: On
Instrument: Operation	
Gas	0.30 LPM (.13 - .50)
pump Rate	5 mL/min (2 - 15) Off
Tip to rinse	

Method: 03-Hg  
Revision: 9  
Date: November 5, 2002  
Page: 19 of 19

**SOP Concurrence Form**  
**for the Distribution and Revision of Standard Operating Procedures**

I have read, understood, and concurred with the Standard Operating Procedure (SOP) described  
above and will perform this procedure as it is written in the SOP.

Print Name	Signature	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

**Method:** 19-Subsampling  
**Revision:** 0  
**Date:** July 26, 1999  
**Page:** 1 of 7

**Document Title:** Subsampling Procedure for Nonvolatile Analysis or Preparation

**Document Control Number:** \_\_\_\_\_

**Organization Name:** ANALYTICAL LABORATORY SERVICES, INC. (ALSI)

**Address:** 34 Dogwood Lane  
Middletown, PA 17057

**Phone:** (717)944-5541

**Approved by:** \_\_\_\_\_  
Susan Magness,  
Quality Assurance Manager

\_\_\_\_\_  
Ray Martrano,  
Laboratory Manager

## TABLE OF CONTENTS



1	Scope and Application .....	2
2	Summary of Method .....	3
3	Interferences .....	3
4	Safety .....	3
5	Apparatus and Materials .....	3
6	Reagents .....	3
7	Glassware Cleaning.....	4
8	Quality Control .....	4
9	Sample Collection, Preservation and Handling .....	4
10	Procedure .....	4
11	Calculations.....	6
12	Reporting Results .....	6
	SOP Concurrence Form .....	6

## **1 Scope and Application**

- 1.1 This standard operating procedure addresses the removal of solid, soil and water samples from sampling containers to ensure representativeness and homogeneity in the aliquot submitted for testing.

- 1.2 Subsamples removal for volatile organic analysis are addressed in the individual analytical SOP's and are not discussed here.

## **2 Summary of Method**

- 2.1 Aliquot removal procedures are described for water, soil and solids.

## **3 Interferences**

- 3.1 The appropriate sampling, preparation or analytical SOP's address the appropriate materials of construction for sampling, measuring or transferring samples.
- 3.2 In general soils should be removed using stainless steel spatulas.
- 3.3 Soil samples should be placed in polypropylene weigh boats for mixing.
- 3.4 Subsampling of liquids for organic analysis should incorporate glass apparatus (i.e. pipets, graduated cylinder) only.
- 3.5 Soils samples are NOT to enter the organic extraction laboratory.

## **4 Safety**

- 4.1 Vinyl or latex gloves must be worn when handling sample containers. All samples should be handled as a potential health hazard.
- 4.2 Samples known or found to contain irritating volatile constituents should be handled in a fume hood.

## **5 Apparatus and Materials**

- 5.1 Weighboats - polypropylene, appropriate sizes.
- 5.2 Spatula - stainless steel.
- 5.3 Pipets - polypropylene transfer or glass Pasteur.
- 5.4 Gloves - latex or vinyl.

## **6 Reagents**

- 6.1 Not applicable.

**7 Glassware Cleaning**

- 7.1 Spatulas are cleaned as described in the glassware washing SOP and “general use” glassware. All other items are single use and disposable.

**8 Quality Control**

- 8.1 Not applicable.

**9 Sample Collection, Preservation and Handling**

- 9.1 Consult the individual sampling SOP.

**10 Procedure**

- 10.1 Aqueous or free flowing samples.

10.1.1 Allow the sample to reach room temperature before aliquoting.

10.1.2 Check that the appropriate preservative has been added by checking the container label. Consult the specific analytical SOP if preservative as presented on the labeling or the pH contradicts that required by the procedure.

10.1.3 Invert the container five times to allow for mixing.

10.1.4 If immiscible layers form that can not be aliquoted proportionally, contact the appropriate customer service representative. The client should decide if each layer is to be analyzed individually.

10.1.5 Transfer the sample into an appropriate container within 10 seconds of inverting.

10.1.6 Return the sample container to the appropriate storage area as soon as possible.

10.1.7 Consult the specific analytical procedure for guidance on the appropriate materials of construction for transferring and holding sample.

10.1.8 Make any necessary comments regarding the sample and the aliquot in the appropriate prep notebook. Be sure to record the actual weight/volume of the final aliquot used for analysis.

- 10.2 Soil and solid samples.

10.2.1 Industrial wastes.

- 10.2.1.1 Industrial wastes (non-soils) may require crushing cutting or shredding before use. Employ whatever means possible to reduce these types of samples to a particle size no greater than 3/8 inch unless some other particle size is defined in the individual analytical SOP. Comment in the analytical or extraction logbook if a method defined particular size can not be achieved.
- 10.2.1.2 Equipment rinsate blanks must be assessed if any mechanical device (i.e., Jaw crusher) is used to crush a sample. These blanks must be analyzed for the same parameters as the sample.

10.2.2 Soil samples.

- 10.2.2.1 Allow the sample to reach room temperature before aliquoting.
- 10.2.2.2 Refer to Section 10.1.4 if immiscible layers are observed.
- 10.2.2.3 Visually inspect the sample in the container. If any stratification of sample is observed by color, particle size or apparent texture, every effort should be made to obtain representative proportions of the sample.
- 10.2.2.4 If the aliquot needed for the specific procedure is 10 grams or less, remove a minimum of 50 grams of the sample from the container using a stainless steel spatula and place in a polypropylene weighboat. If the aliquot needed for the specific procedure is greater than 10 grams, remove a minimum of 100 grams using a stainless steel spatula and place in polypropylene weighboat.
- 10.2.2.5 Mix the sample with the spatula. Break any clumped soil. Mix the soil with the spatula to homogenize any particles that may seem unique in color, particle size or apparent texture.
- 10.2.2.6 Remove an homogenized representative portion of the subsample in the weighboat into the appropriate container as described in the analytical SOP.
- 10.2.2.7 Transfer the remaining subsample from the weighboat back into the sample container.

**Method:** 19-Subsampling  
**Revision:** 0  
**Date:** July 26, 1999  
**Page:** 6 of 7

- 10.2.2.8 Subsample placed in prerinsed glassware is NOT to be returned to the sample container for any reason.
- 10.2.2.9 Cap the sample container immediately and return to storage as soon as possible.
- 10.2.2.10 Make any necessary comment regarding the sample and the aliquot in the appropriate prep notebook. Be sure to record the actual weight/volume of the final aliquot used for analysis.

## **11 Calculations**

11.1 Not applicable.

## **12 Reporting Results**

12.1 Not applicable.

### **SOP Concurrence Form for the Distribution and Revision of Standard Operating Procedures**

I have read, understood, and concurred with the Standard Operating Procedure (SOP) described above and will perform this procedure as it is written in the SOP.

Print Name

Signature

Date

[illegible]