United States
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Agency

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Washington, DC 20460

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EPA

# Innovative Technology Verification Report

# Field Measurement Technology for Mercury in Soil and Sediment

# MTI Inc.'s PDV 6000 Anodic Stripping Voltammetry

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# MTI Inc.'s PDV 6000 Anodic Stripping Voltammetry

Prepared by

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Idaho Falls, ID

Contract No. 68-C-00-179

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Office of Research and Development
U.S. Environmental Protection Agency

# Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here under contract to Science Applications International Corporation. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, DC 20460

## MEASUREMENT AND MONITORING TECHNOLOGY PROGRAM VERIFICATION STATEMENT

TECHNOLOGY TYPE: **Field Measurement Device**

APPLICATION: **Measurement for Mercury**

TECHNOLOGY NAME: **MTI Inc.'s Portable Digital Voltammeter (PDV) 6000**

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### VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) and Measurement and Monitoring Technology (MMT) Programs to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of these programs is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. These programs assist and inform those involved in design, distribution, permitting, and purchase of environmental technologies. This document summarizes results of a demonstration of the Portable Digital Voltammeter (PDV) 6000 developed by Monitoring Technologies International Pty. Ltd. (MTI).

### PROGRAM OPERATION

Under the SITE and MMT Programs, with the full participation of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing demonstration data, and preparing reports. The technologies are evaluated under rigorous quality assurance (QA) protocols to produce well-documented data of known quality. The EPA National Exposure Research Laboratory, which demonstrates field sampling, monitoring, and measurement technologies, selected Science Applications International Corporation as the verification organization to assist in field testing five field measurement devices for mercury in soil and sediment. This demonstration was funded by the SITE Program.

### DEMONSTRATION DESCRIPTION

In May 2003, the EPA conducted a field demonstration of the PDV 6000 and four other field measurement devices for mercury in soil and sediment. Due to inaccurate results on standards (later determined to be an oil contaminant on the disposable beakers that was coating the electrodes), MTI decided to discontinue the field measurements. The demonstration of their PDV 6000 instrument was rescheduled and was conducted in Las Vegas, NV, in June 2003. This verification statement focuses on the PDV 6000; a similar statement has been prepared for each of the other four devices. The performance of the PDV 6000 was compared to that of an off-site laboratory using the reference method,

"Test Methods for Evaluating Solid Waste" (SW-846) Method 7471B (modified). To verify a wide range of performance attributes, the demonstration had both primary and secondary objectives. The primary objectives were:

(1) Determining the instrument sensitivity with respect to the Method Detection Limit (MDL) and Practical Quantitation Limit (PQL);
(2) Determining the analytical accuracy associated with the field measurement technologies;
(3) Evaluating the precision of the field measurement technologies;
(4) Measuring the amount of time required for mobilization and setup, initial calibration, daily calibration, sample analysis, and demobilization; and
(5) Estimating the costs associated with mercury measurements for the following four categories: capital, labor, supplies, and investigation-derived waste (IDW).

Secondary objectives for the demonstration included:

(1) Documenting the ease of use, as well as skills and training required to properly operate the device;
(2) Documenting potential health and safety concerns associated with operating the device;
(3) Documenting the portability of the device;
(4) Evaluating the device durability based on its materials of construction and engineering design; and
(5) Documenting the availability of the device and associated spare parts.

The PDV 6000 analyzed 52 field soil samples, 33 field sediment samples, 35 spiked field samples, and 77 performance evaluation (PE) standard reference material (SRM) samples in the demonstration. The field samples were collected in four areas contaminated with mercury, the spiked samples were from these same locations, and the PE samples were obtained from a commercial provider.

Collectively, the field and PE samples provided the different matrix types and the different concentrations of mercury needed to perform a comprehensive evaluation of the PDV 6000. A complete description of the demonstration and a summary of the results are available in the Innovative Technology Verification Report: "Field Measurement Technology for Mercury in Soil and Sediment — MTI Inc.'s PDV 6000 Anodic Stripping Voltammetry" (EPA/600/R-04/028).

**TECHNOLOGY DESCRIPTION**

The principle of analysis used by the MTI PDV 6000 is Anodic Stripping Voltammetry (ASV). ASV is a simple procedure in which a reducing potential is applied to a "working electrode." When the potential of this working electrode exceeds the ionization potential of the particular metal ion solution in solution, it is reduced to the metal. The metal plates onto the working electrode surface as follows:

$$\mathbf{M^{n+} + ne^{-} \rightarrow M}$$

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. This "deposition" or "accumulation" step concentrates the metal. After sufficient metal has been plated onto the working electrode, the metal is stripped (oxidized) off the electrode by increasing the potential to that electrode at a constant rate. For a given electrolyte solution and electrode, each metal has a specific potential in which the following oxidation reaction will occur:

$$\mathbf{M \rightarrow M^{n+} + ne^{-}}$$

The electrons released by this process form a current that is measured and plotted as a function of the 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 or solution under the same conditions.

During the demonstration, each sample was digested per MTI's standard operating procedure (SOP). Sample preparation consisted of weighing out (in order) 2 grams of sample material, placing that material in a 70-mL digestion

bottle and then pipetting into that bottle 4.0 mL of $HNO_3$, 4.0 mL of $H_2O_2$, 12 mL of deionized (DI) water, and 20 mL of electrolyte solution. The prepared samples were then analyzed with the PDV 6000.

**ACTION LIMITS**

Action limits and concentrations of interest vary and are project specific. There are, however, action limits which can be considered as potential reference points. The EPA Region IX Preliminary Remedial Goals (PRGs) for mercury are 23 mg/kg in residential soil and 310 mg/kg in industrial soil.

**VERIFICATION OF PERFORMANCE**

To ensure data usability, data quality indicators for accuracy, precision, representativeness, completeness, comparability, and sensitivity were assessed for the reference method based on project-specific QA objectives. Key demonstration findings are summarized below for the primary objectives.

***Sensitivity*:** The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Both will vary dependent upon whether the matrix is a soil, waste, or aqueous solution. Only soils/sediments were tested during this demonstration, and therefore, MDL calculations and PQL determinations for this evaluation are limited to those matrices. By definition, values measured below the PQL should not be considered accurate or precise and those below the MDL are not distinguishable from background noise.

Method Detection Limit - The evaluation of an MDL requires seven different measurements of a low concentration standard or sample following the procedures established in the 40 Code of Federal Regulations (CFR) Part 136. The MDL is between 1.67 and 3.67 mg/kg. The equivalent MDL for the referee laboratory is 0.0026 mg/kg. Examples from analyzed samples, however, suggested that the MTI MDL may be closer to 0.811 mg/kg or lower. Values detected at these lower levels would likely be highly inaccurate and should only be considered as a “positive hit” without any implied accuracy or precision.

Practical Quantitation Limit - The low standard calculations suggest that a PQL for the MTI field instrument is 4-8 mg/kg. The percent difference (%D) for the average MTI result for a sample concentration of 4.75 mg/kg, tested as part of the demonstration, is 46%. The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg with a %D <10%.

***Accuracy*:** The results from the PDV 6000 were compared to the 95% prediction interval for the SRM materials and to the referee laboratory results (Method 7471B). MTI data were within the SRM 95% prediction intervals 53% of the time. The comparison between the MTI field data and the referee laboratory results suggest that the two data sets are not different but the similarity for individual samples is often the result of high variability associated with the MTI reported values. The number of MTI average values greater than 50% different from the referee laboratory results or SRM reference values was only 6 for 21 different sample lots with only 2 of those 6 greater than 100% different. These 6 (of the 21) sample lots had results greater than laboratory results, indicating a positive bias. MTI results therefore appear to provide a rough estimate of mercury concentration for field determination and may be affected by interferences not identified by this demonstration. It should be concluded, however, that the MTI PDV 6000 did not compare well to laboratory Method 7471B in terms of obtaining accurate analyses of mercury in soil.

***Precision*:** The precision of the MTI field instrument is not as good as the referee laboratory precision. The overall average RSD for MTI is 35.1% which is above the 25% RSD objective set for the laboratory. The overall laboratory average RSD is 22.3%.

***Measurement Time*:** From the time of sample receipt, MTI required 38 hours to prepare a draft data package containing mercury results for 197 samples. Two persons performed all setup, calibration checks, sample preparation and analysis, and equipment demobilization. Each individual analysis, on average, took 7.5 minutes (from the time the sample was digested until results were displayed), but the total time per analysis averaged approximately 11.6 minutes when all sample preparation, sample analysis, and data package preparation were included in the calculation.

***Measurement Costs*:** The cost per analysis, based on measurement of 197 samples, when incurring a minimum 1-month rental fee for the PDV 6000, was determined to be $43.74 per sample. Excluding the instrument rental cost, the cost for analyzing the 197 samples was determined to be $32.57 per sample. Based on the 3-day field demonstration, the total cost for equipment rental and necessary supplies was estimated at $8,600. The cost breakout by category is: capital costs, 25.5%; supplies, 32.5%; support equipment, 3.2%; labor, 17.4%; and IDW, 21.4%.

Key demonstration findings are summarized below for the secondary objectives.

***Ease of Use*:** Based upon observations made during the demonstration, the PDV 6000 is relatively easy to operate, requiring one field technician with a basic knowledge of chemistry acquired on the job or in a university, basic computer skills, and training on the PDV 6000. A 1-day training course on instrument operation is offered at additional cost; this training should be considered for most potential users having no previous laboratory experience.

***Potential Health and Safety Concerns*:** No significant health and safety concerns were noted during the demonstration; however, during the demonstration, fumes following the addition of acidic solution, during digestion of certain samples, was observed. The digestion procedure involves the use of potentially reactive or aggressive reagents and ultimately there is a potential for vigorous reactions to occur.

***Portability***: The main components of the PDV 6000 consist of a handheld control unit and a cell assembly. The control unit, cell assembly, and other accessories are easily portable due to their size, weight, and method by which they are packed and transported. The handheld control unit, cell assembly, and other pertinent accessories are transported in a hard pelican style case (approximately 36 cm by 25 cm by 15 cm). The portable control unit weighs approximately 700 grams and measures 10 cm by 18 cm by 4 cm. The unit was easy to setup, and it can be taken anywhere by foot. It operates on 110 or 220 volt AC current and also on a rechargeable NiMH battery power supply.

***Durability:*** The PDV 6000 was well designed and constructed of durable plastic. According to MTI, a conformal coating on the instrument's electronics allows for unlimited humidity range; however, the laptop used to run the voltammetric analysis system (VAS) software should be kept dry. The cell assembly is also constructed of durable plastic, and the cell assembly stand is constructed of metal.

***Availability of the Device:*** Per MTI, a stock of instrumentation will be available in the U.S. through the new MTI U.S. operations. Instruments will be available for purchase, rent, or lease and can be delivered within one week of order placement. Spare parts and consumable supplies can be added to the original PDV 6000 order. Supplies not typically provided by MTI (pipetters and a scale) are readily available from laboratory supply firms.

**PERFORMANCE SUMMARY**

In summary, during the demonstration, the PDV 6000 exhibited the following desirable characteristics of a field mercury measurement device: (1) field acceptable accuracy, (2) good precision, (3) good sensitivity compared to the PRGs, (4) high sample throughput, (5) measurement costs comparable to laboratory analytical costs, (6) exceptional portability, and (7) relative ease of use. During the demonstration the PDV 6000 was found to have the following limitations: (1) sample digestion requiring nitric acid and hydrogen peroxide and (2) generation of a secondary waste stream from sample digestion.

**NOTICE**: EPA verifications are based on an evaluation of technology performance under specific, predetermined criteria and appropriate quality assurance procedures. The EPA makes no expressed or implied warranties as to the performance of the technology and does not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements.

# 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 (RCRA) 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 (MMT) 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 MMT Program is managed by the Office of Research and Development's Environmental Sciences Division in Las Vegas, NV.

Gary Foley, Ph. D.
Director
National Exposure Research Laboratory
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# Abstract

MTI's PDV 6000 was demonstrated under the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation Program in June 2003 in Las Vegas, NV. The purpose of the demonstration was to collect reliable performance and cost data for the PDV 6000. Four other field measurement devices for mercury in soil and sediment were evaluated in May 2003 at the Oak Ridge National Laboratory in Oak Ridge, TN. The key objectives of the demonstration were: 1) determine sensitivity of each instrument with respect to a vendor-generated method detection limit (MDL) and practical quantitation limit (PQL); 2) determine analytical accuracy associated with vendor field measurements; 3) evaluate the precision of vendor field measurements using field samples and standard reference materials (SRMs); 4) measure time required to perform mercury measurements; and 5) estimate costs associated with mercury measurements for capital, labor, supplies, and investigation-derived wastes.

The demonstration involved analysis of SRMs, field samples collected from four sites, and spiked field samples for mercury. The performance results for a given field measurement device were compared to those of an off-site laboratory using reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 7471B.

The sensitivity, accuracy, and precision measurements were successfully completed. Results of these measurement evaluations suggest that the MTI field instrument does not perform as well as the laboratory analytical method but does provide a rough estimate of mercury concentrations in soils and sediments often suitable for field analysis. During the demonstration, MTI required 38 hours for analysis of 197 samples. The cost per analysis, based on measurement of 197 samples, when incurring a minimum 1-month rental fee for the PDV 6000, was determined to be $43.74 per sample. Excluding the instrument rental cost, the cost for analyzing the 197 samples was determined to be $32.57 per sample. Based on the 3-day field demonstration, the total cost for equipment rental and necessary supplies was estimated at $8,600.

The PDV 6000 exhibited good ease of use and durability, as well as no major health and safety concerns. However, there is the potential for gas-producing reactions to occur during the digestion procedure used to prepare the samples. MTI sells kits, containing extraction reagents and disposable supplies, for the analyses of samples. When conducting a large number of analyses, purchase of bulk reagents and disposable supplies should be considered to reduce costs.

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# Abbreviations, Acronyms, and Symbols

| | |
|---|---|
| % | Percent |
| %D | Percent difference |
| °C | Degrees Celsius |
| µg/kg | Microgram per kilogram |
| g/L | Gram per liter |
| AC | Alternating current |
| AAS | Atomic absorption spectroscopy |
| ALSI | Analytical Laboratory Services, Inc. |
| ASV | Anodic Stripping Voltammetry |
| bgs | Below ground surface |
| cm | Centimeter |
| CFR | Code of Federal Regulations |
| CI | Confidence Interval |
| COC | Chain of Custody |
| DC | Direct current |
| DI | Deionized (water) |
| DOE | Department of Energy |
| EPA | United States Environmental Protection Agency |
| g | Gram |
| H&S | Health and Safety |
| Hg | Mercury |
| $HgCl_2$ | Mercury (II) chloride |
| IDL | Instrument detection limit |
| IDW | Investigation derived waste |
| ITVR | Innovative Technology Verification Report |
| kg | Kilogram |
| L | Liter |
| LCS | Laboratory control sample |
| LEFPC | Lower East Fork Poplar Creek |
| m | Meter |
| MDL | Method detection limit |
| mg | Milligram |
| mg/kg | Milligram per kilogram |
| mL | Milliliter |
| mm | Millimeter |
| MS/MSD | Matrix spike/matrix spike duplicate |
| MMT | Monitoring and Measurement Technology |
| MTI | Monitoring Technologies International |
| NERL | National Exposure Research Laboratory |

## Abbreviations, Acronyms, and Symbols (Continued)

| | |
|---|---|
| NiMH | Nickel metal halide |
| nm | Nanometer |
| ORD | Office of Research and Development |
| ORR | Oak Ridge Reservation |
| ORNL | Oak Ridge National Laboratory |
| OSWER | Office of Solid Waste and Emergency Response |
| PDV | Portable Digital Voltammeter |
| PPE | Personal protective equipment |
| ppb | Parts per billion |
| ppm | Parts per million |
| ppt | Parts per trillion |
| PQL | Practical quantitation limit |
| QA | Quality assurance |
| QAPP | Quality Assurance Project Plan |
| QC | Quality control |
| RPD | Relative percent difference |
| RSD | Relative standard deviation |
| SAIC | Science Applications International Corporation |
| SITE | Superfund Innovative Technology Evaluation |
| SOP | Standard operating procedure |
| SRM | Standard reference material |
| SW-846 | Test Methods for Evaluating Solid Waste; Physical/Chemical Methods |
| TOC | Total organic carbon |
| TOM | Task Order Manager |
| UL | Underwriters Laboratory |
| UEFPC | Upper East Fork of Poplar Creek |
| Y-12 | Y-12 Oak Ridge Security Complex, Oak Ridge, TN |
| VAS | Voltammetric analysis system |
| V | Volt |

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This document was QA reviewed by George Brilis of the EPA National Exposure Research Laboratory.

# Chapter 1
# Introduction

The U.S. Environmental Protection Agency (EPA) under the Office of Research and Development (ORD), National Exposure Research Laboratory (NERL), conducted a demonstration to evaluate the performance of innovative field measurement devices for their ability to measure mercury concentrations in soils and sediments. This Innovative Technology Verification Report (ITVR) presents demonstration performance results and associated costs of MTI's Portable Digital Voltammeter (PDV) 6000 anodic stripping voltammetry instrument. The vendor-prepared comments regarding the demonstration are presented in Appendix A.

The demonstration was conducted as part of the EPA Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) Program. Mercury contaminated soils and sediments, collected from four sites within the continental U.S., comprised the majority of samples analyzed during the evaluation. Some soil and sediment samples were spiked with mercury (II) chloride ($HgCl_2$) to provide concentrations not occurring in the field samples. Certified standard reference material (SRM) samples were also used to provide samples with certified mercury concentrations and to increase the matrix variety.

The demonstration was conducted at the Department of Energy (DOE) Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN during the week of May 5, 2003. The purpose of the demonstration was to obtain reliable performance and cost data for field measurement devices in order to 1) provide potential users with a better understanding of the devices' performance and operating costs under well-defined field conditions and 2) provide the instrument vendors with documented results that can assist them in promoting acceptance and use of their devices. The results obtained using the five field mercury measurement devices were compared to the mercury results obtained for identical sample sets (samples, spiked samples, and SRMs) analyzed at a referee laboratory. The referee laboratory, which was selected prior to the demonstration, used a well-established EPA reference method.

## 1.1 Description of the SITE Program

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 EPA's Office of Solid Waste and Emergency Response (OSWER) and ORD under the Superfund Amendments and Reauthorization Act of 1986.

The overall goal of the SITE Program is to conduct performance verification 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 program is designed to meet three main 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 the use of innovative technologies at Superfund sites, as well as at other waste sites or commercial facilities.

The SITE Program includes the following elements:

- The MMT Program evaluates innovative technologies that sample, detect, monitor, or measure hazardous and toxic substances in soil, water, and sediment samples. 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 conventional technologies.

- The Remediation Technology Program conducts demonstrations of innovative treatment technologies to provide reliable performance, cost, and applicability data for site cleanups.
- The 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 in the support of the technologies. A significant number of these activities are performed by EPA's Technology Innovation Office.

The Field Analysis of Mercury in Soils and Sediments demonstration was performed under the MMT Program. The MMT Program provides developers of innovative hazardous waste sampling, detection, monitoring, and measurement devices with an opportunity to demonstrate the performance of their devices under actual field conditions. The main 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 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 NERL in Las Vegas, NV. The NERL is the EPA center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. The NERL mission components include 1) developing and evaluating methods and technologies for sampling, monitoring, and characterizing water, air, soil, and sediment; 2) supporting regulatory and policy decisions; and 3) providing technical support to ensure the effective implementation of environmental regulations and strategies.

## 1.2 Scope of the Demonstration

The demonstration project consisted of two separate phases: Phase I involved obtaining information on prospective vendors having viable mercury detection instrumentation. Phase II consisted of field and planning activities leading up to and including the demonstration activities. The following subsections provide detail on both of these project phases.

### *1.2.1 Phase I*

Phase I was initiated by making contact with knowledgeable sources on the subject of “mercury in soil” detection devices. Contacts included individuals within EPA, Science Applications International Corporation (SAIC), and industry where measurement of mercury in soil was known to be conducted. Industry contacts included laboratories and private developers of mercury detection instrumentation. In addition, the EPA Task Order Manager (TOM) provided contacts for "industry players" who had participated in previous MMT demonstrations. SAIC also investigated university and other research-type contacts for knowledgeable sources within the subject area.

These contacts led to additional knowledgeable sources on the subject, which in turn led to various Internet searches. The Internet searches were very successful in finding additional companies involved with mercury detection devices.

All in all, these research activities generated an original list of approximately 30 companies potentially involved in the measurement of mercury in soils. The list included both international and U.S. companies. Each of these companies was contacted by phone or email to acquire further information. The contacts resulted in 10 companies that appeared to have viable technologies.

Due to instrument design (i.e., the instrument’s ability to measure mercury in soils and sediments), business strategies, and stage of technology development, only 5 of those 10 vendors participated in the field demonstration portion of phase II.

### *1.2.2 Phase II*

Phase II of the demonstration project involved strategic planning, field-related activities for the demonstration, data analysis, data interpretation, and preparation of the ITVRs.

Phase II included pre-demonstration and demonstration activities, as described in the following subsections.

#### 1.2.2.1 Pre-Demonstration Activities

The pre-demonstration activities were completed in the fall 2002. There were six objectives for the pre-demonstration:

- Establish concentration ranges for testing vendors' analytical equipment during the demonstration.
- Collect soil and sediment field samples to be used in 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.
- Provide soil and sediment samples to the vendors for self-evaluation of their instruments, as a precursor to the demonstration.

As an integral part of meeting these objectives, a pre-demonstration sampling event was conducted in September 2002 to collect field samples of soils and sediments containing different levels of mercury. The field samples were obtained from the following locations:

- Carson River Mercury site - near Dayton, NV
- Y-12 National Security Complex - Oak Ridge, TN
- A confidential manufacturing facility - eastern U.S.
- Puget Sound - Bellingham Bay, WA

Immediately after collecting field sample material from the sites noted above, the general mercury concentrations in the soils and sediments were confirmed by quick turnaround laboratory analysis of field-collected subsamples using method SW-7471B. The field sample materials were then shipped to a soil preparation laboratory for homogenization. Additional pre-demonstration activities are detailed in Chapter 4.

#### 1.2.2.2 Demonstration Activities

Specific objectives for this SITE demonstration were developed and defined in a Field Demonstration and Quality Assurance Project Plan (QAPP) (EPA Report # EPA/600/R-03/053). The Field Demonstration QAPP is available through the EPA ORD web site (http://www.epa.gov/ORD/SITE) or from the EPA Project Manager. The demonstration objectives were subdivided into two categories: primary and secondary. Primary objectives are goals of the demonstration study that need to be achieved for technology verification. The measurements used to achieve primary objectives are referred to as critical. These measurements typically produce quantitative results that can be verified using inferential and descriptive statistics.

Secondary objectives are additional goals of the demonstration study developed for acquiring other information of interest about the technology that is not directly related to verifying the primary objectives. The measurements required for achieving secondary objectives are considered to be noncritical. Therefore, the analysis of secondary objectives is typically more qualitative in nature and often uses observations and sometimes descriptive statistics.

The field portion of the demonstration involved evaluating the capabilities of five mercury-analyzing instruments to measure mercury concentrations in soil and sediment. During the demonstration, each instrument vendor received three types of samples 1) homogenized field samples referred to as "field samples", 2) certified SRMs, and 3) spiked field samples (spikes).

Spikes were prepared by adding known quantities of $HgCl_2$ to field samples. Together, the field samples, SRMs, and spikes are referred to as "demonstration samples" for the purpose of this ITVR. All demonstration samples were independently analyzed by a carefully selected referee laboratory. The experimental design for the demonstration is detailed in Chapter 4.

## 1.3 Mercury Chemistry and Analysis

### *1.3.1 Mercury Chemistry*

Elemental mercury is the only metal that occurs as a liquid at ambient temperatures. Mercury naturally occurs, primarily within the ore, cinnabar, as mercury sulfide (HgS). Mercury easily forms amalgams with many other metals, including gold. As a result, mercury has historically been used to recover gold from ores.

Mercury is ionically stable; however, it is very volatile for a metal. Table 1-1 lists selected physical and chemical properties of elemental mercury.

**Table 1-1. Physical and Chemical Properties of Mercury**

| Properties | Data |
|---|---|
| Appearance | Silver-white, mobile, liquid. |
| Hardness | Liquid |
| Abundance | 0.5% in Earth's crust |
| Density @ 25 ˚C | 13.53 g/mL |
| Vapor Pressure @ 25 ˚C | 0.002 mm |
| Volatilizes @ | 356 ˚C |
| Solidifies @ | -39 ˚C |

Source: Merck Index, 1983

Historically, mercury releases to the environment included a number of industrial processes such as chloralkali manufacturing, copper and zinc smelting operations, paint application, waste oil combustion, geothermal energy plants, municipal waste incineration, ink manufacturing, chemical manufacturing, paper mills, leather tanning, pharmaceutical production, and textile manufacturing. In addition, industrial and domestic mercury-containing products, such as thermometers, electrical switches, and batteries, are disposed of as solid wastes in landfills (EPA, July 1995). Mercury is also an indigenous compound at many abandoned mining sites and is, of course, found as a natural ore.

At mercury-contaminated sites, mercury exists in mercuric form ($Hg^{2+}$), mercurous form ($Hg_2^{2+}$), elemental form ($Hg^0$), and alkylated form (e.g., methyl or ethyl mercury). $Hg_2^{2+}$ and $Hg^{2+}$ are the more stable forms under oxidizing conditions. Under mildly reducing conditions, both organically bound mercury and inorganic mercury may be degraded to elemental mercury, which can then be converted readily to methyl or ethyl mercury by biotic and abiotic processes. Methyl and ethyl mercury are the most toxic forms of mercury; the alkylated mercury compounds are volatile and soluble in water.

Mercury (II) forms relatively strong complexes with $Cl^-$ and $CO_3^{2-}$. Mercury (II) also forms complexes with inorganic ligands such as fluoride ($F^-$), bromide ($Br^-$), iodide ($I^-$), sulfate ($SO_4^{2-}$), sulfide ($S^{2-}$), and phosphate ($PO_4^{3-}$) and forms strong complexes with organic ligands, such as sulfhydryl groups, amino acids, and humic and fulvic acids. The insoluble HgS is formed under mildly reducing conditions.

### *1.3.2 Mercury Analysis*

There are several laboratory-based, EPA promulgated methods for the analysis of mercury in solid and liquid hazardous waste matrices. In addition, there are several performance-based methods for the determination of various mercury species. Table 1-2 summarizes the commonly used methods for measuring mercury in both solid and liquid matrices, as identified through a review of the EPA Test Method Index and SW-846. A discussion of the choice of reference method is presented in Chapter 4.

**Table 1-2. Methods for Mercury Analysis in Solids or Aqueous Soil Extracts**

| Method | Analytical Technology | Type(s) of Mercury analyzed | Approximate Concentration Range | Comments |
|---|---|---|---|---|
| SW-7471B | CVAAS | • inorganic mercury<br>• organo-mercury | 10-2,000 ppb | Manual cold vapor technique widely used for total mercury determinations |
| SW-7472 | ASV | • inorganic mercury<br>• organo-mercury | 0.1-10,000 ppb | Newer, less widely accepted method |
| SW-7473 | TD, amalgamation, and AAS | • inorganic mercury<br>• organo-mercury | 0.2 - 400 ppb | Allows for total decomposition analysis |
| SW-7474 | AFS | • inorganic mercury<br>• organo-mercury | 1 ppb - ppm | Allows for total decomposition analysis; less widely used/reference |
| EPA 1631 | CVAFS | • inorganic mercury<br>• organo-mercury | 0.5 - 100 ppt | Requires “trace” analysis procedures; written for aqueous matrices; Appendix A of method written for sediment/soil samples |
| EPA 245.7 | CVAFS | • inorganic mercury<br>• organo-mercury | 0.5 - 200 ppt | Requires “trace” analysis procedures; written for aqueous matrices; will require dilutions of high-concentration mercury samples |
| EPA 6200 | FPXRF | • inorganic mercury | >30 mg/kg | Considered a screening protocol |

AAS = Atomic Absorption Spectrometry
AAF = Atomic Fluorescence Spectrometry
AFS = Atomic Fluorescence Spectrometry
ASV = Anodic Stripping Voltammetry
CVAAS = Cold Vapor Atomic Absorption Spectrometry
CVAFS = Cold Vapor Atomic Fluorescence Spectrometry
FPXRF = Field Portable X-ray Fluorescence
EPA = U.S. Environmental Protection Agency
mg/kg = milligram per kilogram
ppb = parts per billion
ppm = parts per million
ppt = parts per trillion
SW = solid waste
TD = thermal decomposition

# Chapter 2
# Technology Description

This chapter provides a detailed description of 1) anodic stripping voltammetry (ASV), which is the type of technology on which MTI's instrument is based, and 2) a detailed description of the actual MTI PDV 6000 instrument.

## 2.1 Description of Anodic Stripping Voltammetry

The principle of analysis used by the MTI PDV 6000 is ASV. ASV is a sensitive method that can be used for the analysis of trace concentrations of metals in solution, including digestion solutions from metal-contaminated soils and sediments. The method involves initially plating metals onto an electrode by applying a negative voltage, then stripping the metals back into solution by applying a positive voltage to the electrode. The ramping of the positive voltage generates a small but measurable current (MTI, 2002).

The ASV technique was first discovered in the 1920s by Jaroslav Heyrovsky, who won the Nobel prize in 1959 (MTI, 2002). The technique was originally developed with a hanging Hg drop electrode. However, to limit the quantity of Hg needed, thin Hg films can be pre-deposited onto an electrode such as glassy carbon, or co-deposited with the analyte metal ions. With such films, sensitivities in the low part-per-billion (ppb) range can be achieved. A negative potential is applied to the glassy carbon 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:

$$\mathbf{M^{n+} + ne^{-} \rightarrow M}$$

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

The first step of the process is referred to as the "deposition" or "accumulation" step. This step involves concentrating the metal on the electrode. The longer the potential is applied, the more metal is reduced and plated onto the surface of the electrode. The deposition time is predetermined. When sufficient metal has been plated onto the working electrode, the metal is stripped (oxidized) off the electrode by applying, 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:

$$\mathbf{M \rightarrow M^{n+} + ne^{-}}$$

The electrons released by this process form a current. The current is measured and may be plotted as a function of the 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, and laboratory versions of an ASV device can measure concentrations in the parts per trillion (ppt) range. The length of the plating step can be varied to suit the analyte concentration of the sample. For example, analysis of a 10-ppb solution of Pb

may require a 3-5 minute accumulation step, while a solution in the parts per million range would require less than 1 minute.

## 2.2 Description of the MTI PDV 6000

The PDV 6000 Portable Analyzer is an instrument that can be used for field screening or laboratory analysis of heavy metal ions such as silver, arsenic, gold, cadmium, chromium, copper, iron, mercury, manganese, nickel, lead, tin, and zinc. The instrument can be used for metal ion detection in a wide variety of matrixes, including chemicals, materials, food, beverages, water, industrial effluent, and pharmaceuticals. The PDV 6000 consists of two major components: 1) the main instrument control unit and 2) the cell assembly. Figure 2-1 is a schematic of the top of the cell assembly. Within the cell assembly, there are three separate electrodes surrounding a stirrer motor. The reference electrode, found in the cell's assembly with the other electrodes, is a critical component of the PDV 6000.

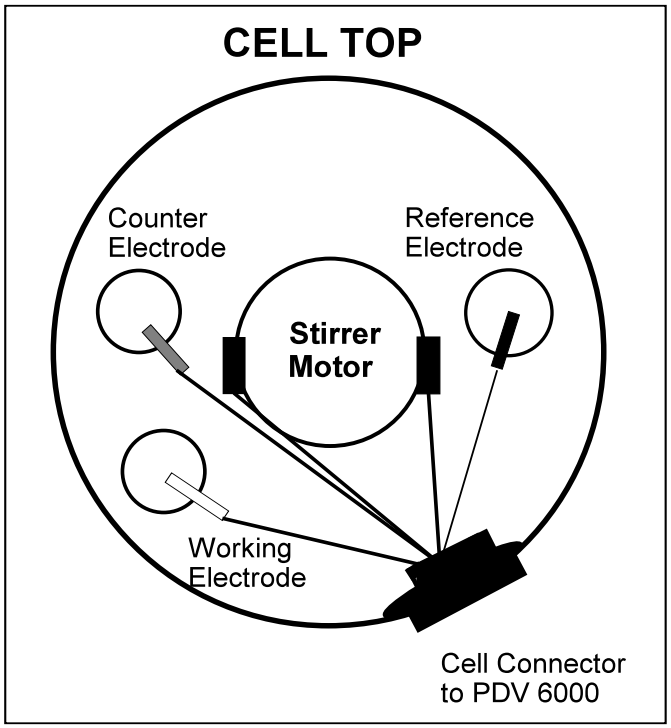


**Figure 2-1. PDV 6000 cell assembly.**

**Applications and Specifications** - The MTI PDV 6000 can be operated as a stand-alone instrument or attached to a laptop or desktop computer to run accompanying voltammetric analysis system (VAS) software. The VAS software incorporates features such as standard addition calibration, simultaneous multi-element analysis, and storage of data. For stand-alone use, the control unit is programmed to analyze 10 metals in the concentration range of 10 ppb to 30 ppm. According to MTI, the stand-alone unit should only be used for screening purposes (i.e., determining whether a sample may be above or below a particular threshold).

According to MTI, the VAS software allows for better detection limits and more accurate analysis. A specific electrolyte and electrode combination are used to optimize results for specific metals. This is essential for detection limits in the low mg/kg range. Where the detection range is in the g/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. High silver concentrations can interfere with mercury determinations.

**Operation** - The PDV 6000 control unit is a hand-held portable device, weighing approximately 700 g, and has a dimension of 10 cm by 18 cm by 4 cm. When used in the field (Figure 2-2), the PDV 6000 should only be used to indicate the approximate concentration range of the metal of interest. This is true for all field analysis since many factors can reduce the accuracy and precision of any analysis. (When used in the laboratory, the vendor reports the PDV 6000 can provide accurate and reproducible data). According to MTI, it is realistic to expect the PDV 6000 to obtain data from the field that is within 20% of the true value. For this reason, it is best to use the PDV 6000 to classify samples as "above a threshold concentration" or "below a threshold concentration."

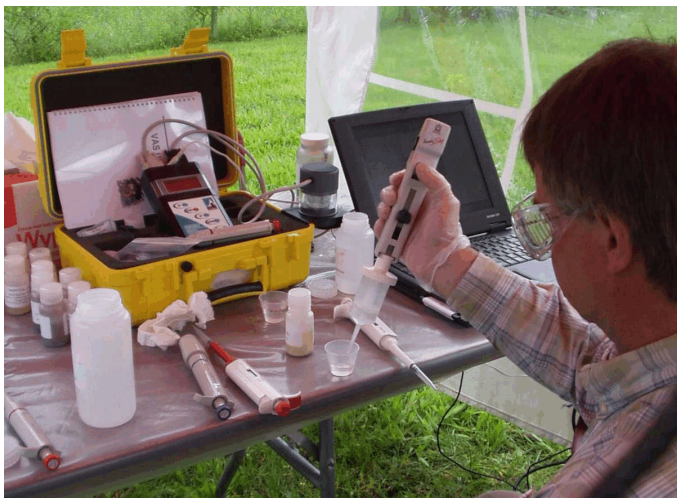

**Figure 2-2. Photograph of the PDV 6000 during the field demonstration.**

Certain field conditions may affect the accuracy and precision of results. These include the following:

- Sample homogeneity
- Sampling handling errors
- Pipetting errors
- Unpredictable matrix effects
- Sample and cell contamination

**Essential Components and Supplies** – For typical use as a field instrument, the PDV 6000 is shipped with a carrying case, the handheld control unit, cell assembly and cell stand, Ag/AgCl reference electrode, platinum counter electrode, glassy carbon working electrode, cable to link the analytical cell to the control unit, a DB9 serial cable to link the control unit to a computer, a reference electrode plating accessory, a main-powered 12 volt (V) direct current (DC) supply, a nickel metal halide (NiMH) battery pack and battery pack charger, the PDV 6000 operation manual, and VAS software installation disks and the VAS User's Guide.

For solids analysis, ancillary supplies are required to conduct extractions. These include a portable scale for measuring the correct sample mass to extract; a set of air displacement pipetters (50-500 µL, 100-1000 µL, and 200-1000 µL); a repeating pipetter (0.5-50 mL); and extraction reagents. It is recommended that kits be purchased to supply the extraction reagents and disposable supplies (e.g., bottles) necessary to extract and analyze the samples. 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).

**Power Supply** – The PDV 6000 can operate using either a 110 V alternating current (AC) source or direct current battery. The specific power supply options for the PDV 6000, as presented in Table 2-1, affect the number of analyses that may be performed on a daily basis.

**Table 2-1. Power Supply Options for the PDV 6000**

| Power Source | No. of Analyses |
|---|---|
| 9V PP3 | 10-20 |
| Rechargeable Battery Pack | 50 |
| 9V main power supply [a] | Continuous |

a Main power supply also recharges the battery pack and powers the reference electrode plating accessory.

**Instrument Calibration** – The standard curve method compares the sample response with that of one or more known standards. Voltage readings can allow calibration curves of between 1-10 standards to be constructed and then compared with up to 15 samples. Generally, calibration is based on a single point comparison, whereby the voltage generated by the standard is compared to the voltage generated by the sample. The response for a particular analyte is proportional to its concentration in the analytical cell; therefore, 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 reanalyzing that solution. The same sample can be spiked and reanalyzed once or several times, as necessary. The spiking enables the result to be calculated by the method of standard additions. The results from the sample and spiked sample runs are then plotted, and a line of regression is fitted and used to calculate the sample concentration.

**VAS Software** – The use of the supplied VAS software allows more flexible and accurate analyses, even in the field. This software incorporates features such as multiple point calibration curves or standard addition calibration, simultaneous multi-element analysis, easy parameter optimization and manual baseline, and peak center adjustment. It also stores data, and allows comments to be added about the sample location and a description of the sample. The VAS software requires a computer that has a minimum specification of a 300 Mhz 586 processor (Pentium or equivalent), 64 MB RAM, 10 MB of free hard disk space, and runs Windows 98, ME, NT, 2000, or XP.

## 2.3 Developer Contact Information

Additional information about the PDV 6000 can be obtained from the following source:

**International Contact**
Monitoring Technologies International Pty. Ltd.
1/7 Collingwood Street
Osborne Park, Perth
West Australia 6017
Internet email: support@mti.com.au
Web address: www.monitoring-technologies.com.

**U.S. Contact**
Felicia Owen, MTI Inc.
1609 Ebb Drive
Wilmington, NC 28409
Telephone: (910) 392-5714 Fax: (910) 392-4320
email: fowen@owenscientific.com

# Chapter 3
# Field Sample Collection Locations and Demonstration Site

As previously described in Chapter 1, the demonstration in part tested the ability of all five vendor instruments to measure mercury concentrations in demonstration samples. The demonstration samples consisted of field-collected samples, spiked field samples, and SRMs. The field-collected samples comprised the majority of demonstration samples. This chapter describes the four sites from which the field samples were collected, the demonstration site, and the sample homogenization laboratory. Spiked samples were prepared from these field samples.

Screening of potential mercury-contaminated field sample sites was conducted during Phase I of the project. Four sites were selected for acquiring mercury-contaminated samples that were diverse in appearance, consistency, and mercury concentration. A key criterion was the source of the contamination. These sites included:

- Carson River Mercury site - near Dayton, NV
- The Y-12 National Security Complex (Y-12) - Oak Ridge, TN
- A confidential manufacturing facility - eastern U.S.
- Puget Sound - Bellingham Bay, WA

**Site Diversity** – Collectively, the four sites provided sampling areas with both soil and sediment, having variable physical consistencies and variable ranges of mercury contamination. Two of the sites (Carson River and Oak Ridge) provided both soil and sediment samples. A third site (a manufacturing facility) provided just soil samples and a fourth site (Puget Sound) provided only sediment samples.

**Access and Cooperation** – Site representatives were instrumental in providing site access, and in some cases, guidance on the best areas to collect samples from relatively high and low mercury concentrations. In addition, representatives from the host demonstration site (ORNL) provided a facility for conducting the demonstration.

At three of the sites, the soil and/or sediment sample was collected, homogenized by hand in the field, and subsampled for quick turnaround analysis. These subsamples were sent to analytical laboratories to determine the general range of mercury concentrations at each of the sites. (The Puget Sound site did not require confirmation of mercury contamination due to recently acquired mercury analytical data from another, ongoing research project.) The field-collected soil and sediment samples from all four sites were then shipped to SAIC's GeoMechanics Laboratory for a more thorough sample homogenization (see Section 4.3.1) and subsampled for redistribution to vendors during the pre-demonstration vendor self-evaluations.

All five of the technology vendors performed a self-evaluation on selected samples collected and homogenized during this pre-demonstration phase of the project. For the self-evaluation, the laboratory results and SRM values were supplied to the vendor, allowing the vendor to determine how well it performed the analysis on the field samples. The results were used to gain a preliminary understanding of the field samples collected and to prepare for the demonstration.

Table 3-1 summarizes key characteristics of samples collected at each of the four sites. Also included are the sample matrix, sample descriptions, and sample depth intervals. The analytical results presented in Table 3-1 are based on referee laboratory mercury results for the demonstration samples.

**Table 3-1. Summary of Site Characteristics**

| Site Name | Sampling Area | Sample Matrix | Depth | Description | Hg Concentration Range |
|---|---|---|---|---|---|
| Carson River Mercury site | Carson River | Sediment | water/sediment interface | Sandy silt, with some organic debris present (plant stems and leaves) | 10 ppb - 50 ppm |
| | Six Mile Canyon | Soil | 3 - 8 cm bgs | Silt with sand to sandy silt | 10 ppb - 1,000 ppm |
| Y-12 National Security Complex | Old Hg Recovery Bldg. | Soil | 0 - 1 m bgs | Silty-clay to sandy-gravel | 0.1 - 100 ppm |
| | Poplar Creek | Sediment | 0 - 0.5 m bgs | Silt to coarse sandy gravel | 0.1 - 100 ppm |
| Confidential manufacturing site | Former plant building | Soil | 3.6 -9 m bgs | Silt to sandy silt | 5 - 1,000 ppm |
| Puget Sound - Bellingham Bay | Sediment layer | Sediment | 1.5 - 1.8 m thick | Clayey-sandy silt with various woody debris | 10 - 400 ppm |
| | Underlying Native Material | Sediment | 0.3 m thick | Medium-fine silty sands | 0.16 - 10 ppm |

bgs = below ground surface.

## 3.1 Carson River

### *3.1.1 Site Description*

The Carson River Mercury site begins near Carson City, NV, and extends downstream to the Lahontan Valley and the Carson Desert. During the Comstock mining era of the late 1800s, 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 Nevada 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 (EPA Region 9, 1994).

Mercury contamination is present at Carson River as either elemental mercury and/or inorganic mercury sulfides with less than 1%, if any, methylmercury. Mercury contamination exists in soils present at the former gold and silver mining mill sites; waterways adjacent to the mill sites; and sediment, fish, and wildlife over more than a 50-mile length of the Carson River. Mercury is also present 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 (EPA, 2002a).

### *3.1.2 Sample Collection*

The Carson River Mercury site provided both soil and sediment samples across the range of contaminant concentrations desired for the demonstration. Sixteen near-surface soil samples were collected between 3-8 cm below ground surface (bgs). Two sediment samples were collected at the water-to-sediment interface. All 18 samples were collected on September 23-24, 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 3 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-liter (L) sealable bags identified with a permanent marker. The sediment samples were also collected with a shovel, screened through a 6.3-mm sieve to remove larger material, and collected in 4-L sealable bags identified with a permanent marker. Each of the 4-L sealable bags was placed into a second 4-L

sealable bag, and the sample label was placed onto the outside bag. The sediment samples were then placed into 10-L buckets, lidded, and identified with a sample label.

## 3.2 Y-12 National Security Complex

### *3.2.1 Site Description*

The Y-12 site is located at the DOE ORNL in Oak Ridge, TN. 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 (ORR) adjacent to the city of Oak Ridge, TN. 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 development of 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.

Soils at the Y-12 facility are contaminated with mercury in many areas. One of the areas of known high levels of mercury-contaminated soils is in the vicinity of a former mercury use facility (the "Old Mercury Recovery Building" – Building 8110). At this location, mercury-contaminated material and soil were processed in a Nicols-Herschoff roasting furnace to recover mercury. Releases of mercury from this process, and from a building sump used to secure the mercury-contaminated materials and the recovered mercury, have contaminated the surrounding soils (Rothchild, et al., 1984). Mercury contamination also occurred in the sediments of the East Fork of Poplar Creek (DOE, 1998). The Upper East Fork of Poplar Creek (UEFPC) drains the entire Y-12 complex. Releases of mercury via building drains connected to the storm sewer system, building basement dewatering sump discharges, and spills to soils, all contributed to contamination of UEFPC. Recent investigations showed that bank soils containing mercury along the UEFPC were eroding and contributing to mercury loading. Stabilization of the bank soils along this reach of the creek was recently completed.

### *3.2.2 Sample Collection*

Two matrices were sampled at Y-12 in Oak Ridge, TN, creek sediment and soil. A total of 10 sediment samples was collected; one sediment sample was collected from the Lower East Fork of Poplar Creek (LEFPC) and nine sediment samples were collected from the UEFPC. A total of six soil samples was collected from the Building 8110 area. The sampling procedures that were 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 a commercially available clam-shell sonar dredge attached to a rope. The dredge was slowly lowered to the creek bottom surface, where it was pushed by foot into the sediment. Several drops of the sampler (usually seven or more) 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. One creek sample consisted of creek bank sediments, which was collected using a stainless steel trowel.

The collected sediment was then poured onto a 6.3-mm sieve to remove oversize sample material. Sieved samples were then placed in 12-L sealable plastic buckets. The sediment samples in these buckets were homogenized with a plastic ladle and subsamples were collected in 20-milliliter (mL) vials for quick turnaround analyses.

**Soil** – Soil samples were collected from pre-selected boring locations September 25, 2002. All samples were collected in the immediate vicinity of the Building 8110 foundation 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 soil was transferred to an aluminum pan, homogenized by hand, and subsampled to a 20-mL vial. The remaining soil was transferred to 4-L plastic containers.

## 3.3 Confidential Manufacturing Site

### *3.3.1 Site Description*

A confidential manufacturing site, located in the eastern U.S., was selected for participation in this demonstration. The site contains elemental mercury, mercury amalgams, and mercury oxide in shallow sediments (less than 0.3 m deep) and deeper soils (3.65 to 9 m bgs). This site provided soil with concentrations from 5-1,000 mg/kg.

The site is the location of three former processes that resulted in mercury contamination. The first process

involved amalgamation of zinc with mercury. The second process involved the manufacturing of zinc oxide. The third process involved 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. Mercury values have been measured ranging from 0.05 to over 5,000 mg/kg, with average values of approximately 100 mg/kg.

### *3.3.2 Sample Collection*

Eleven subsurface soil samples were collected on September 24, 2002. All samples were collected with a Geoprobe® unit using plastic sleeves. All samples were collected at the location of a former facility plant. Drilling locations were determined based on historical data provided by the site operator. The intention was to gather soil samples across a range of concentrations. Because the surface soils were from 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 9 m bgs. Individual cores were 1-m long. The plastic sleeve for each 1-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 premixing 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, by using a wooden spatula, oversize materials were manually 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-L sample container for each chosen sample interval. A subsample of the mixed soil was transferred into a 20-mL vial, and it was sent for quick turnaround mercury analysis. This process was repeated for each subsequent sample interval.

## 3.4 Puget Sound

### *3.4.1 Site Description*

The Puget Sound site consists of contaminated offshore sediments. The particular area of the site used for collecting demonstration samples is identified as the Georgia Pacific, Inc. Log Pond. The Log Pond is located within the Whatcom Waterway in Bellingham Bay, WA, a well-established heavy industrial land use area with a maritime shoreline designation. Log Pond sediments measure approximately 1.5 to 1.8-m thick, and contain various contaminants including mercury, phenols, polyaromatic hydrocarbons, polychlorinated biphenyls, and wood debris. Mercury was used as a preservative in the logging industry. The area was capped in late 2000 and early 2001 with an average of 7 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 Environmental, 2001).

Mercury concentrations have been measured ranging from 0.16 to 400 mg/kg (dry wt). The majority (98%) of the mercury detected in near-shore ground waters and sediments of the Log Pond is believed to be comprised of complexed divalent ($Hg^{2+}$) forms such as mercuric sulfide (Bothner, et al., 1980 and Anchor Environmental, 2000).

### *3.4.2 Sample Collection*

Science Applications International Corporation (SAIC) is currently performing a SITE remedial technology evaluation in the Puget Sound (SAIC, 2002). As part of ongoing work at that site, SAIC collected additional sediment for use during this MMT project. Sediment samples collected on August 20-21, 2002 from the Log Pond in Puget Sound were obtained beneath approximately 3-6 m of water, using a vibra-coring system capable of capturing cores to 0.3 m 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 into 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.

The following criteria were used to verify whether an acceptable core sample was collected:

- Target penetration depth (i.e., into native material) was achieved.

- Sediment recovery of at least 65% of the penetration depth was achieved.
- Sample appeared undisturbed and intact without any evidence of obstruction/blocking within the core tube or 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. 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.

## 3.5 Demonstration Site

The demonstration was conducted in a natural environment, outdoors, in Oak Ridge, TN. The area was a grass covered hill with some parking areas, all of which were surrounded by trees. Building 5507, in the center of the demonstration area, provided facilities for lunch, break, and sample storage for the project and personnel.

Most of the demonstration was performed during rainfall events ranging from steady to torrential. Severe puddling of rain occurred to the extent that boards needed to be placed under chairs to prevent them from sinking into the ground. Even when it was not raining, the relative humidity was high, ranging from 70.6 to 98.3 percent. Between two and four of the tent sides were used to keep rainfall from damaging the instruments. The temperature in the afternoons ranged from 65-70 degrees Fahrenheit, and the wind speed was less than 10 mph. The latitude is 36°N, the longitude 35°W, and the elevation 275 m. (Figure 3-1 is a photograph of the site during the demonstration and Figure 3-2 is a photograph of the location.)

**Figure 3-1. Tent and field conditions during the demonstration at Oak Ridge, TN.**

**Figure 3-2. Demonstration site and Building 5507.**

## 3.6 SAIC GeoMechanics Laboratory

Sample homogenization was completed at the SAIC GeoMechanics Laboratory in Las Vegas, NV. This facility is an industrial-type building with separate facilities for personnel offices and material handling. The primary function of the laboratory is for rock mechanics studies. The laboratory has rock mechanics equipment, including sieves, rock crushers, and sample splitters. The personnel associated with this laboratory are experienced in the areas of sample preparation and sample homogenization. In addition to the sample homogenization equipment, the laboratory contains several benches, tables, and open space. Mercury air monitoring equipment was used during the sample preparation activities for personnel safety.

# Chapter 4
# Demonstration Approach

This chapter describes the demonstration approach that was used for evaluating the field mercury measurement technologies at ORNL in May 2003 and in Las Vegas in June 2003. It presents the objectives, design, sample preparation and management procedures, and the reference method confirmatory process used for the demonstration.

## 4.1 Demonstration Objectives

The primary goal of the SITE MMT Program is to develop reliable performance and cost data on innovative, field-ready measurement technologies. A SITE demonstration must provide detailed and reliable performance and cost data in order that potential technology users have adequate information needed to make sound judgements regarding an innovative technology's applicability to a specific site and to be able to compare the technology to conventional technologies.

Table 4-1 summarizes the project objectives for this demonstration. In accordance with *QAPP Requirements for Applied Research Projects (EPA,1998)*, the technical project objectives for the demonstration were categorized as primary and secondary.

**Table 4-1. Demonstration Objectives**

| Objective | Description | Method of Evaluation |
|---|---|---|
| Primary Objectives | | |
| Primary Objective # 1 | Determine sensitivity of each instrument with respect to vendor-generated MDL and PQL. | Independent laboratory confirmation of SRMs, field samples, and spiked field samples. |
| Primary Objective # 2 | Determine potential analytical accuracy associated with vendor field measurements. | |
| Primary Objective # 3 | Evaluate the precision of vendor field measurements. | |
| Primary Objective # 4 | Measure time required to perform five functions related to mercury measurements: 1) mobilization and setup, 2) initial calibration, 3) daily calibration, 4) sample analysis, and 5) demobilization. | Documentation during demonstration; vendor-provided information. |
| Primary Objective # 5 | Estimate costs associated with mercury measurements for the following four categories: 1) capital, 2) labor, 3) supplies, and 4) investigation-derived wastes. | |
| Secondary Objectives | | |
| Secondary Objective # 1 | Document ease of use, skills, and training required to operate the device properly. | Documentation of observations during demonstration; vendor-provided information. |
| Secondary Objective # 2 | Document potential H&S concerns associated with operating the device. | |
| Secondary Objective # 3 | Document portability of the device. | |
| Secondary Objective # 4 | Evaluate durability of device based on materials of construction and engineering design. | |
| Secondary Objective # 5 | Document the availability of the device and its spare parts. | Post-demonstration investigation. |

Critical data support primary objectives and noncritical data support secondary objectives. With the exception of the cost information, primary objectives required the use of quantitative results to draw conclusions regarding the technology performance. Secondary objectives pertained to information that was useful and did not necessarily require the use of quantitative results to draw conclusions regarding technology performance.

## 4.2 Demonstration Design

### *4.2.1 Approach for Addressing Primary Objectives*

The purpose of this demonstration was to evaluate the performance of the vendor's instrumentation against a standard laboratory procedure. In addition, an overall average relative standard deviation (RSD) was calculated for all measurements made by the vendor and the referee laboratory. RSD comparisons used descriptive statistics, not inferential statistics, between the vendor and laboratory results. Other statistical comparisons (both inferential and descriptive) for sensitivity, precision, and accuracy were used, depending upon actual demonstration results.

The approach for addressing each of the primary objectives is discussed in the following subsections. A detailed explanation of the precise statistical determination used for evaluating primary objectives No. 1 through No. 3 is presented in Chapter 6.

#### 4.2.1.1 Primary Objective #1: Sensitivity

Sensitivity is the ability of a method or instrument to discriminate between small differences in analyte concentration (EPA, 2002b). It can be discussed in terms of an instrument detection limit (IDL), a method detection limit (MDL), and as a practical quantitation limit (PQL). MDL is not a measure of sensitivity in the same respect as an IDL or PQL. It is a measure of precision at a predetermined, usually low, concentration. The IDL pertains to the ability of the instrument to determine with confidence the difference between a sample that contains the analyte of interest at a low concentration and a sample that does not contain that analyte. The IDL 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 and with an adequate degree of certainty.

The IDL is not rigidly defined in terms of matrix, method, laboratory, or analyst variability, and it is not usually associated with a statistical level of confidence. IDLs are, thus, usually lower than MDLs and rarely serve a purpose in terms of project objectives (EPA, 2002b). The PQL defines a specific concentration with an associated level of accuracy. The MDL defines a lower limit at which a method measurement can be distinguished from background noise. The PQL is a more meaningful estimate of sensitivity. The MDL and PQL were chosen as the two distinct parameters for evaluating sensitivity. The approach for addressing each of these indicator parameters is discussed separately in the following paragraphs.

**MDL**

MDL is the estimated measure of sensitivity as defined in 40 Code of Federal Regulations (CFR) Part 136. The purpose of the MDL measurement is to estimate the concentration at which an individual field instrument is 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, 2002b).

The determination of a MDL usually 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 is as follows:

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

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

**PQL**

The PQL is another important measure of sensitivity. The PQL is defined in EPA G-5i as the lowest level an instrument is capable of producing a result that has significance in terms of precision and bias. (Bias is the difference between the measured value and the true value.) It is generally considered the lowest standard on the instrument calibration curve. It is often 5-10 times higher than the MDL, depending upon the analyte, the instrument being used, and the method for analysis; however, it should not be rigidly defined in this manner.

During the demonstration, the PQL was to be defined by the vendor's reported calibration or based upon lower

concentration samples or SRMs. The evaluation of vendor-reported results for the PQL included a determination of the percent difference (%D) between their calculated value and true value. The true value is considered the value defined by the referee laboratory for field samples or spiked field samples, or, in the case of SRMs, the certified value reported by the supplier. The equation used for the %D calculation is:

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

where: $C_{true}$ = true concentration as determined by the referee laboratory or SRM reference value

$C_{calculated}$ = calculated test sample concentration

The PQL and %D were reported for the vendor. The %D for the referee laboratory, at the same concentration, was also reported for purposes of comparison. No statistical comparison was made between these two values; only a descriptive comparison was made for purposes of this evaluation. (The %D requirement for the referee laboratory was defined as 10% or less. The reference method PQL was approximately 10 µg/kg.)

#### 4.2.1.2 Primary Objective #2: Accuracy

Accuracy was calculated by comparing the measured value to a known or true value. For purposes of this demonstration, three separate standards were used to evaluate accuracy. These included: 1) SRMs, 2) field samples collected from four separate mercury-contaminated sites, and 3) spiked field samples. Four sites were used for evaluation of the MTI field instrument. Samples representing all three standard types were prepared at the SAIC GeoMechanics Laboratory. In order to prevent cross contamination, SRMs were prepared in a separate location. Each of these standards is discussed separately in the following paragraphs.

**SRMs**

The primary standards used to determine accuracy for this demonstration were SRMs. SRMs provided very tight statistical comparisons, although they did not provide all matrices of interest nor all ranges of concentrations. The SRMs were obtained from reputable suppliers, and had reported concentrations at associated 95% confidence intervals (CIs) and 95% prediction intervals. Prediction intervals were used for comparison because they represent a statistically infinite number of analyses, and therefore, would include all possible correct results 95% of the time. All SRMs were analyzed by the referee laboratory and selected SRMs were analyzed by the vendor, based upon instrument capabilities and concentrations of SRMs that could be obtained. Selected SRMs covered an appropriate range for each vendor. Replicate SRMs were also analyzed by the vendor and the laboratory.

The purpose for SRM analysis by the referee laboratory was 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 to ensure 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 analyzed SRMs as an ongoing check for laboratory bias.

Evaluation of vendor and laboratory analysis of SRMs was performed as follows. Accuracy was reported for individual sample concentrations of replicate measurements made at the same concentration.

Two-tailed 95% CIs were computed according to the following equation:

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

where: $t_{(n-1,\ 0.975)}$ = 97.5$^{th}$ percentile of the t-distribution with n–1 degrees of freedom

n = number of measurements

s = standard deviation of replicate measurements

The number of vendor-reported SRM results and referee laboratory-reported SRM results that were within the associated 95% prediction interval were evaluated. Prediction intervals were computed in a similar fashion to the CI, except that the Student's "t" value use "n" equal to infinity and, because prediction intervals represented "n" approaching infinity, the square root of "n" was dropped from the equation.

A final measure of accuracy determined from SRMs is a frequency distribution that shows the percentage of vendor-reported measurements that are within a specified window of the reference value. For example, a distribution within a 30% window of a reported concentration, within a 50%

window, and outside a 50% window of a reported concentration. This distribution aspect could be reported as average concentrations of replicate results from the vendor for a particular concentration and matrix compared to the same sample from the laboratory. These are descriptive statistics and are used to better describe comparisons, but they are not intended as inferential tests.

**Field Samples**

The second accuracy standard used for this demonstration was actual field samples collected from four separate mercury-contaminated sites. This accuracy determination consisted of a comparison of vendor-reported results for field samples to the referee laboratory results for the same field samples. The field samples were used to ensure that "real-world" samples were tested for each vendor. The field samples consisted of variable mercury concentrations within varying soil and sediment matrices. The referee laboratory results are considered the standard for comparison to each vendor.

Vendor sample results for a given field sample were compared to replicates analyzed by the laboratory for the same field sample. (A hypothesis test was used with alpha = 0.01. The null hypothesis was that sample results were similar. Therefore, if the null hypothesis is rejected, then the sample sets are considered different.) Comparisons for a specific matrix or concentration were made in order to provide additional information on that specific matrix or concentration. Comparison of the vendor values to laboratory values were similar to the comparisons noted previously for SRMs, except that a more definitive or inferential statistical evaluation was used. Alpha = 0.01 was used to help mitigate inter-laboratory variability. Additionally, an aggregate analysis was used to mitigate statistical anomalies (see Section 6.1.2).

**Spiked Field Samples**

The third accuracy standard for this demonstration was spiked field samples. These spiked field samples were analyzed by the vendors and by the referee laboratory in replicate in order to provide additional measurement comparisons to a known value. Spikes were prepared to cover additional concentrations not available from SRMs or the samples collected in the field. They were grouped with the field sample comparison noted above.

#### 4.2.1.3 Primary Objective #3: Precision

Precision can be defined as the degree of mutual agreement of independent measurements generated through repeated application of a process under specified conditions. Precision is usually thought of as repeatability of a specific measurement, and it is often reported as RSD. The RSD is computed from a specified number of replicates. The more replications of a measurement, the more confidence is 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, dependent upon the degree of confidence desired in the specified result. 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 experimental design for this demonstration included a mechanism to evaluate the precision of the vendors' technologies. Field samples from the four mercury-contaminated field sites were evaluated by each vendor's analytical instrument. During the demonstration, concentrations were predetermined only as low, medium, or high. Ranges of test samples (field samples, SRMs, and spikes) were selected to cover the appropriate analytical ranges of the vendor's instrumentation. It was known prior to the demonstration that not all vendors were capable of measuring similar concentrations (i.e., some instruments were better at measuring low concentrations and others were geared toward higher concentration samples or had other attributes such as cost or ease of use that defined specific attributes of their technology). Because of this fact, not all vendors analyzed the same samples.

During the demonstration, the vendor's instrument was tested with samples from the four different sites, having different matrices when possible (i.e., depending upon available concentrations) and having different concentrations (high, medium, and low) using a variety of samples. Sample concentrations for an individual instrument were chosen based upon vendor attributes in terms of expected low, medium, and high concentrations that the particular instrument was capable of measuring.

The referee laboratory measured replicates of all samples. The results were used for precision comparisons to the individual vendor. The RSD for the vendor and the laboratory was calculated individually, using the following equation:

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

where: S = standard deviation of replicate results
$\bar{x}$ = mean value of replicate results

Using descriptive statistics, differences between vendor RSD and referee laboratory RSD were determined. This included RSD comparisons based upon concentration, SRMs, field samples, and different sites. In addition, an overall average RSD was calculated for all measurements made by the vendor and the laboratory. RSD comparisons were based upon descriptive statistical evaluations between the vendor and the laboratory, and results were compared accordingly.

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

The amount of time required for performing the analysis was measured and reported for five categories:

- Mobilization and setup
- Initial calibration
- Daily calibration
- Sample analyses
- Demobilization

Mobilization and setup included the time needed to unpack and prepare the instrument for operation. Initial calibration included the time to perform the vendor recommended on-site calibrations. Daily calibration included the time to perform the vendor-recommended calibrations on subsequent field days. (Note that this could have been the same as the initial calibration, a reduced calibration, or none.) Sample analyses included the time to prepare, measure, and calculate the results for the demonstration and the necessary quality control (QC) samples performed by the vendor.

The time per analysis was determined by dividing the total amount of time required to perform the analyses by the number of samples analyzed (197). In the numerator, sample analysis time included preparation, measurement, and calculation of results for demonstration samples and necessary QC samples performed by the vendor. In the denominator, the total number of analyses included only demonstration samples analyzed by the vendor, not QC analyses nor reanalyses of samples.

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

Unique time measurements are also addressed in this report (e.g., if soil samples were analyzed directly, and sediment samples required additional time to dry before the analyses started, then a statement was made noting that soil samples were analyzed in X amount of hours, and that sediment samples required drying time before analysis).

Recorded times were rounded to the nearest 15-minute interval. The number of vendor personnel used was noted and factored into the time calculations. No comparison on time per analysis is made between the vendor and the referee laboratory.

#### 4.2.1.5 Primary Objective #5: Cost

The following four cost categories were considered to estimate costs associated with mercury measurements:

- Capital costs
- Labor costs
- Supply costs
- Investigation-derived waste (IDW) disposal costs

Although both vendor and laboratory costs are presented, the calculated costs were not compared with the referee laboratory. A summary of how each cost category was estimated for the measurement device is provided below.

- The capital cost was estimated based on published price lists for purchasing, renting, or leasing each field measurement device. If the device was purchased, the capital cost estimate did not include salvage value for the device after work was completed.
- The labor cost was based on the number of people required to analyze samples during the demonstration. The labor rate was based on a standard hourly rate for a technician or other appropriate operator. During the demonstration, the skill level required was confirmed based on vendor input regarding the operation of the device to produce mercury concentration results and observations made in the field. The labor costs were based on: 1) the actual number of hours required to complete all analyses, quality assurance (QA), and reporting; and 2) the assumption that a technician who worked for a portion of a day was paid for an entire 8-hour day.
- The supply costs were based on any supplies required to analyze the field and SRM samples during the demonstration. Supplies consisted of items not included in the capital category, such as extraction

solvent, glassware, pipettes, spatulas, agitators, and similar materials. The type and quantity of all supplies brought to the field and used during the demonstration were noted and documented.

Any maintenance and repair costs during the demonstration were documented or provided by the vendor. Equipment costs were estimated based on this information and standard cost analysis guidelines used in the SITE Program.

- The IDW disposal costs included decontamination fluids and equipment, mercury-contaminated soil and sediment samples, and used sample residues. Contaminated personal protective equipment (PPE) normally used in the laboratory was placed into a separate container. The disposal costs for the IDW were included in the overall analytical costs for each vendor.

After all of the cost categories were estimated, the cost per analysis was calculated. This cost value was based on the number of analyses performed. As the number of samples analyzed increased, the initial capital costs and certain other costs were distributed across a greater number of samples. Therefore, the per unit cost decreased. For this reason, two costs were reported: 1) the initial capital costs and 2) the operating costs per analysis. No comparison to the referee laboratory's method cost was made; however, a generic cost comparison was made. Additionally, when determining laboratory costs, the associated cost for laboratory audits and data validation should be considered.

### 4.2.2 Approach for Addressing Secondary Objectives

Secondary objectives were evaluated based on observations made during the demonstration. Because of the number of vendors involved, technology observers were required to make simultaneous observations of two vendors each during the demonstration. Four procedures were implemented to ensure that these subjective observations made by the observers were as consistent as possible.

First, forms were developed for each of the five secondary objectives. These forms assisted in standardizing the observations. Second, the observers met each day before the evaluations began, at significant break periods, and after each day of work to discuss and compare observations regarding each device. Third, an additional observer was assigned to independently evaluate only the secondary objectives in order to ensure that a consistent approach was applied in evaluating these objectives. Finally, the SAIC TOM circulated among the evaluation staff during the demonstration to ensure that a consistent approach was being followed by all personnel. Table 4-2 summarizes the aspects observed during the demonstration for each secondary objective. The individual approaches to each of these objectives are detailed further in the following subsections.

**Table 4-2. Summary of Secondary Objective Observations Recorded During the Demonstration**

| | SECONDARY OBJECTIVE | | | |
|---|---|---|---|---|
| General Information | Secondary Objective # 1<br>Ease of Use | Secondary Objective # 2<br>H&S Concerns | Secondary Objective # 3<br>Instrument Portability | Secondary Objective # 4<br>Instrument Durability |
| - Vendor Name<br>- Observer Name<br>- Instrument Type<br>- Instrument Name<br>- Model No.<br>- Serial No. | - No. of Operators<br>- Operator Names/Titles<br>- Operator Training<br>- Training References<br>- Instrument Setup Time<br>- Instrument Calibration Time<br>- Sample Preparation Time<br>- Sample Measurement Time | - Instrument Certifications<br>- Electrical Hazards<br>- Chemicals Used<br>- Radiological Sources<br>- Hg Exposure Pathways<br>- Hg Vapor Monitoring<br>- PPE Requirements<br>- Mechanical Hazard<br>- Waste Handling Issues | - Instrument Weight<br>- Instrument Dimensions<br>- Power Sources<br>- Packaging<br>- Shipping & Handling | - Materials of Construction<br>- Quality of Construction<br>- Max. Operating Temp.<br>- Max. Operating Humidity<br>- Downtime<br>- Maintenance Activities<br>- Repairs Conducted |

H&S = Health and Safety
PPE = Personal Protective Equipment

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

The skills and training required for proper device operation were noted; these included any degrees or specialized training required by the operators. This information was gathered by interviews (i.e., questioning) of the operators. The number of operators required was also noted. This objective was also evaluated by subjective observations regarding the ease of equipment use and major peripherals required to measure mercury concentrations in soils and sediments. The operating manual was evaluated to determine if it is easily useable and understandable.

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

Health and safety (H&S) concerns associated with device operation were noted during the demonstration. Criteria included 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 was evaluated, based upon equipment design. Other H&S concerns, such as basic electrical and mechanical hazards, were also noted. Equipment certifications, such as Underwriters Laboratory (UL), were documented.

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

The portability of the device was evaluated by observing transport, measuring setup and tear down time, determining the size and weight of the unit and peripherals, and assessing the ease with which the instrument was repackaged for movement to another location. The use of battery power or the need for an AC outlet was also noted.

#### 4.2.2.4 Secondary Objective #4: Instrument Durability

The durability of each device and major peripherals was assessed by noting the quality of materials and construction. All device failures, routine maintenance, repairs, and downtime were documented during the demonstration. No specific tests were performed to evaluate durability; rather, subjective observations were made using a field form as guidance.

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

The availability of each device was evaluated by determining whether additional units and spare parts are readily available from the vendor or retail stores. The vendor's office (or a web page) and/or a retail store was contacted to identify and determine the availability of supplies of the tested measurement device and spare parts. This portion of the evaluation was performed after the field demonstration, in conjunction with the cost estimate.

## 4.3 Sample Preparation and Management

### *4.3.1 Sample Preparation*

#### 4.3.1.1 Field Samples

Field samples were collected during the pre-demonstration portion of the project, with the ultimate goal of producing a set of consistent test soils and sediments to be distributed among all participating vendors and the referee laboratory for analysis during the demonstration. Samples were collected from the following four sites:

- Carson River Mercury site (near Dayton, NV)
- Y-12 National Security Complex (Oak Ridge, TN)
- Manufacturing facility (eastern U.S.)
- Puget Sound (Bellingham, WA)

The field samples collected during the pre-demonstration sampling events comprised a variety of matrices, ranging from material having a high clay content to material composed mostly of gravelly, coarse sand. The field samples also differed with respect to moisture content; several were collected as wet sediments. Table 4-3 shows the number of distinct field samples that were collected from each of the four field sites.

Prior to the start of the demonstration, the field samples selected for analysis during the demonstration were processed at the SAIC GeoMechanics Laboratory in Las Vegas, NV. The specific sample homogenization procedure used by this laboratory largely depended on the moisture content and physical consistency of the sample. Two specific sample homogenization procedures were developed and tested by SAIC at the GeoMechanics Laboratory during the pre-demonstration portion of the project. The methods included a non-slurry sample procedure and a slurry sample procedure.

A standard operating procedure (SOP) was developed detailing both methods. The procedure was found to be satisfactory, based upon the results of replicate samples during the pre-demonstration. This SOP is included as Appendix A of the *Field Demonstration Quality Assurance Project Plan* (SAIC, August 2003, EPA/600/R-03/053). Figure 4-1 summarizes the homogenization steps of the SOP, beginning with sample mixing. This procedure was

used for preparing both pre-demonstration and demonstration samples. Prior to the mixing process (i.e., Step 1 in Figure 4-1), all field samples being processed were visually inspected to ensure that oversized materials were removed and that there were no clumps that would hinder homogenization. Non-slurry samples were air-dried in accordance with the SOP so that they could be passed multiple times through a riffle splitter. Due to the high moisture content of many of the samples, they were not easily air-dried and could not be passed through a riffle splitter while wet. Samples with very high moisture contents, termed "slurries," were not air-dried, and bypassed the riffle splitting step. The homogenization steps for each type of matrix are briefly summarized as follows.

**Table 4-3. Field Samples Collected from the Four Sites**

| Field Site | No. of Samples / Matrices Collected | Areas For Collecting Sample Material | Volume Required |
|---|---|---|---|
| Carson River | 12 Soil<br>6 Sediment | Tailings Piles (Six Mile Canyon)<br>River Bank Sediments | 4 L each for soil<br>12 L each for sediment |
| Y-12 | 10 Sediment<br>6 Soil | Poplar Creek Sediments<br>Old Mercury Recovery Bldg. Soils | 12 L each for sediment<br>4 L each for soil |
| Manufacturing Site | 12 Soil | Subsurface Soils | 4 L each |
| Puget Sound | 4 Sediment | High-Level Mercury (below cap)<br>Low-Level Mercury (native material) | 12 L each |

**Preparing Slurry Matrices**

For slurries (i.e., wet sediments), the mixing steps were sufficiently thorough that the sample containers could be filled directly from the mixing vessel. There were two separate mixing steps for the slurry-type samples. Each slurry was initially mixed mechanically within the sample container (i.e., bucket) in which the sample was shipped to the SAIC GeoMechanics Laboratory. A subsample of this premixed sample was transferred to a second mixing vessel. A mechanical drill equipped with a paint mixing attachment was used to mix the subsample. As shown in Figure 4-1, slurry samples bypassed the sample riffle splitting step. To ensure all sample bottles contained the same material, the entire set of containers to be filled was submerged into the slurry as a group. The filled vials were allowed to settle for a minimum of two days, and the standing water was removed using a Pasteur pipette. The removal of the standing water from the slurry samples was the only change to the homogenization procedure between the pre-demonstration and the demonstration.

**Preparing "Non-Slurry" Matrices**

Soils and sediments having no excess moisture were initially mixed (Step 1) and then homogenized in the sample riffle splitter (Step 2). Prior to these steps, the material was air-dried and subsampled to reduce the volume of material to a size that was easier to handle. As shown in Figure 4-1 (Step 1), the non-slurry subsample was manually stirred with a spoon or similar equipment until the material was visually uniform. Immediately following manual mixing, the subsample was mixed and split six times for more complete homogenization (Step 2). After the sixth and final split, the sample material was leveled to form a flattened, elongated rectangle and cut into transverse sections to fill the containers (Steps 3 and 4). After homogenization, 20-mL sample vials were filled and prepared for shipment (Step 5).

For the demonstration, the vendor analyzed 197 samples, which included replicates of up to 7 samples per sample lot. The majority of the samples distributed had concentrations within the range of the vendor's technology. Some samples had expected concentrations at or below the estimated level of detection for each of the vendor instruments. These samples were designed to evaluate the reported MDL and PQL and also to assess the prevalence of false positives. Field samples distributed to the vendor included sediments and soils collected from all four sites and prepared by both the slurry and dry homogenization procedures. The field samples were segregated into broad sample sets: low, medium, and high mercury concentrations. This gave the vendor the same general understanding of the sample to be analyzed as they would typically have for field application of their instrument.

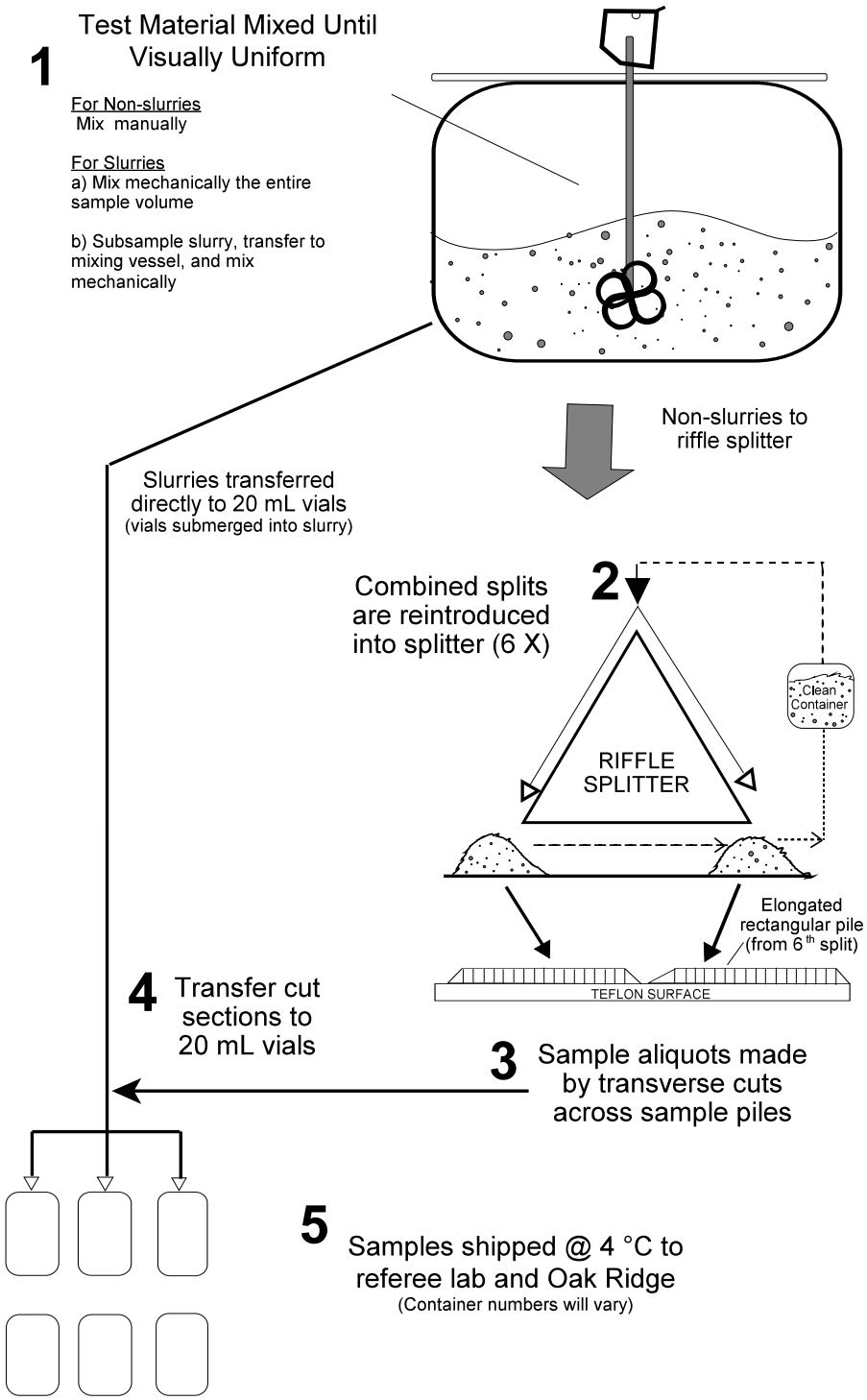


**Figure 4-1. Test sample preparation at the SAIC GeoMechanics Laboratory.**

In addition, selected field samples were spiked with mercury (II) chloride to generate samples with additional concentrations and test the ability of the vendor's instrumentation to measure the additional species of mercury. Specific information regarding the vendor's sample distribution is included in Chapter 6.

#### 4.3.1.2 Standard Reference Materials

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

The SRMs selected were designed to encompass the same contaminant ranges indicated previously: low-, medium-, and high-level mercury concentrations. In addition, SRMs of varying matrices were included in the demonstration to challenge the vendor technology as well as the referee laboratory. The referee laboratory analyzed all SRMs. SRM samples were intermingled with site field samples and labeled in the same manner as field samples.

#### 4.3.1.3 Spiked Field Samples

Spiked field samples were prepared by the SAIC GeoMechanics Laboratory using mercury (II) chloride. Spikes were prepared using field samples from the selected sites. Additional information was gained by preparing spikes at concentrations not previously obtainable. The SAIC GeoMechanics Laboratory's ability to prepare spikes was tested prior to the demonstration and evaluated in order to determine expected variability and accuracy of the spiked sample. The spiking procedure was evaluated by preparing several different spikes using two different spiking procedures (dry and wet). Based upon results of replicate analyses, it was determined that the wet, or slurry, procedure was the only effective method of obtaining a homogeneous spiked sample.

### *4.3.2 Sample Management*

#### 4.3.2.1 Sample Volumes, Containers, and Preservation

A subset from the pre-demonstration field samples was selected for use in the demonstration based on the sample's mercury concentration range and sample type (i.e., sediment versus soil). The SAIC GeoMechanics Laboratory prepared individual batches of field sample material to fill sample containers for each vendor. Once all containers from a field sample were filled, each container was labeled and cooled to 4 °C. Because mercury analyses were to be performed both by the vendors in the field and by the referee laboratory, adequate sample size was taken into account. Minimum sample size requirements for the vendors varied from 0.1 g or less to 8-10 g. Only the referee laboratory analyzed separate sample aliquots for parameters other than mercury. These additional parameters included arsenic, barium, cadmium, chromium, lead, selenium, silver, copper, zinc, oil and grease, and total organic carbon (TOC). Since the mercury method (SW-846 7471B) being used by the referee laboratory requires 1 g for analysis, the sample size sent to all participants was a 20-mL vial (approximately 10 g), which ensured a sufficient volume and mass for analysis by all vendors.

#### 4.3.2.2 Sample Labeling

The sample labeling used for the 20-mL vials consisted of an internal code developed by SAIC. This "blind" code was used throughout the entire demonstration. The only individuals who knew the key to the coding of the homogenized samples to the specific field samples were the SAIC TOM, the SAIC GeoMechanics Laboratory Manager, and the SAIC QA Manager.

#### 4.3.2.3 Sample Record Keeping, Archiving, and Custody

Samples were shipped to the laboratory and the demonstration site the week prior to the demonstration. A third set of vials was archived at the SAIC GeoMechanics Laboratory as reserve samples.

The sample shipment to Oak Ridge was retained at all times in the custody of SAIC at their Oak Ridge office until arrival of the demonstration field crew. Samples were shipped under chain-of-custody (COC) and with custody seals on both the coolers and the inner plastic bags. Once the demonstration crew arrived, the coolers were retrieved from the SAIC office. The custody seals on the plastic bags inside the cooler were broken by the vendor upon transfer.

Upon arrival at the ORNL site, the vendor set up the instrumentation at the direction and oversight of SAIC. At the start of sample testing, the vendor was provided with a sample set representing field samples collected from a particular field site, intermingled with SRM and spiked samples. Due to variability of vendor instrument

measurement ranges for mercury detection, not all vendors received samples from the same field material. All samples were stored in an ice cooler prior to demonstration startup and were stored in an on-site sample refrigerator during the demonstration. Each sample set was identified and distributed as a set with respect to the site from which it was collected. This was done because, in any field application, the location and general type of the samples would be known.

The vendor was responsible for analyzing all samples provided, performing any dilutions or reanalyses as needed, calibrating the instrument if applicable, performing any necessary maintenance, and reporting all results. Any samples that were not analyzed during the day were returned to the vendor for analysis at the beginning of the next day. Once analysis of the samples from the first location were completed by the vendor, SAIC provided a set of samples from the second location. Samples were provided at the time that they were requested by the vendor. Once again, the transfer of samples was documented using a COC form.

This process was repeated for samples from each location. SAIC maintained custody of all remaining sample sets until they were transferred to the vendor. SAIC maintained custody of samples that already had been analyzed and followed the waste handling procedures in Section 4.2.2 of the Field Demonstration QAPP to dispose of these wastes.

## 4.4 Reference Method Confirmatory Process

The referee laboratory analyzed all samples that were analyzed by the vendor technologies in the field. The following subsections provide information on the selection of the reference method, selection of the referee laboratory, and details regarding the performance of the reference method in accordance with EPA protocols. Other parameters that were analyzed by the referee laboratory are also discussed briefly.

### *4.4.1 Reference Method Selection*

The selection of 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 1-2 summarizes the methods evaluated, as identified through a review of the EPA Test Method Index and SW-846).

In selecting which of the potential methods would be suitable as a reference method, consideration was given to the following questions:

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

Based on the above considerations, it was determined that SW-846 Method 7471B [analysis of mercury in solid samples by cold-vapor atomic absorption spectrometry (AAS)] would be the best reference method. SW-846 method 7474, (an atomic fluorescence spectrometry method using Method 3052 for microwave digestion of the solid) had also been considered a likely technical candidate; however, because this method was not as widely used or referenced, Method 7471B was considered the better choice.

### *4.4.2 Referee Laboratory Selection*

During the planning of the pre-demonstration phase of this project, nine laboratories were sent a statement of work (SOW) for the analysis of mercury to be performed as part of the pre-demonstration. Seven of the nine laboratories responded to the SOW with appropriate bids. 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. 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: 1) the laboratory's interest in continuing in the demonstration, 2) the laboratory-reported SRM results, 3) the laboratory MDL for the reference method selected, 4) the precision of the laboratory calibration curve, 5) the laboratory's ability to support the demonstration (scheduling conflicts, backup instrumentation, etc.), and 6) cost.

One of the three candidate laboratories was eliminated from selection based on a technical consideration. It was determined that this laboratory would not be able to meet demonstration quantitation limit requirements. (Its lower calibration standard was approximately 50 µg/kg and the vendor comparison requirements were well below this value.) Two candidates thus remained, including the eventual demonstration laboratory, Analytical Laboratory Services, Inc. (ALSI):

Analytical Laboratory Services, Inc.
Ray Martrano, Laboratory Manager
34 Dogwood Lane
Middletown, PA 17057
(717) 944-5541

In order to make a final decision on selecting a referee laboratory, a preliminary audit was performed by the SAIC QA Manager at the remaining two candidate laboratories. 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% CI for the SRM.

Calibration curves from each laboratory were reviewed carefully. This included calibration curves generated from previously performed analyses and those generated for other laboratory clients. There were two QC requirements regarding calibration curves; the correlation coefficient had to be 0.995 or greater and the lowest point on the calibration curve had to 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, an analysis of seven standards was reviewed for MDLs. Both laboratories were able to achieve an MDL that was below 1 µg/kg.

It should be noted that vendor sensitivity claims impacted how low this lower quantitation standard should be. These claims were somewhat vague, and the actual quantitation limit each vendor could achieve was uncertain prior to the demonstration (i.e., some vendors claimed a sensitivity as low as 1 µg/kg, but it was uncertain at the time if this limit was actually a PQL or a detection limit). Therefore, it was determined that, if necessary, the laboratory actually should be able to achieve even a lower PQL than 10 µg/kg.

For both laboratories, SOPs based upon SW-846 Method 7471B were reviewed. Each SOP followed this reference method. In addition, interferences were discussed because there was some concern that organic interferences may have been 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 how these interferences would be eliminated. This is discussed at the end of this subsection.

Sample throughput was somewhat important because the selected laboratory was to receive all demonstration samples at the same time (i.e., the samples were to be analyzed at the same time in order to eliminate any question of variability associated with loss of contaminant due to holding time). This meant that the laboratory would receive approximately 400 samples for analysis over the period of a few days. 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 used a Leeman mercury analyzer for analysis. One of the two laboratories had backup instrumentation in case of problems. Each laboratory indicated that its 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 they have previously participated in the program. A second aspect of the SITE program is that it generally requires analysis of relatively "dirty" samples and many laboratories are not use to analyzing such "dirty" samples. Both laboratories have been longtime participants in this program.

Other QC-related issues examined during the audits included 1) analyses of other SRM samples not previously examined, 2) laboratory control charts, and 3) precision

and accuracy results. Each of these issues was closely examined. Also, because of the desire to increase the representativeness of the samples for the demonstration, each laboratory was asked if sample aliquot sizes could be increased to 1 g (the method requirement noted 0.2 g). Based upon previous results, both laboratories routinely increased sample size to 0.5 g, and each laboratory indicated that increasing the sample size would not be a problem. Besides these QC issues, 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.

**Selection Summary**

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

- ALSI had backup instrumentation available. Even though neither laboratory reported any problems with its primary instrument (the Leeman mercury analyzer), ALSI did have a backup 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 the vendor was able to analyze at concentrations as low as 1 µg/kg with precise and accurate determinations, ALSI was able to perform analyses at lower concentrations as part of the demonstration. ALSI used a second, lower calibration curve for any analyses required below 0.05 mg/kg. Very few vendors were able to analyze samples at concentrations at this low a level.
- Management practices and analyst experience were similar at both laboratories. ALSI had participated in a few more SITE demonstrations than the other laboratory, but this difference was not significant because both laboratories had proven themselves capable of handling the additional QC requirements for the SITE program. In addition, both laboratories had internal QA management procedures to provide the confidence needed to achieve SITE requirements.
- Interferences for the samples previously analyzed were discussed and data were reviewed. ALSI performed two separate analyses for each sample. This included analyses with and 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, an analysis 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 reviewed indicated 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 was chosen as the referee laboratory for the demonstration.

### *4.4.3 Summary of Analytical Methods*

#### 4.4.3.1 Summary of Reference Method

The critical measurement for this study was the analysis of mercury in soil and sediment samples. Samples analyzed by the laboratory included field samples, spiked field samples, and SRM samples. Detailed laboratory procedures for subsampling, extraction, and analysis were provided in the SOPs included as Appendix B of the Field Demonstration QAPP. These are briefly summarized below.

Samples were 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 stripped/volatilized from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of the AA 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 at 254 nm. Free chlorine is removed by using an excess (25 mL) of hydroxylamine sulfate reagent. Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary analysis without reagents can determine if this type of interference is present.

Prior to analysis, the contents of the sample container are 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 biochemical 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. An analysis without stannous chloride is also included as an interference check when organic contamination is suspected. In the event of positive results of the non-stannous chloride analysis, the laboratory was to report those results to SAIC so that a determination of organic interferences could be made.

#### 4.4.3.2 Summary of Methods for Non-Critical Measurements.

A selected set of non-critical parameters was also measured during the demonstration. These parameters were measured to provide a better insight into the chemical constituency of the field samples, including the presence of potential interferents. The results of the tests for potential interferents were reviewed to determine if a trend was apparent in the event that inaccuracy or low precision was observed. Table 4-4 presents the analytical method reference and method type for these non-critical parameters.

**Table 4-4. Analytical Methods for Non-Critical Parameters**

| Parameter | Method Reference | Method Type |
|---|---|---|
| Arsenic, barium, cadmium, chromium, lead, selenium, silver, copper, and zinc | SW-846 3050/6010 | Acid digestion, ICP |
| Oil and Grease | EPA 1664 | n-Hexane extraction, Gravimetric analysis |
| TOC | SW-846 9060 | Carbonaceous analyzer |
| Total Solids | EPA 2540G | Gravimetric |

## 4.5 Deviations from the Demonstration Plan

Three deviations to the demonstration plan occurred. The first was that the demonstration was to be conducted in Oak Ridge, TN, on May 5-8, 2003. On the morning of May 6, MTI was able to confirm, through the analyses of standards, that the obtained results were erroneous. While several possibilities existed as to why erroneous results were being generated, the exact reason could not be determined and corrected in time to complete the analyses during the scheduled demonstration. Several discussions ensued between the EPA TOM, SAIC personnel on-site, and MTI personnel. These discussions resulted in an agreement that if the cause of the erroneous results could be identified and a new location and date could be arranged, then MTI would be given a second attempt at the demonstration.

During the following weeks, MTI traced the source of the problem to disposable beakers that were used in the analyses. The beakers had an oil film in them that gradually coated the electrodes, preventing accurate readings. In order to correct the problem, MTI disposed of the beakers in stock, and added to the operating procedure a sodium hydroxide rinse between samples that prevented the buildup of residues on the electrodes.

While in Oak Ridge, MTI only received samples from the Oak Ridge sampling site. None of the results from this first demonstration are presented or discussed in this ITVR. All samples were collected from MTI and returned to the SAIC GeoMechanics Laboratory for storage purposes. Samples

that were opened by MTI were replaced with unopened sample bottles held in reserve by SAIC, when available.

The second demonstration for MTI was held in Las Vegas, NV, June 14-17, 2003.

A second and third deviation occurred in the distribution of the samples (second deviation) and an unforeseen and unrelated emergency (third deviation). The intent in the demonstration plan was to give the samples from one sampling site to the vendors and, when that sample set was completed, the next sample set would be given to the vendor. This process was repeated until all four sample sets were completed by the vendor. MTI's two personnel on-site divided the workload into two parts. The first individual extracted the samples and the second individual analyzed the samples with the PDV 6000. When the extraction of the first set of samples was completed, the second set of samples was given to MTI for extraction. The extraction was faster than the analysis; therefore, the first individual completed all of the extractions in two days. The second individual completed the analyses in three days. This was complicated by an unrelated emergency, which prevented any work from being performed on the third day at the site; therefore, no sample preparation or analyses were performed on June 16. All samples were prepared June 14-15. Sample analyses were completed June 14, 15, and 17. MTI personnel are unsure as to whether the one day delay would have any effect on results; however, it is common practice to analyze low concentration mercury samples as soon as possible upon preparation.

# Chapter 5
# Assessment of Laboratory Quality Control Measurements

## 5.1 Laboratory QA Summary

QA may be defined as a system of activities, the purpose of which is to provide assurance that defined standards of quality are met with a stated level of confidence. A QA program is a means of integrating the quality planning, quality assessment, QC, and quality improvement efforts to meet user requirements. The objective of the QA program is to reduce measurement errors to agreed-upon limits, and to produce results of acceptable and known quality. The QAPP specified the necessary guidelines to ensure that the measurement system for laboratory analysis was in control, and provided detailed information on the analytical approach to ensure that data of high quality could be obtained to achieve project objectives. The laboratory analyses were critical to project success, as the laboratory results were used as a standard for comparison to the field method results. The field methods are of unknown quality, and therefore, for comparison purposes the laboratory analysis needed to be a known quantity. The following sections provide information on the use of data quality indicators, and a detailed summary of the QC analyses associated with project objectives.

## 5.2 Data Quality Indicators for Mercury Analysis

To assess the quality of the data generated by the referee laboratory, two important data quality indicators of primary concern are precision and accuracy. Precision can be defined as the degree of mutual agreement of independent measurements generated through repeated application of the process under specified conditions. Accuracy is the degree of agreement of a measured value with the true or expected value. Both accuracy and precision were measured by the analysis of matrix spike/matrix spike duplicates (MS/MSDs). The precision of the spiked duplicates is evaluated by expressing, as a percentage, the difference between results of the sample and sample duplicate results. The relative percent difference (RPD) is calculated as:

$$RPD = \frac{(\text{Maximum Value} - \text{Minimum Value})}{(\text{Maximum Value} + \text{Minimum Value})/2} \times 100$$

To determine and evaluate accuracy, known quantities of the target analytes were spiked into selected field samples. All spikes were post-digestion spikes because of the high sample concentrations encountered during the demonstration. Pre-digestion spikes, on high-concentration samples would either have been diluted or would have required additional studies to determine the effect of spiking more analyte and subsequent recovery values. To determine matrix spike recovery, and hence measure accuracy, the following equation was applied:

$$\%R = \frac{C_{ss} - C_{us}}{C_{sa}} \times 100$$

where,

| | | |
|---|---|---|
| $C_{ss}$ | = | Analyte concentration in spiked sample |
| $C_{us}$ | = | Analyte concentration in unspiked sample |
| $C_{sa}$ | = | Analyte concentration added to sample |

Laboratory control samples (LCSs) were used as an additional measure of accuracy in the event of significant

matrix interference. To determine the percent recovery of LCS analyses, the equation below was used:

$$\%R = \frac{\text{Measured Concentration}}{\text{Theoretical Concentration}} \times 100$$

While several precautions were taken to generate data of known quality through control of the measurement system, the data must also be representative of true conditions and comparable to separate sample aliquots. Representativeness refers to the degree with which analytical results accurately and precisely reflect actual conditions present at the locations chosen for sample collection. Representativeness was evaluated as part of the pre-demonstration and combined with the precision measurement in relation to sample aliquots. Sample aliquoting by the SAIC GeoMechanics Laboratory tested the ability of the procedure to produce homogeneous, representative, and comparable samples. All samples were carefully homogenized in order to ensure comparability between the laboratory and the vendor. Therefore, the RSD measurement objective of 25% or less for replicate sample lot analysis was intended to assess not only precision but representativeness and comparability.

Sensitivity was another critical factor assessed for the laboratory method of analysis. This was measured as a practical quantitation limit and was determined by the low standard on the calibration curve. Two separate calibration curves were run by the laboratory when necessary. The higher calibration curve was used for the majority of the samples and had a lower calibration limit of 25 µg/kg. The lower calibration curve was used when samples were below this lower calibration standard. The lower calibration curve had a lower limit standard of 5 µg/kg. The lower limit standard of the calibration curve was run with each sample batch as a check standard and was required to be within 10% of the true value (QAPP QC requirement). This additional check on analytical sensitivity was performed to ensure that this lower limit standard was truly representative of the instrument and method practical quantitation limit.

## 5.3 Conclusions and Data Quality Limitations

Critical sample data and associated QC analyses were reviewed to determine whether the data collected were of adequate quality to provide proper evaluation of the project's technical objectives. The results of this review are summarized below.

Accuracy objectives for mercury analysis by Method 7471B were assessed by the evaluation of 23 spiked duplicate pairs, analyzed in accordance with standard procedures in the same manner as the samples. Recovery values for the critical compounds were well within objectives specified in the QAPP, except for two spiked samples summarized in Table 5-1. The results of these samples, however, were only slightly outside specified limits, and given the number of total samples (46 or 23 pairs), this is an insignificant number of results that did not fall within specifications. The MS/MSD results therefore, are supportive of the overall accuracy objectives.

**Table 5-1. MS/MSD Summary**

| Parameter | Value |
|---|---|
| QC Limits | 80%- 120% |
| Recovery Range | 85.2% - 126% |
| Number of Duplicate Pairs | 23 |
| Average Percent Recovery | 108% |
| No. of Spikes Outside QC Specifications | 2 |

An additional measure of accuracy was LCSs. These were analyzed with every sample batch (1 in 20 samples) and results are presented in Table 5-2. All results were within specifications, thereby supporting the conclusion that QC assessment met project accuracy objectives.

**Table 5-2. LCS Summary**

| Parameter | Value |
|---|---|
| QC Limits | 90%- 110% |
| Recovery Range | 90% - 100% |
| Number of LCSs | 24 |
| Average Percent Recovery | 95.5% |
| No. of LCSs Outside QC Specifications | 0 |

Precision was assessed through the analysis of 23 duplicate spike pairs for mercury. Precision specifications were established prior to the demonstration as a RPD less

than 20%. All but two sample pairs were within specifications, as noted in Table 5-3. The results of these samples, however, were only slightly outside specified limits, and given the number of total samples (23 pairs), this is an insignificant number of results that did not fall within specifications. Therefore, laboratory analyses met precision specifications.

**Table 5-3. Precision Summary**

| Parameter | Value |
|---|---|
| QC Limits | RPD< 20% |
| MS/MSD RPD Range | 0.0% to 25% |
| Number of Duplicate Pairs | 23 |
| Average MS/MSD RPD | 5.7% |
| No. of Pairs Outside QC Specifications | 2 |

Sensitivity results were within specified project objectives. The sensitivity objective was evaluated as the PQL, as assessed by the low standard on the calibration curve. For the majority of samples, a calibration curve of 25-500 µg/kg was used. This is because the majority of samples fell within this calibration range (samples often required dilution). There were, however, some samples below this range and a second curve was used. The calibration range for this lower curve was 5-50 µg/kg. In order to ensure that the lower concentration on the calibration curve was a true PQL, the laboratory ran a low check standard (lowest concentration on the calibration curve) with every batch of samples. This standard was required to be within 10% of the specified value. The results of this low check standard are summarized in Table 5-4.

**Table 5-4. Low Check Standards**

| Parameter | Value |
|---|---|
| QC Limits | Recovery 90% - 110% |
| Recovery Range | 88.6% - 111% |
| Number of Check Standards Analyzed | 23 |
| Average Recovery | 96% |

There were a few occasions where this standard did not meet specifications. The results of these samples, however, were only slightly outside specified limits, and given the number of total samples (23), this is an insignificant number of results that did not fall within specifications. In addition, the laboratory reanalyzed the standard when specifications were not achieved, and the second determination always fell within the required limits. Therefore laboratory objectives for sensitivity were achieved according to QAPP specifications.

As noted previously, comparability and representativeness were assessed through the analysis of replicate samples. Results of these replicates are presented in the discussion on primary project objectives for precision. These results show that data were within project and QA objectives.

Completeness objectives were achieved for the project. All samples were analyzed and data were provided for 100% of the samples received by the laboratory. No sample bottles were lost or broken.

Other measures of data quality included method blanks, calibration checks, evaluation of linearity of the calibration curve, holding time specifications, and an independent standard verification included with each sample batch. These results were reviewed for every sample batch run by ALSI, and were within specifications. In addition, 10% of the reported results were checked against the raw data. Raw data were reviewed to ensure that sample results were within the calibration range of the instrument, as defined by the calibration curve. A 6-point calibration curve was generated at the start of each sample batch of 20. A few data points were found to be incorrectly reported. Recalculations were performed for these data, and any additional data points that were suspected outliers were checked to ensure correct results were reported. Very few calculation or dilution errors were found. All errors were corrected so that the appropriate data were reported.

Another measure of compliance were the non-stannous chloride runs performed by the laboratory for every sample analyzed. This was done to check for organic interference. There were no samples that were found to have any organic interference by this method. Therefore, these results met expected QC specifications and data were not qualified in any fashion.

Total solids data were also reviewed to ensure that calculations were performed appropriately and dry weights reported when required. All of these QC checks met

QAPP specifications. In summary, all data quality indicators and QC specifications were reviewed and found to be well within project specifications. Therefore, the data are considered suitable for purposes of this evaluation.

## 5.4 Audit Findings

The SAIC SITE QA Manager conducted audits of both field activities and of the subcontracted laboratory as part of the QA measures for this project. The results of these technical system reviews are discussed below.

The field audit resulted in no findings or non-conformances. The audit performed at the subcontract laboratory was conducted during the time of project sample analysis. One non-conformance was identified and corrective action was initiated. It was discovered that the laboratory PQL was not meeting specifications due to a reporting error. The analyst was generating the calibration curves as specified above; however, the lower limit on the calibration curve was not being reported. This was immediately rectified and no other findings or non-conformances were identified.

# Chapter 6
# Performance of the PDV 6000

MTI analyzed samples on May 5-6, 2003 in Oak Ridge, TN. As discussed in Section 4.5, on the morning of May 6, MTI determined through the analyses of standards that the results they were obtaining were erroneous. A second demonstration was performed in Las Vegas from June 14-17, 2003, and it proved successful in accomplishing the specified objectives. The observations conducted as part of this second attempt at the demonstration were reviewed, and the primary and secondary objectives were completed. The results of the primary and secondary objectives, identified in Chapter 1, are discussed in Sections 6.1 and 6.2, respectively.

Due to an unrelated emergency during the second demonstration, analysis activities were not able to be performed on June 16. For this reason, samples that were analyzed on June 17 had been extracted on June 15, and stored in plastic bottles. This may have resulted in a reduced mercury concentration in the extract, especially for low concentration samples. The extracts that remained for analysis on June 17 were from low concentration samples. There was, however, no additional study performed to determine if time elapsed between extraction and analysis influenced mercury concentrations, and it is believed that this short time period was not significant in the overall evaluation of results.

The distribution of the samples prepared for MTI and the referee laboratory is presented in Table 6-1. From the four sites, MTI received samples at 36 different concentrations for a total of 197 samples. These 197 samples consisted of 22 concentrations in replicates of 7, 13 concentrations in replicates of 3, and 1 concentration in a replicate of 4. Although all these samples were analyzed by MTI, a few samples were not used as part of the evaluation. Some sample results were judged invalid by MTI field personnel and some were found to be below MTI's detection limit, as explained in more detail in the following sections.

**Table 6-1. Distribution of Samples Prepared for MTI and the Referee Laboratory**

| Site | Concentration Range | Sample Type | | | |
|---|---|---|---|---|---|
| | | Soil | Sediment | Spiked Soil | SRM |
| Carson River | Low (1-500 ppb) | 3 | 10 | 7 | 0 |
| (Subtotal = 48) | Mid (0.5-50 ppm) | 0 | 0 | 0 | 7 |
| | High (50->1,000 ppm) | 0 | 0 | 7 | 14 |
| Puget Sound | Low (1 ppb - 10 ppm) | 13 | 0 | 7 | 3 |
| (Subtotal = 51) | High (10-500 ppm) | 0 | 10 | 7 | 11 |
| Oak Ridge | Low (0.1-10 ppm) | 0 | 3 | 0 | 14 |
| (Subtotal = 54) | High (10-800 ppm) | 13 | 10 | 0 | 14 |
| Manufacturing (Subtotal = 44) | General (5-1,000 ppm) | 23 | 0 | 7 | 14 |
| Subtotal (Total = 197) | | 52 | 33 | 35 | 77 |

## 6.1 Primary Objectives

### *6.1.1 Sensitivity*

Sensitivity objectives are explained in Chapter 4. The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Determinations of these two measurements are explained in the paragraphs below, along with a comparison to the referee laboratory. These determinations set the standard for the evaluation of accuracy and precision for the MTI field instrument. Any sample analyzed by MTI and subsequently reported as below their level of detection was not used as part of any additional evaluations. This was done because of the expectation that values below the lower limit of instrument sensitivity would not reflect the true instrument accuracy and precision.

The sensitivity measurements of MDL and PQL are both dependent upon the matrix and method. Hence, the MDL and PQL will vary, depending upon whether the matrix is a soil, waste, or water. Only soils and sediments were tested during this demonstration and, therefore, MDL calculations for this evaluation reflect soil and sediment matrices. PQL determinations are not independent calculations, but are dependent upon results provided by the vendor for the samples they tested.

Comparison of the MDL and PQL to laboratory sensitivity required that a standard evaluation be performed for all instruments tested during this demonstration. PQL, as previously noted, is defined in EPA G-5i as the lowest level of method and instrument performance with a specified accuracy and precision. This is often defined by the lowest point on the calibration curve. Our approach was to let the vendor provide the lower limit of quantitation as determined by their particular standard operating procedure, and then test this limit by comparing results of samples analyzed at this low concentration to the referee laboratory results, or comparing the results to a standard reference material, if available. Comparison of these data are, therefore, presented for the lowest concentration sample results, as provided by the vendor. If the vendor provided "non-detect" results, then no formal evaluation of that sample was presented. In addition, the sample(s) was not used in the evaluation of precision and accuracy.

**Method Detection Limit** – The standard procedure for determining MDLs is to analyze a low standard or reference material seven times, calculate the standard deviation, and multiply the standard deviation by the "t" value for seven measurements at the 99$^{th}$ percentile (alpha = 0.01). (This value is 3.143, as determined from a standard statistics table.) This procedure for determination of an MDL is defined in 40 CFR Part 136, and while determinations for MDLs may be defined differently for other instruments, this method was previously noted in the demonstration QAPP and is intended to provide a comparison to other MDL evaluations. The purpose is to provide a lower level of detection with a statistical confidence at which the instrument will detect the presence of a substance above its noise level. There is no associated accuracy or precision determined or implied.

Several blind standards and field samples were provided to MTI at their estimated lower limit of sensitivity. The MTI lower limit of sensitivity was previously estimated at 0.100 mg/kg. Because there are several different SRMs and field samples at concentrations close to the MDL, evaluation of the MDL was performed using more than a single concentration. Samples chosen for calculation were based upon: 1) concentration and how close it was to the estimated MDL, 2) number of analyses performed for the same sample (e.g., more than 4), and 3) if non-detects were reported by MTI for a sample used to calculate the MDL. Then the next highest concentration sample was selected based upon the premise that a non-detect result reported for one of several samples indicates the selected sample is on the "edge" of the instruments detection capability.

Seven replicates were analyzed by MTI of a sample for which the laboratory reported an average concentration of 0.734 mg/kg. (Sample lot 57 from the Puget Sound site.) The average concentration reported by MTI for this sample was 1.58 mg/kg, and the standard deviation was 1.17 mg/kg. An SRM with a reference value of 0.62 mg/kg (sample lot 38) was analyzed seven times by MTI, with a reported average concentration of 2.71 mg/kg and a standard deviation of 0.632 mg/kg. Calculations of the respective MDLs based upon each of these standards are 3.67 and 1.99 mg/kg.

As a further check of the MDL, both MTI and the referee laboratory analyzed sample lot 56 from the Carson River samples. The referee laboratory reported an average concentration of 0.231 mg/kg, and MTI reported "non-detect" for 6 of 7 replicates analyzed. This confirms that the MTI field instrument sensitivity is above this sample concentration. The referee laboratory reported a concentration of 0.811 mg/kg for sample lot 11 (from the Puget Sound samples), while MTI reported an average concentration of 3.15 mg/kg for three replicate analyses, with a standard deviation of 1.96 mg/kg. Therefore, it appears that the method detection limit for this instrument

is between 0.231 and 0.811 mg/kg. Also, based on results from sample lots 57 and 38 (noted above in the MDL calculation), there is additional evidence that sample concentrations in this range can be detected but not accurately quantitated by the MTI field instrument. The referee laboratory reported an average value of 0.06 mg/kg for sample lot 2 from the Puget Sound site, while the MTI average value for seven separate results was 1.61 mg/kg, with a standard deviation of 0.534 mg/kg. While this is 2 orders of magnitude above the value reported by the referee laboratory, it does indicate that, for this sample, MTI was able to detect a much lower concentration than indicated by the MDL calculations noted above. Therefore, MTI instrumentation is sometimes able to detect lower concentrations of mercury, but this appears to be inconsistent based on the results for sample lot 56 (referee laboratory measured value of 0.231 mg/kg) that resulted primarily in reported data as "non-detects." This apparent difference in the MDL is probably attributable to the fact that, when analyzing samples on the PDV 6000, the operator selects a concentration, based upon the expected sample set concentration range, and prepares and analyzes a standard at the selected concentration.

The MDL is between 1.67 and 3.67 mg/kg. This calculation, however, did not prove accurate for instrument/method sensitivity. As noted by the results above, the MTI field instrument was able to detect concentrations well below this calculated value. It should be noted, however, that in one sample MTI detected mercury at 0.06 mg/kg (as determined by the referee laboratory result), but in another sample it was unable to detect mercury at 0.231 mg/kg. The reason for this discrepancy is unknown. It should be concluded, however, that values below 0.811 mg/kg may or may not be detected by the MTI field instrument and that these values, if detected, would likely be highly inaccurate and should only be considered as a "positive hit" and do not represent a value that is close to the true concentration.

**Practical Quantitation Limit** – This value is usually calculated by determining a low standard on the instrument calibration curve, and it is estimated as the lowest standard at which the instrument will accurately and precisely determine a given concentration within specified QC limits. The PQL is often around 5-10 times the MDL. This PQL estimation, however, is method- and matrix- dependent. In order to determine the PQL, several low standards were provided to MTI and subsequent %Ds were calculated.

The lower limit of sensitivity previously provided by the vendor (0.10 mg/kg) appears to be an inaccurate estimate of instrument sensitivity, but, as noted above, sometimes the MTI field instrument may be able to detect values close to this lower concentration. If one considers the MDL around 0.8 mg/kg, then the PQL could be between 4 and 8 mg/kg. This, however, is only an estimate. The relationship between sensitivity and precision is such that the lower the concentration, the higher the variation in reported sample results. The PQL should have a precision and accuracy that match the instrument capabilities within a certain operating range of analysis.

Values in the range between 4 and 8 mg/kg were chosen for estimating the PQL and associated %D between the MTI reported average and the reference value if it is an SRM or the average value reported by the referee laboratory. Also compared are the 95% CIs for additional descriptive information. In addition, values below the estimated value of 4 mg/kg are included to determine if the instrument capabilities can provide an even lower PQL.

Sample lot 14 (Oak Ridge site) has an average value of 4.75 mg/kg reported by the referee laboratory, with a standard deviation of 1.31 mg/kg. The 95% CI for this sample is 3.38 to 6.12 mg/kg. The MTI average value is 6.95 mg/kg, which is just outside the range of the 95% CI. The %D between this value and that obtained from the referee laboratory is 46.3%.

Sample lot 57 (Puget Sound) has an average value of 0.734 mg/kg reported by the referee laboratory, with a standard deviation of 0.119 mg/kg. The 95% CI for this sample is 0.624 to 0.844 mg/kg. The MTI average value is 1.58 mg/kg, which is outside the range of the 95% CI. The %D between this value and that of the referee laboratory is 115%.

These results suggest that the instrument PQL is 4-8 mg/kg. Given the information associated with the MDL determination, the PQL is probably above the MDL range noted previously as between 1.67 and 3.67 mg/kg.

**Sensitivity Summary**

The low standard calculations suggest that a PQL for the MTI field instrument is 4-8 mg/kg. The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg. The %D for the average MTI result for the sample concentration of 4.75 mg/kg is 46%. The range for the calculated MDL is between 1.67 and 3.67 mg/kg, based on the results of seven replicate analyses for low standards. The equivalent MDL for the referee laboratory is 0.0026 mg/kg. The MDL determination, however, is only a statistical calculation that has been used in the past by EPA and is currently not considered a "true" MDL by

SW-846 methodology. SW-846 is suggesting that performance-based methods be used and that PQLs be determined using low standard calculations.

More definitive information for the PQL is unavailable because additional standards in the calculated range of the PQL are not available. Vendor estimations of the PQL were actually much lower than determined during the demonstration; therefore, several lower standards below MTI's PQL were provided for analysis (see accuracy tables below) and subsequently, additional standards or samples in the actual PQL range were not tested.

### *6.1.2 Accuracy*

Accuracy is the instrument measurement compared to a standard or true value. For this demonstration, three separate standards were used for determining accuracy. The primary standard is SRMs. The SRMs are traceable to national systems. These were obtained from reputable suppliers with reported concentration and an associated 95% CI and 95% prediction interval. The CI from the reference material is used as a measure of comparison with the CI calculated from replicate analyses for the same sample analyzed by the laboratory or vendor. Results are considered comparable if CIs of the SRM overlap with the CIs computed from the replicate analyses by the vendor. While this is not a definitive measure of comparison, it provides some assurance that the two values are equivalent.

Prediction intervals are intended as a measure of comparison for a single laboratory or vendor result with the SRM. When computing a prediction interval, the equation assumes an infinite number of analyses, and it is used to compare individual sample results. A 95% prediction interval would, therefore, predict the correct result from a single analysis 95% of the time for an infinite number of samples, if the result is comparable to that of the SRM. It should be noted that the corollary to this statement is that 5% of the time a result will be outside the prediction interval if determined for an infinite number of samples. If several samples are analyzed, the percentage of results within the prediction interval will be slightly above or below 95%. The more samples analyzed, the more likely the percentage of correct results will be close to 95% if the result for the method being tested is comparable to the SRM.

All SRMs were analyzed in replicates of three or seven by both the vendor and by the referee laboratory. In some instances, analyses performed by the vendor were determined to be invalid measurements and were, therefore, not included with the reported results. There were 9 different SRMs analyzed by both the vendor and the laboratory, for a total of 53 data points by the vendor and 63 data points by the laboratory. One SRM (sample lot 44) was not included because 6 of 7 analyses performed by the vendor were judged to be invalid, and this would not provide a sufficient number of analyses for comparison.

The second accuracy determination used a comparison of vendor results of field samples and SRMs to the referee laboratory results for these same samples. Field samples were used to ensure that "real-world" samples were tested for each vendor. The referee laboratory result is considered as the standard for comparison to the vendor result. This comparison is in the form of a hypothesis test with alpha = 0.01. (Detailed equations along with additional information about this statistical comparison is included in Appendix B.)

It should be noted that a laboratory bias is evident. This bias was determined by comparing average laboratory values to SRM reference values and is discussed below. The laboratory bias is low in comparison to the reference value. A bias correction was not made when comparing individual samples (replicate analyses) between the laboratory and vendor; however, setting alpha = 0.01 helps mitigate for this possible bias by widening the range of acceptable results between the two data sets.

An aggregate analysis, or unified hypothesis test, was also performed for all 32 sample lots. (A detailed discussion of this statistical comparison is included in Appendix B.) This analysis provides additional statistical evidence in relation to the accuracy evaluation. A bias term is included in this calculation in order to account for the laboratory data bias previously noted.

The third measure of accuracy is obtained by the analysis of spiked field samples. These were analyzed by the vendor and the laboratory in replicate in order to provide additional measurement comparisons and are treated in the same manner as the other field samples. Spikes were prepared to cover additional concentrations not available from SRMs or field samples. There is no comparison to the spiked concentration, only a comparison between the vendor and the laboratory reported value.

The purpose for SRM analyses 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 ensure that a competent laboratory would be used for the demonstration. The pre-demonstration laboratory qualification showed that the laboratory was within

prediction intervals for all SRMs analyzed. Because of the need to provide confidence in laboratory analysis during the demonstration, the referee laboratory also analyzed SRMs as an ongoing check of laboratory bias. As noted in Table 6-3, not all laboratory results were within the prediction interval. This is discussed in more detail below. All laboratory QC checks, however, were found to be within compliance (see Chapter 5).

Evaluation of vendor and laboratory analysis of SRMs is performed in the following manner. Accuracy was determined by comparing the 95% CI of the sample analyzed by the vendor and laboratory to the 95% CI for the SRM. (95% CIs around the true value are provided by the SRM supplier.) This is provided in Tables 6-2 and 6-3, with notations when the CIs overlap, suggesting comparable results. In addition, the number of SRM results for the vendor's analytical instrumentation and the referee laboratory that are within the associated 95% prediction interval are reported. This is a more definitive evaluation of laboratory and vendor accuracy. The percentage of total results within the prediction interval for the vendor and laboratory are reported in Tables 6-2 and 6-3, respectively.

**Table 6-2. MTI SRM Comparison**

| Sample Lot No. | SRM Value/ 95% CI | MTI Avg./ 95% CI | CI Overlap (yes/no) | No. of Samples Analyzed | 95% Prediction Interval | MTI No. w/in Prediction Interval |
|---|---|---|---|---|---|---|
| 37 | 0.158 / 0.132 - 0.184 | 2.12 / 0.767 - 3.47 | no | 6 | 0 - 0.357 | 0 |
| 35 | 0.017 / 0.010 - 0.024 | 1.11/ 0 - 2.87 | yes | 3 | 0 - 0.0358 [a] | 1 |
| 48 | 77.8 / 71.5 - 84.0 | 62.6 / 20.9 - 104 | yes | 3 | 45.6 - 110 | 2 |
| 50 | 203 / 183 - 223 [b] | 188 / 121 - 255 | yes | 7 | 97.4 - 308 | 7 |
| 38 | 0.62 / 0.61 - 0.63 [b] | 2.71 / 2.05 - 3.37 | no | 6 | 0.54 - 0.70 | 0 |
| 53 | 910 / 821 - 999 [b] | 323 / 253 - 393 | no | 7 | 437 - 1380 | 1 |
| 54 | 1120 / 1009 - 1231 [b] | 733 / 511 - 955 | no | 7 | 582 - 1701 | 5 |
| 49 | 99.8 / 81.9 - 118 | 123 / 90.8 - 155 | yes | 7 | 31.3 - 168 | 7 |
| 52 | 608 / 490 - 726 [b] | 390 / 270 - 510 | yes | 7 | 292 - 924 | 5 |
| | Total Samples | | | 53 | | 28 |
| | % of samples w/in prediction interval | | | | | 53% |

a Prediction interval is estimated based upon n=30. A 95% CI was provided by the SRM supplier but no prediction interval was given.
b CI is estimated based upon n=30. A 95% prediction interval was provided by the SRM supplier but no CI was given.

**Table 6-3. ALSI SRM Comparison**

| Sample Lot No. | SRM Value/ 95% CI | ALSI Avg./ 95% CI | CI Overlap (yes/no) | No. of Samples Analyzed | 95% Prediction Interval | ALSI No. w/in Prediction Interval |
|---|---|---|---|---|---|---|
| 37 | 0.158 / 0.132 - 0.184 | 0.139 / 0.093 - 0.185 | yes | 7 | 0 - 0.357 | 7 |
| 35 | 0.017 / 0.010 - 0.024 | 0.00874 / 0.00782 - 0.00966 | no | 7 | 0 - 0.0358 [a] | 7 |
| 48 | 77.8 / 71.5 - 84.0 | 82.9 / 56.7 - 109 | yes | 7 | 45.6 - 110 | 5 |
| 50 | 203 / 183 - 223[b] | 167 / 140 - 194 | yes | 7 | 97.4 - 308 | 7 |
| 38 | 0.62 / 0.61 - 0.63 [b] | 0.533 / 0.502 - 0.564 | no | 7 | 0.54 - 0.70 | 7 |
| 53 | 910 / 821 - 999 [b] | 484 / 325 - 643 | no | 7 | 437 - 1380 | 4 |
| 54 | 1120 / 1009 - 1231 [b] | 711 / 552 - 870 | no | 7 | 582 - 1701 | 5 |
| 49 | 99.8 / 81.9 - 118 | 84.2 / 74.5 - 93.9 | yes | 7 | 31.3 - 168 | 7 |
| 52 | 608 / 490 - 726 [b] | 424 / 338 - 510 | yes | 7 | 292 - 924 | 7 |
| | Total Samples | | | 63 | | 56 |
| | % of samples w/in prediction interval | | | | | 89% |

a Prediction interval is estimated based upon n=30. A 95% CI was provided by the SRM supplier but no prediction interval was given.
b CI is estimated based upon n=30. A 95% prediction interval was provided by the SRM supplier but no CI was given.

The single most important number from these tables is the percentage of samples within the 95% prediction interval. As noted for the MTI data, this percentage is only 53% with n = 53. As seen from the tabulated data, average results for MTI fall evenly both above and below the reference value. (Four results are above and five results are below.) This would suggest that there is no particular high or low bias.

SRM values of 0.017, 0.158, and 0.62 mg/kg show a percent difference between the MTI result and the reference value greater than 300%, indicating that MTI results in this range are not accurate. The sensitivity evaluation suggested that the MTI PQL may be somewhere between 4 and 8 mg/kg. If these results are not included in the accuracy evaluation, 27 of 38, or 71%, of the MTI results are within the prediction interval. (Considerably greater than the 53% noted for all results.) Also, 25 of these 38 samples, or 66%, are within 50% of the SRM reference value, and 16 of these 38 samples or 42% are within 30% of the SRM value. Therefore, there is a correlation with accuracy and concentration, at least for the very low concentrations.

The percentage of samples within the 95% prediction interval for the laboratory data is 89% with n = 63. For 8 of the 9 different SRMs, ALSI average results are below the reference value. This would suggest that the ALSI data are biased low. Because of this bias, the percentage of samples outside the prediction interval is slightly below the anticipated number of results, given that the number of samples analyzed (63) is relatively high. Nonetheless, the referee laboratory data should be considered accurate and not significantly different from the SRM value. Because there is no bias correction term in the individual hypothesis tests (Table 6-4), alpha is set at 0.01 to help mitigate for laboratory bias. This in effect widens the scope of vendor data that would fall within an acceptable range of the referee laboratory.

**Table 6-4. Accuracy Evaluation by Hypothesis Testing**

| Sample Lot No./ Site | Avg. Conc. mg/kg | RSD or CV | Number of Measurements | Significantly Different at Alpha = 0.01 | Relative Percent Difference (MTI to ALSI) |
|---|---|---|---|---|---|
| 14/ Oak Ridge | | | | no | 38.7% |
| MTI | 6.95 | 37.5% | 3 | | |
| ALSI | 4.75 | 27.5% | 7 | | |
| 21/ Oak Ridge | | | | no | 109 % |
| MTI | 38.3 | 118% | 3 | | |
| ALSI | 11.2 | 23.8% | 3 | | |
| 22/ Oak Ridge | | | | no | -21.2% |
| MTI | 65.9 | 31.1% | 3 | | |
| ALSI | 81.6 | 9.44% | 3 | | |
| 24/ Oak Ridge | | | | no | -4.2% |
| MTI | 212 | 22.7% | 7 | | |
| ALSI | 221 | 44.8% | 7 | | |
| 26/ Oak Ridge | | | | no | 62.8% |
| MTI | 147 | 56.4% | 7 | | |
| ALSI | 77.0 | 13.2% | 7 | | |
| 31/ Oak Ridge | | | | no | 24.5% |
| MTI | 1211 | 12.9% | 3 | | |
| ALSI | 947 | 13.2% | 3 | | |
| 37/Oak Ridge | | | | no | 175% |
| MTI | 2.12 | 60.8% | 6 | | |
| ALSI | 0.14 | 36.4% | 7 | | |
| 67/Oak Ridge | | | | no | 36.1% |
| MTI | 1203 | 5.1% | 6 | | |
| ALSI | 835 | 14.8% | 7 | | |
| 02/Puget Sound | | | | yes | 174% |
| MTI | 1.61 | 33.2% | 7 | | |
| ALSI | 0.06 | 23.6% | 4 | | |
| 05/Puget Sound | | | | yes | 160% |
| MTI | 1.87 | 9.8% | 3 | | |
| ALSI | 0.21 | 33.3% | 2 | | |
| 11/Puget Sound | | | | no | 118% |
| MTI | 3.15 | 62.3% | 3 | | |
| ALSI | 0.81 | 32.7% | 7 | | |

**Table 6-4. Continued**

| Sample Lot No./ Site | Avg. Conc. mg/kg | RSD or CV | Number of Measurements | Significantly Different at Alpha = 0.01 | Relative Percent Difference (MTI to ALSI) |
|---|---|---|---|---|---|
| 25/Puget Sound | | | | no | 109% |
| MTI | 56.6 | 70.9% | 3 | | |
| ALSI | 16.6 | 12.3% | 3 | | |
| 27/Puget Sound | | | | yes | 50.6% |
| MTI | 76.7 | 25.5% | 7 | | |
| ALSI | 45.7 | 22.2% | 7 | | |
| 35/Puget Sound | | | | yes | 198% |
| MTI | 1.61 | 11.4% | 3 | | |
| ALSI | 0.009 | 6.3% | 7 | | |
| 48/Puget Sound | | | | no | -27.9% |
| MTI | 62.6 | 26.8% | 3 | | |
| ALSI | 82.9 | 34.2% | 7 | | |
| 50/Puget Sound | | | | no | 73.3% |
| MTI | 188 | 38.2% | 7 | | |
| ALSI | 167 | 17.7% | 7 | | |
| 57/Puget Sound | | | | no | 73.6% |
| MTI | 1.58 | 74.1% | 6 | | |
| ALSI | 0.73 | 16.2% | 7 | | |
| 62/Puget Sound | | | | yes | 61.6% |
| MTI | 27.6 | 21.1% | 7 | | |
| ALSI | 14.6 | 28.3% | 7 | | |
| 04/Carson River | | | | no | 90% |
| MTI | 0.29 | 56.0% | 3 | | |
| ALSI | 0.11 | 9.1% | 7 | | |
| 38/Carson River | | | | yes | 134% |
| MTI | 2.71 | 23.5% | 6 | | |
| ALSI | 0.53 | 6.2% | 7 | | |
| 53/Carson River | | | | no | -39.9% |
| MTI | 323 | 23.5% | 7 | | |
| ALSI | 484 | 35.5% | 7 | | |
| 54/Carson River | | | | no | 3.0% |
| MTI | 733 | 32.7% | 7 | | |
| ALSI | 711 | 21.0% | 7 | | |
| 63/Carson River | | | | no | 30.6% |
| MTI | 230 | 34.8% | 7 | | |
| ALSI | 169 | 6.6% | 7 | | |
| 17/Manufacturing Site | | | | no | 24.3% |
| MTI | 13.4 | 16.9% | 2 | | |
| ALSI | 10.5 | 14.6% | 7 | | |
| 20/Manufacturing Site | | | | no | -18.3% |
| MTI | 53.2 | 20.9% | 7 | | |
| ALSI | 63.9 | 25.3% | 7 | | |
| 32/Manufacturing Site | | | | no | 38.7% |
| MTI | 876 | 40.2% | 7 | | |
| ALSI | 592 | 12.7% | 7 | | |
| 33/Manufacturing Site | | | | no | -13.8% |
| MTI | 1048 | 36.6% | 6 | | |
| ALSI | 1204 | 13.3% | 7 | | |
| 49/Manufacturing Site | | | | no | 37.5% |
| MTI | 123 | 28.2% | 7 | | |
| ALSI | 84.2 | 12.5% | 7 | | |
| 52/Manufacturing Site | | | | no | -8.4% |
| MTI | 390 | 33.1% | 7 | | |
| ALSI | 424 | 21.9% | 7 | | |
| 66/Manufacturing Site | | | | no | 6.2% |
| MTI | 949 | 26.6% | 6 | | |
| ALSI | 892 | 11.2% | 7 | | |

CV = Coefficient of variance

**Hypothesis Testing**

Sample results from field and spiked field samples for the vendor compared to similar tests by the referee laboratory are used as another accuracy check. Spiked samples were used to cover concentrations not found in the field samples, and they are considered the same as the field samples for purposes of comparison. Because of the limited data available for determining the accuracy of the spiked value, these were not considered the same as reference standards. Therefore, these samples were evaluated in the same fashion as field samples, but they were not compared to individual spiked concentrations.

Using a hypothesis test with alpha = 0.01, vendor results for all samples were compared to laboratory results to determine if sample populations are the same or significantly different. This was performed for each sample lot separately. Because this comparison does not separate precision from bias, if MTI's or ALSI's computed standard deviation was large due to a highly variable result (indication of poor precision), the two CIs could overlap. Therefore, the fact that there was no significant difference between the two results could be due to high sample variability. Accordingly, associated RSDs have also been reported in Table 6-4, along with results of the hypothesis testing for each sample lot.

Of the 31 sample lots (including results below 8 mg/kg), 6 results are significantly different, based upon the hypothesis test noted above. Of these six results, four are at concentrations of 0.5 mg/kg, or less. This is due to the inability of the MTI field instrument to accurately measure results in this low range, as was noted previously. Therefore, only two results within the range of the MTI analysis capability are significantly different than the laboratory results. This suggests that there is no difference between these two data sets.

The most striking feature of the information in Table 6-4 is the high variability in reported RSDs for the MTI data. This high variability is a major reason that the comparison between vendor and referee laboratory data are not found to be different. Discounting the results that are too low to accurately quantitate, there appears to be very little difference between MTI and referee laboratory data. It is not, however, a result of the MTI instrument accurately determining sample concentrations. As was noted in the discussion of SRMs, the MTI field analysis was successful at measuring accurate concentrations of mercury only about 50% of the time. The increased similarity noted between MTI and the laboratory is a result of the inability of the hypothesis test to note a difference between the two results when sample variability is high.

Most of the relative percent differences are positive, which indicates that the MTI result is generally higher than the laboratory result. This is indicative of the previously noted low bias associated with the laboratory data. There are some MTI results that are less than the laboratory result; therefore, no overall MTI high or low bias is apparent. It appears that MTI data are subject to more random variability.

In determining the number of results significantly above or below the value reported by the referee laboratory, only 6 of 21 MTI average results were found to have relative percent differences greater than 50% for sample concentrations above the estimated PQL of 8 mg/kg. Only 2 of 21 MTI average results have relative percent differences greater than 100% for this same group of samples (see Table 6-5). Interferences may be a problem but, because of the random variability associated with the data, no interferences are specifically apparent from the data collected. Table 6-6 shows the results of additional data collected for these same samples.

In addition to the statistical summary presented above, data plots (Figures 6-1, 6-2, and 6-3) are included in order to present a visual interpretation of the accuracy. Three separate plots have been included for the MTI data. These three plots are divided based upon sample concentration in order to provide a more detailed presentation. Concentrations of samples analyzed by MTI ranged approximately from 0.01 to over 1,200 mg/kg. The previous statistical summary eliminated some of these data based upon whether concentrations were interpreted to be in the analytical range of the MTI field instrument. This graphical presentation presents all data points. It shows MTI data compared to ALSI data plotted against concentration. Sample groups are shown by connecting lines. Breaks between groups indicate a different set of samples at a different concentration. Sample groups were arranged from lowest to highest concentration.

As can be seen by this presentation, samples analyzed by MTI below about 50 mg/kg did not match well with the ALSI results with some exceptions. For higher concentrations, sample results were much closer to ALSI with some deviations present. This is only a visual interpretation and does not provide statistical significance. It does, however, provide a visual interpretation that supports the previous statistical results for accuracy, as presented above.

**Table 6-5. Number of Sample Lots Within Each %D Range**

| | <30% | >30%, <50% | >50%, <100% | >100% | Total |
|---|---|---|---|---|---|
| Positive %D | 4 | 4 | 4 | 2 | 14 |
| Negative %D | 6 | 1 | 0 | 0 | 7 |
| Total | 10 | 5 | 4 | 2 | 21 |

Only those sample lots with the average result greater than the PQL are tabulated.

**Table 6-6. Concentration (in mg/kg) of Non-Target Analytes**

| Lot # | Site | TOC | O&G | Ag | As | Ba | Cd | Cr | Cu | Pb | Se | Sn | Zn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Carson River | 870 | 190 | <0.5 | 9 | 210 | <0.5 | 19 | 13 | 3 | <2 | <5 | 60 | 0.19 |
| 2 | Puget Sound | 3500 | 290 | <0.5 | 3 | 23 | <0.5 | 16 | 10 | 1 | <2 | <5 | 24 | 0.04 |
| 4 | Carson River | 2400 | 200 | <0.5 | 8 | 240 | <0.5 | 17 | 32 | 12 | <2 | <5 | 66 | 0.10 |
| 5 | Puget Sound | 3500 | 210 | <0.5 | 3 | 28 | <0.5 | 18 | 11 | 3 | <2 | <5 | 28 | 0.16 |
| 6 | Carson River | 7200 | 200 | <0.5 | 4 | 32 | <0.5 | 16 | 9 | 1 | <2 | <5 | 24 | 0.23 |
| 11 | Puget Sound | 3800 | 130 | <0.5 | 4 | 20 | <0.5 | 18 | 8 | 1 | <2 | <5 | 24 | 0.63 |
| 13 | Manufacturing Site | 3200 | 100 | <0.5 | 2 | 110 | <0.5 | 42 | 51 | 7 | <2 | <5 | 61 | 5.5 |
| 14 | Oak Ridge | 7800 | 180 | 0.32 | 2 | 41 | 0.4 | 16 | 9 | 11 | <2 | <4 | 74 | 78 |
| 17 | Manufacturing Site | 2400 | 90 | <0.5 | <2 | 180 | <0.5 | 48 | 20 | 15 | <2 | <5 | 120 | 10 |
| 20 | Manufacturing Site | 2000 | <50 | <0.5 | <2 | 150 | <0.5 | 35 | 52 | 5 | 2 | <5 | 68 | 83 |
| 21 | Oak Ridge | 7800 | 320 | 1.9 | 4 | 150 | 2.8 | 22 | 40 | 23 | <2 | <4 | 340 | 14 |
| 22 | Oak Ridge | 6600 | 190 | 1.7 | 5 | 120 | <0.5 | 44 | 36 | 23 | <2 | <5 | 160 | 88 |
| 24 | Oak Ridge | 6600 | 250 | <0.5 | 5 | 89 | <0.5 | 6.3 | 7 | 10 | <2 | <5 | 31 | 220 |
| 25 | Puget Sound | 46000 | 1200 | <0.5 | 2 | 46 | 0.7 | 35 | 33 | 31 | <2 | 6 | 98 | 35 |
| 26 | Oak Ridge | 88000 | 340 | 9.1 | 10 | 140 | 1.9 | 47 | 73 | 82 | <2 | 5 | 250 | 100 |
| 27 | Puget Sound | 37000 | 1100 | <0.5 | 3 | 33 | 0.7 | 39 | 29 | 31 | <2 | 5 | 110 | 120 |
| 31 | Oak Ridge | 5000 | 80 | 0.59 | 4 | 120 | <0.5 | 41 | 32 | 16 | <2 | <5 | 96 | 870 |
| 32 | Manufacturing Site | 4700 | 120 | <0.5 | 2 | 160 | <0.5 | 190 | 47 | 6 | <2 | <5 | 78 | 650 |
| 33 | Manufacturing Site | <470 | 120 | <0.5 | <2 | 340 | <0.5 | 9.7 | 31 | 8 | <2 | <5 | 110 | 1300 |
| 35 | SRM Canmet S0-3 | NR | NR | NR | NR | 300 | NR | 26 | 17 | 14 | NR | NR | 52 | 0.02 |
| 37 | SRM CRM-016 | NR | NR | 0.7 | 7.8 | 79 | 0.47 | 14 | 16 | 14 | 1 | NR | 70 | 0.16 |
| 38 | SRM NWRI TH-2 | NR | NR | 5.8 | 8.7 | 570 | 5.2 | 120 | 120 | 190 | 0.83 | NR | 900 | 0.62 |
| 44 | SRM CRM 021 | NR | NR | 6.5 | 25 | 590 | 1.2 | 11 | 4800 | 6500 | NR | 300 | 550 | 4.7 |
| 46 | SRM CRM 032 | NR | NR | 81 | 370 | 120 | 130 | 15 | 590 | 4600 | 170 | 1300 | 2600 | 21 |
| 48 | SRM CRM 023 | NR | NR | NR | 380 | 76 | 0.92 | 31 | 8.9 | 210 | 120 | NR | 94 | 78 |
| 49 | SRM CRM 025 | NR | NR | 130 | 340 | 1800 | 370 | 440 | 7.8 | 1450 | 520 | NR | 52 | 100 |
| 50 | SRM RTC spec. | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | 200 |
| 52 | SRM RTC spec. | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | 600 |
| 53 | SRM RTC spec. | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | 900 |
| 54 | SRM RTC spec. | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | NR | 1100 |
| 56 | Spiked Lot 1 | 870 | 190 | <0.5 | 9 | 210 | <0.5 | 19 | 13 | 3 | <2 | <5 | 60 | 0.20 |
| 57 | Spiked PS- X1,X4 | 3500 | 290 | <0.5 | 3 | 23 | <0.5 | 16 | 10 | 1 | <2 | <5 | 24 | 0.61 |
| 62 | Spiked Lot 5 | 3500 | 210 | <0.5 | 3 | 28 | <0.5 | 18 | 11 | 3 | <2 | <5 | 28 | 23 |
| 63 | Spiked Lot 23 | 5700 | 100 | 37 | 11 | 280 | 0.9 | 25 | 170 | 140 | <2 | <5 | 170 | 270 |
| 66 | Spiked MS-SO-08 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 980 |
| 67 | Spiked Lot 26 | 88000 | 340 | 9.1 | 10 | 145 | 1.9 | 47 | 73 | 82 | <2 | 5 | 250 | 740 |

CRM = Canadian Reference Material
RTC = Resource Technology Corporation
NA = Not Analyzed
NR = Not Reported by Standard Supplier

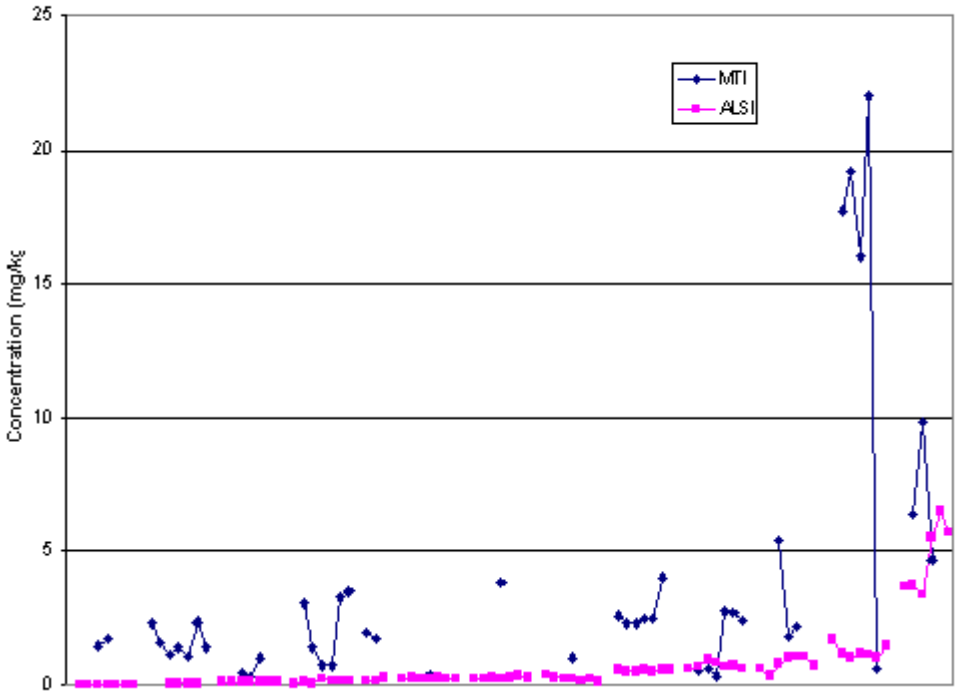


**Figure 6-1. Data plot for low concentration sample results.**

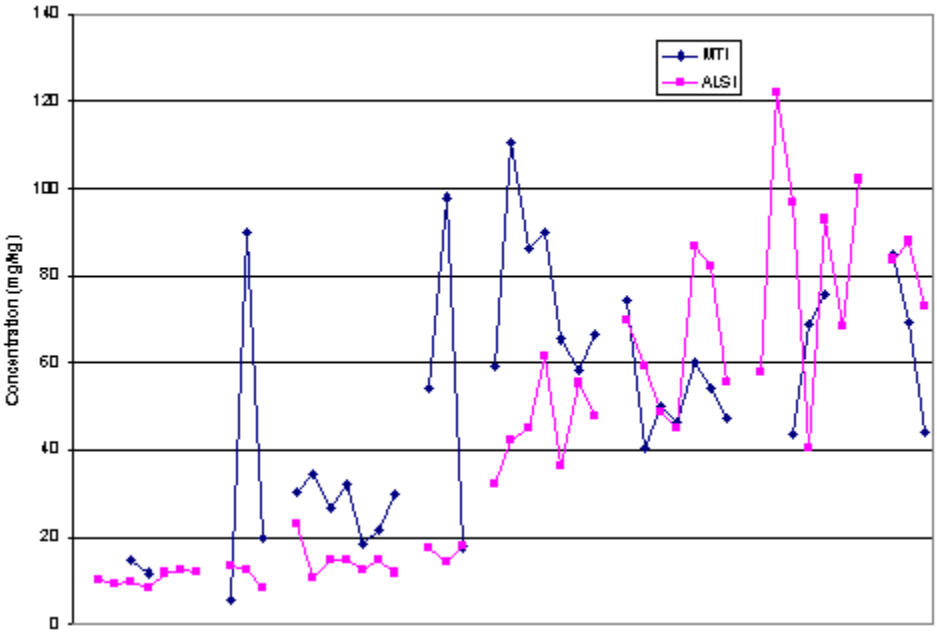


**Figure 6-2. Data plot for medium concentration sample results.**

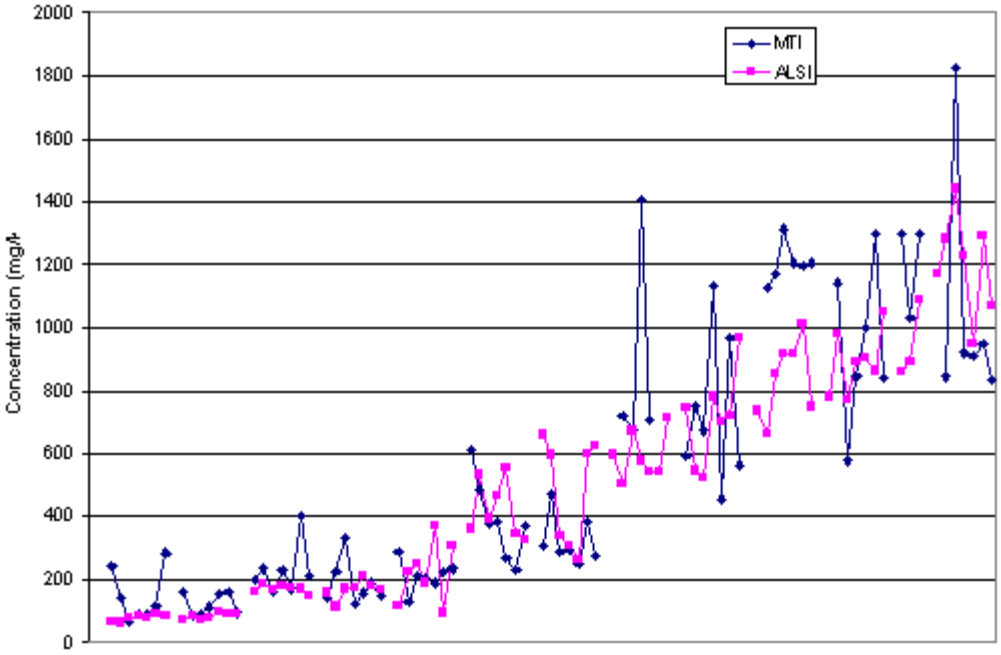


**Figure 6-3. Data plot for high concentration sample results.**

**Unified Hypothesis Test**

SAIC performed a unified hypothesis test analysis to assess the comparability of analytical results provided by MTI and those provided by ALSI. (See appendix B for a detailed description of this test.) MTI and ALSI both supplied multiple assays on replicates derived from a total of 31 different sample lots, consisting of field materials and reference materials. The MTI and ALSI data from these assays formed the basis of this assessment.

Results from this analysis suggest that the two data sets are not the same. The null hypothesis tested was that, on average, MTI and ALSI produce the same results within a given sample lot. The null hypothesis is rejected in part because MTI results tended to exceed those from ALSI for the same sample lot. Even when a bias term is used to correct this discrepancy, the null hypothesis is still rejected. Additional information about this statistical evaluation is included in Appendix B.

**Accuracy Summary**

In summary, MTI data were only within SRM 95% prediction intervals about 50% of the time, which suggests significant non-equivalence. ALSI data, however, compared favorably to SRM values and were within the 95% prediction interval 89% of the time, indicating statistical parity found to be biased low.

The comparison between the MTI field data and the ALSI results suggest that the two data sets are not different, but this similarity between individual samples is often the result of high variability associated with the MTI reported values. When a unified hypothesis test is performed, the results suggest that the two data sets are in fact not the same. MTI data was found to be both above and below referee laboratory concentrations; however, the sample lot distribution shown in Table 6-5 implies a positive bias when compared to the low bias previously noted for the laboratory reported results. The number of MTI average values greater than 50% different from the referee laboratory results or SRM reference values, however, was only 6 of 21 different sample lots and those greater than 100% different were only 2 of 21 different sample lots. MTI results therefore appear to provide a rough estimate of accuracy for field determination and may be affected by interferences not identified by this demonstration.

### *6.1.3 Precision*

Precision is usually thought of as repeatability of a specific measurement, and it is often reported as RSD. The RSD is computed from a specified number of replicates. The

more replications of a measurement, the higher 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. Most samples were analyzed seven times by both MTI and the referee laboratory. In some cases, samples may have been analyzed as few as three times and some MTI results were judged invalid and were not used. This was often the situation when it was believed that the chosen sample, or SRM, was likely to be below the vendor quantitation limit. The precision goal for the referee laboratory, based upon pre-demonstration results, is an RSD of 25% or less. A descriptive evaluation for the differences between MTI RSDs and the referee laboratory RSDs was determined. In Table 6-7, the RSD for each separate sample lot is shown for MTI compared to the referee laboratory. The average RSD was then computed for all measurements made by MTI, and this value was compared to the average RSD for the laboratory.

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. To evaluate precision for clearly different matrices, an overall average RSD for the SRMs is calculated and compared to the average RSD for the field samples. This comparison is also included in Table 6-7 and shown for both MTI and the referee laboratory.

The purpose of this evaluation is to determine the field instrument's capability to precisely measure analyte concentrations under real-life conditions. Instrument repeatability was measured using samples from each of four different sites. Within each site, there may be two separate matrices, soil and sediment. Not all sites have both soil and sediment matrices, nor are there necessarily high, medium, and low concentrations for each sample site. Therefore, spiked samples were included to cover additional ranges.

Table 6-7 shows results from Oak Ridge, Puget Sound, Carson River, and the manufacturing site. It was thought that because these four different field sites represented different matrices, measures of precision may vary from site to site. The average RSD for each site is shown in Table 6-7 and compared between MTI and the referee laboratory. SRM RSDs are not included in this comparison because SRMs, while grouped with different sites for purposes of ensuring that the samples remained blind during the demonstration, were not actually samples from that site, and were, therefore, compared separately.

The RSDs of various concentrations are compared by noting the RSD of the individual sample lots. The ranges of test samples (field, SRMs, and spikes) were selected to cover the appropriate analytical ranges of MTI's instrumentation. Average referee laboratory values for sample concentrations are included in the table, along with SRM values, when appropriate. These are discussed in detail in Section 6.1.2 describing the accuracy evaluation and are included here for purposes of precision comparison. Sample concentrations were separated into approximate ranges: low, medium, and high, as noted in Table 6-7 and Table 6-1. Samples reported by MTI as below their approximated MDL were not included in Table 6-7. Also not included in this table are samples where a high number of results were reported as invalid by MTI. Other than the low concentrations previously noted, there appears to be no correlation between concentration (low, medium, or high) and RSD; therefore, no other formal evaluations of this comparison were performed.

The referee laboratory analyzed replicates of all samples analyzed by MTI. This was used for purposes of precision comparison to MTI. RSD for the vendor and the laboratory were calculated individually and shown in Table 6-7.

**Table 6-7. Evaluation of Precision**

| Sample Lot No. MTI and Lab | Avg. Conc. or Reference SRM value | RSD | Number of Samples | w/in 25% RSD Goal? |
|---|---|---|---|---|
| | | OAK RIDGE | | |
| Lot no. 14 | 4.75 (medium) | | | |
| MTI | | 37.5% | 3 | no |
| ALSI | | 27.5% | 7 | yes |
| Lot no. 21 | 11.2 (medium) | | | |
| MTI | | 118% | 3 | no |
| ALSI | | 23.8% | 3 | yes |
| Lot no. 22 | 81.6 (high) | | | |
| MTI | | 31.1% | 3 | no |
| ALSI | | 9.4% | 3 | yes |

**Table 6-7. Continued**

| Sample Lot No. MTI and Lab | Avg. Conc. or Reference SRM value | RSD | Number of Samples | w/in 25% RSD Goal? |
|---|---|---|---|---|
| Lot no. 24 | 221 (high) | | | |
| MTI | | 22.7% | 7 | yes |
| ALSI | | 44.8% | 7 | no |
| Lot no. 26 | 77.0 (high) | | | |
| MTI | | 56.4% | 7 | no |
| ALSI | | 13.2% | 7 | yes |
| Lot no. 31 | 947 (high) | | | |
| MTI | | 12.9% | 3 | yes |
| ALSI | | 13.2% | 3 | yes |
| Lot no. 37 | 0.11 (low) | | | |
| MTI | | 60.8% | 6 | no |
| ALSI | | 36.4% | 7 | no |
| Lot no. 67 | 835 (high) | | | |
| MTI | | 5.0% | 6 | yes |
| ALSI | | 14.8% | 7 | yes |
| Oak Ridge Avg. RSD | | | | |
| MTI | | 40.6% | | no |
| ALSI | | 20.9% | | yes |
| PUGET SOUND | | | | |
| Lot no. 05 | 0.21 (low) | | | |
| MTI | | 9.8% | 3 | yes |
| ALSI | | 33.3% | 2 | no |
| Lot no. 11 | 0.81 (low) | | | |
| MTI | | 62.3% | 3 | no |
| ALSI | | 32.7% | 7 | no |
| Lot no. 25 | 16.6 (medium) | | | |
| MTI | | 70.9% | 3 | no |
| ALSI | | 12.3% | 3 | yes |
| Lot no. 27 | 45.7 (medium) | | | |
| MTI | | 25.5% | 7 | no |
| ALSI | 0.11 (low) | 22.2% | 7 | yes |
| Lot no. 35 | 0.017 (lo | | | |
| MTI | | 11.4% | 3 | yes |
| ALSI | | 6.3% | 7 | yes |
| Lot no. 48 | 77.78 (high) | | | |
| MTI | | 26.8% | 3 | no |
| ALSI | | 34.2% | 7 | no |
| Lot no. 50 | 200 (high) | | | |
| MTI | | 38.2% | 7 | no |
| ALSI | | 17.7% | 7 | yes |
| Lot no. 57 | 0.73 (low) | | | |
| MTI | | 74.1% | 6 | no |
| ALSI | | 16.2% | 7 | yes |
| Lot no. 62 | 14.6 (medium) | | | |
| MTI | | 21.1% | 7 | yes |
| ALSI | | 28.5% | 7 | no |
| Puget Sound/ Avg. RSD | | | | |
| MTI | | 44.0% | | no |
| ALSI | | 24.1% | | yes |
| CARSON RIVER | | | | |
| Lot no. 04 | 0.11 (low) | | | |
| MTI | | 56.0% | 3 | no |
| ALSI | | 9.1% | 7 | yes |
| Lot no. 38 | 0.62 (high) | | | |
| MTI | | 23.3% | 6 | yes |
| ALSI | | 6.2% | 7 | yes |

**Table 6-7. Continued**

| Sample Lot No. MTI and Lab | Avg. Conc. or Reference SRM value | RSD | Number of Samples | w/in 25% RSD Goal? |
|---|---|---|---|---|
| Lot no. 53 | 900 (high) | | | |
| MTI | | 23.5% | 7 | yes |
| ALSI | | 35.5% | 7 | no |
| Lot no. 54 | 1100 (high) | | | |
| MTI | | 32.6% | 7 | no |
| ALSI | | 21.0% | 7 | yes |
| Lot no. 63 | 169 (high) | | | |
| MTI | | 34.8% | 7 | no |
| ALSI | | 6.6% | 7 | yes |
| Carson River/ Avg. RSD | | | | |
| MTI | | 49.3% | | no |
| ALSI | | 16.3% | | yes |
| MANUFACTURING SITE | | | | |
| Lot no. 17 | 10.5 (medium) | | | |
| MTI | | 16.9% | 2 | yes |
| ALSI | | 14.6% | 7 | yes |
| Lot no. 20 | 63.9 (high) | | | |
| MTI | | 20.9% | 7 | yes |
| ALSI | | 25.4% | 7 | yes |
| Lot no. 32 | 592 (high) | | | |
| MTI | | 40.2% | 7 | no |
| ALSI | | 12.7% | 7 | yes |
| Lot no. 33 | 1204 (high) | | | |
| MTI | | 36.6% | 6 | no |
| ALSI | | 13.3% | 7 | yes |
| Lot no. 49 | 99.8 (high) | | | |
| MTI | | 28.2% | 7 | no |
| ALSI | | 12.5% | 7 | yes |
| Lot no. 52 | 600 (high) | | | |
| MTI | | 33.1% | 7 | no |
| ALSI | | 21.9% | 7 | yes |
| Lot no. 66 | 892 (high) | | | |
| MTI | | 26.6% | 6 | no |
| ALSI | | 11.2% | 7 | yes |
| Manufacturing Site/ Avg. RSD | | | | |
| MTI | | 28.2% | | no |
| ALSI | | 15.4% | | yes |
| SUMMARY STATISTICS | | | | |
| Overall Avg. RSD | | | | |
| MTI | | 35.1% | | no |
| ALSI | | 22.3% | | yes |
| Field Samples/ Avg. RSD | | | | |
| MTI | | 39.4% | | no |
| ALSI | | 19.4% | | yes |
| SRMs/ Avg. RSD | | | | |
| MTI | | 30.9% | | no |
| ALSI | | 25.1% | | yes |

As noted from Table 6-7, MTI precision is often more variable than the referee laboratory. The single most important measure of precision provided in Table 6-7, overall average RSD, is 22.3% for the referee laboratory, compared to the MTI average RSD of 35.1%. Only the laboratory RSD is within the predicted 25% RSD objective for precision expected from both analytical and sampling variance.

In addition, field sample precision compared to SRM precision shows that there may be some difference between these two sample lots (field sample RSD is 19.4% for ALSI and 39.4% for MTI; SRM RSD is 25.1% for ALSI and 30.9% for MTI), but that this difference is likely not significant. For purposes of this analysis, spiked samples are considered the same as field samples because these were similar field matrices, and the resulting variance was expected to be equal to field samples. The replicate sample RSDs confirm the pre-demonstration results, showing that sample homogenization procedures met their originally stated objectives.

There appears to be no significant site variation between Oak Ridge, Puget Sound, and the Carson River sites. (See Table 6-7 showing average RSDs for each of these sample lots. These average RSDs are computed using only the results of the field samples and not the SRMs.) The manufacturing site had a lower average RSD for both the vendor and the laboratory, but this difference was not significant in results from different vendors and, therefore, may not be significant.

**Precision Summary**

The precision of the MTI field instrument is not as good as the measured laboratory precision. The overall RSD for MTI is 35.1%, which is above the 25% RSD objective set for the laboratory. The overall laboratory RSD is 22.3%. Because MTI precision shows a wider variance in sample results, MTI data did not prove to be significantly different from the ALSI data when performing a hypothesis test procedure for data comparison.

### *6.1.4 Time Required for Mercury Measurement*

During the demonstration, the time required for mercury measurement activities was measured. The following specific activities were timed: instrument setup, sample preparation, sample analysis, and instrument disassembly. Two MTI technical representatives performed these operations during the demonstration; one individual performed sample preparation (i.e., acid digestion of the soil and sediment samples) and the other individual conducted instrument setup/disassembly and all sample analyses with the PDV 6000.

Setup and disassembly times were measured once. Sample preparation and analytical time were measured separately each day. Combined, sample preparation and sample analysis comprised the operational time. Recording of sample preparation time began when the first aliquot of sample material was weighed out on a portable scale and continued until the last digestion bottle was completed at the end of the day. Recording of analytical time began with preparation and initial analysis of the mercury standard and continued until the last sample analysis was completed at the end of the day.

To acquire the total operational time for all three days, the sum of the total sample preparation time and total sample analysis time was divided by the total number of analyses performed over the 3-day demonstration. For this calculation, analyses of blanks and calibration standards and reanalyses of samples were not included in the total number of samples. Any downtime (i.e., lunch breaks) was noted and subtracted from the total daily operational time.

Setup time for the PDV 6000 consisted of 1) transporting the PDV 6000 carrying case, preparation kits, laptop computer, and other ancillary equipment from a rental vehicle to the measurement site; 2) unpacking and spreading the items out on a on a level working surface; 3) connecting the cell assembly to the PDV 6000 control unit and connecting other peripheral devices, such as the serial cable used to link the PDV 6000 to the laptop computer; and 4) securing all power connections.

It should be noted that the VAS software was already installed on MTI's laptop computer. If this were not the case for potential users, then the software installation would add to the setup time.

The main components of the PDV 6000 were contained within a hard shell, pelican-style carrying case. These components included the main PDV 6000 control unit, the cell assembly with stirrer, the cell stand, a Ag/AgCl reference electrode, a platinum counter electrode, a glassy carbon working electrode, a connecting cable to link the analytical cell to the control unit, a DB9 male/female serial cable link for connecting the PDV 6000 to a computer, a reference electrode plating accessory, a main powered 12 VDC supply (plug pack), a NiMH rechargeable battery pack and battery pack charger, the PDV 6000 operation manual, VAS software installation disks, and a printed VAS User's Guide and warranty card.

Of these components, the reference electrode plating accessory, the NiMH battery pack, and the charger were not used during the demonstration. (The pre-plating procedure is not required for mercury analysis and the instrument was powered by line electricity.)

In addition to the main instrument components, there was ancillary equipment that was unpacked as part of setup. Most of this equipment related directly to sample digestion procedures. These included the following items:

- Portable scale
- Air displacement pipettes (5-50 µL, 100-1000 µL, and 200-1000 µL)
- Repeating pipetter (0.5 - 50 mL)
- Sample processing kits
- Incidentals (i.e., paper wipes, felt labeling pens, etc.)

These items, along with other supplies, were transported in a cardboard box. Setup of all of the necessary equipment and supplies took approximately 15 minutes.

It should be noted that, although MTI utilized two people during the demonstration, one person could perform both the sample preparations and sample analyses. According to MTI, the number of individuals required for conducting full analyses should be based on the number of samples to be analyzed. For instance, if there are 15 samples or less per day to be analyzed, MTI would advise that one person would be sufficient; if there were to be more than 15 samples analyzed daily, the user may decide to use two people. In the case of the demonstration, where over 50 samples were analyzed daily, two people were deemed necessary by MTI to efficiently process the samples.

Individual sample analysis times were not measured during the demonstration. Analysis time was estimated by recording start and stop times each day and accounting for any instrument downtime due to operator breaks or device failure and maintenance activities. Therefore, the total time for analyses included preparing a mercury standard and an electrolyte standard solution each day, analyzing blanks and the calibration standards, and conducting reanalyses on certain samples; however, the total number of analyses performed includes only demonstration samples (i.e., samples, spikes, and SRMs). The sample total does not include blanks, calibration standards, or reanalyses. Table 6-8 presents the time measurements recorded for each of the three days of PDV 6000 operation.

**Table 6-8. Time Measurements for MTI** (minutes)[a].

| Activity | Day 1 | Day 2 | Day 3 | 3-Day Totals |
|---|---|---|---|---|
| Instrument Setup | 15 | -- | -- | 15 |
| Sample Preparation | 370 | 430 | 0 | 800 |
| Sample Analysis | 370 | 560 | 550 | 1,480 |
| Operation Time [b] | 740 | 990 | 550 | 2,280 |
| Disassembly | -- | -- | 10 | 10 |

a Times are rounded to nearest 15 minutes.
b Operation Time = Sample Preparation Time + Sample Analysis Time.

Disassembly of the instrument and ancillary equipment was measured from the completion time of the last sample analyses until the instrument components were disassembled and placed back into the original shipping container. Disassembly of the PDV 6000 involved turning off the power, disconnecting the electrical power source, the serial cable link between the control unit and laptop computer, and removal of the cable link connecting the analytical cell to the control unit. This complete process took about 15 minutes (earlier stated 15-minute rounding).

Packaging for shipping is not included in the time measurement; however, the PDV 6000 carrying case appears durable enough to ship as is or in a box, without the need for reinforced corners and buffer spaces. The pipettes, scale, and any unused supplies would also need to be packaged for shipment. It is estimated that this complete process would take approximately 1 hour, including the time to ship any returnable items to suppliers.

**Analysis Time Summary**

In total, MTI analyzed 197 samples during the demonstration. Sample preparation took a total of 800 minutes (roughly 4 minutes per sample) and sample analysis took 1,480 minutes (7.5 minutes per analysis). Using the total operational time reported in Table 6-8 (2,280 minutes), 11.6 minutes is the estimated time per complete sample analysis for the demonstration. As previously noted, the number of analyses does not include blanks, standards, and reanalyzed samples.

It is realized that actual times will vary from site to site depending on project goals. For example, if the results can be reported as “greater than” or “less than” a specific target concentration, then the time per sample analysis could be significantly reduced. On the other hand, if high

concentration samples require one or more dilutions, or heterogeneous samples require duplicate analysis, the sample time per analysis may increase. If project goals require all samples to be quantified, the number of reanalyses and blanks required could be higher, thus also increasing the time per analysis. During the demonstration, no "greater than values" were reported; however, some "less than values" were reported.

### *6.1.5 Cost*

Background information, assumptions used in the cost analysis, demonstration results, and a cost estimate, are provided in Chapter 7.

## 6.2 Secondary Objectives

This section discusses the performance results for the PDV 6000 in terms of the secondary objectives described in Section 4.1. These secondary objectives were addressed based on observations of the PDV 6000 made during the demonstration and information provided by MTI during and after the demonstration.

### *6.2.1 Ease of Use*

**Documents the ease of use, as well as the skills and training required to properly operate the device.**

**Based on observations made during the demonstration and review of the PDV 6000 operation manual, the instrument appears to be easy to operate as a stand-alone unit or in conjunction with the VAS software. Training on the unit and software would be recommended for first-time users. A laboratory or field technician with a basic knowledge of chemistry and basic computer knowledge could operate the equipment after a 1-day training course.**

The vendor provides a SOP that summarizes the sample preparation and sample analysis procedures for the PDV 6000. Also provided with the unit is the PDV 6000 Operations Manual, version 2.2 (47 pages in length), and the VAS User's Guide, version 2.1 (50 pages in length). This SOP was evaluated during the demonstration and the step-by-step procedures were easy to understand.

The analysis portion of the MTI mercury measurement process may require analytical experience to gain efficiency in the field. Familiarity with calibrating analytical instruments, running blanks before processing samples, running calibration standards, and overall familiarity with sample peaks, would be an advantage for a prospective user. The VAS User's Guide does provide some examples of sample peaks in the chapter titled "Analyzing Data." There is also some discussion of peak measurement within the PDV 6000 Operations Manual in Chapter 3 (Introduction to Voltammetry).

In addition to providing the written instructions, MTI provides a 1-day training course on the PDV 6000 for up to eight individuals (at the purchaser's cost). Currently, there is no specific training course for the VAS software. The combination of instrument training, the field SOP, the PDV 6000 Operations Manual, and the VAS User's Guide should provide a user with adequate direction on basic use of the PDV 6000. Once in the field, MTI does supply some ongoing support. MTI has a phone number for domestic support (910-617-8367) and an Internet email support address with support provided from Australia. Chapter 8 of the PDV 6000 Operations Manual does include information on troubleshooting. Neither the training course nor email support was evaluated during the demonstration.

MTI chose to operate the PDV 6000 with two MTI representatives during the demonstration. One individual who conducted the sample preparation held B.S. degrees in biology and chemistry. The other individual conducting the analysis held a degree in chemistry/pharmacology. The two MTI representatives were able to perform sample preparation and analysis on a somewhat continuous basis, although sample preparation was more routine and, thus, a quicker operation. The sample digestion procedure kept far enough ahead of the sample analysis that all 197 samples were prepared for analysis more than a day ahead of completing all the analyses. The separation of sample extraction and analysis is not recommended by MTI; however, it was performed by MTI as a means of completing the 197 samples over the 3-day time frame.

Sample preparation took approximately four minutes per sample. Sample preparation consisted of weighing out a specific mass of sample material, placing the material into a 70-mL digestion bottle, and then pipetting the following into the bottle.

- 4 mL of $HNO_3$
- 4 mL of $H_2O_2$ (1 mL at a time)
- 12 mL of DI water
- 20 mL of electrolyte solution

This procedure was easy to understand, and could be performed by a trained technician. The two main

peripheral items used during the sample preparation procedure are a portable analytical scale and one or more pipettes.

MTI typically would not supply the analytical balance and pipettes, although the company indicates that these items could be purchased as part of an accessory kit; however, MTI does supply disposable pipette tips within the sample preparation kits. The reader should note that brands and models of the balance and pipettes, other than those used for the demonstration, may be adequate for use.

Sample analysis on average took approximately 10-12 minutes per sample. Because sample analysis was a separate procedure and involved running blanks, calibration standards, and some reanalysis, the procedure lagged behind sample preparation. If a single individual were to perform both preparation and analysis, it would be advantageous to prepare several samples in advance of conducting analyses.

The sample analysis process is more involved than the sample preparation procedure and should be performed by a technician trained in using the PDV 6000 with the VAS software. As samples are analyzed, VAS software screens do allow the analyst to track the stage at which the analytical process is progressing, which would be especially beneficial to the novice user. Figure 6-4 is an example of the PDV 6000 run log screen with open data windows. Figure 6-5 shows the sample graph screen for a mercury analysis and Figure 6-6 has a sample graph and data for a sample analyzed by the method of standard additions.

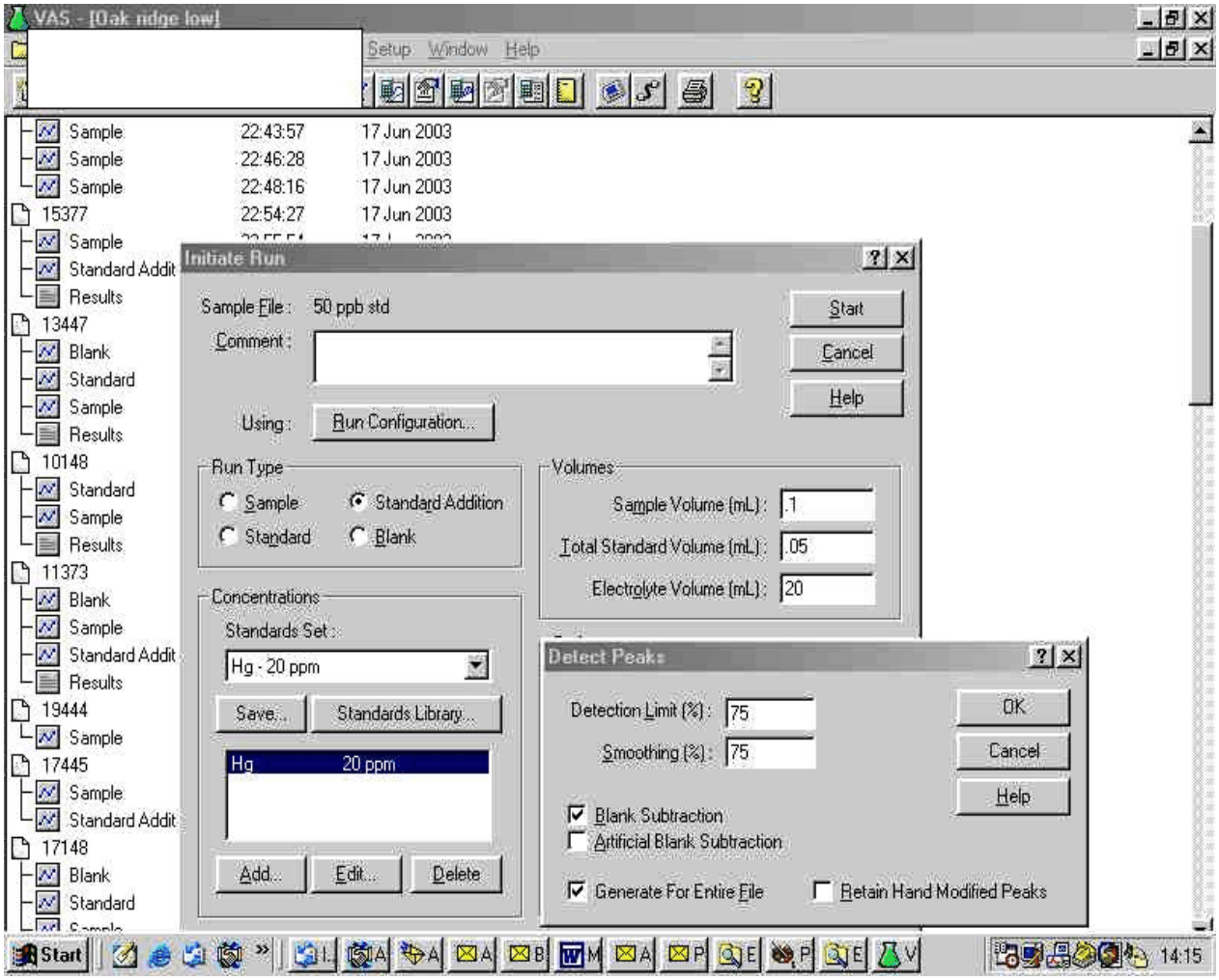

**Figure 6-4. PDV 6000 sample run log with open data windows.**

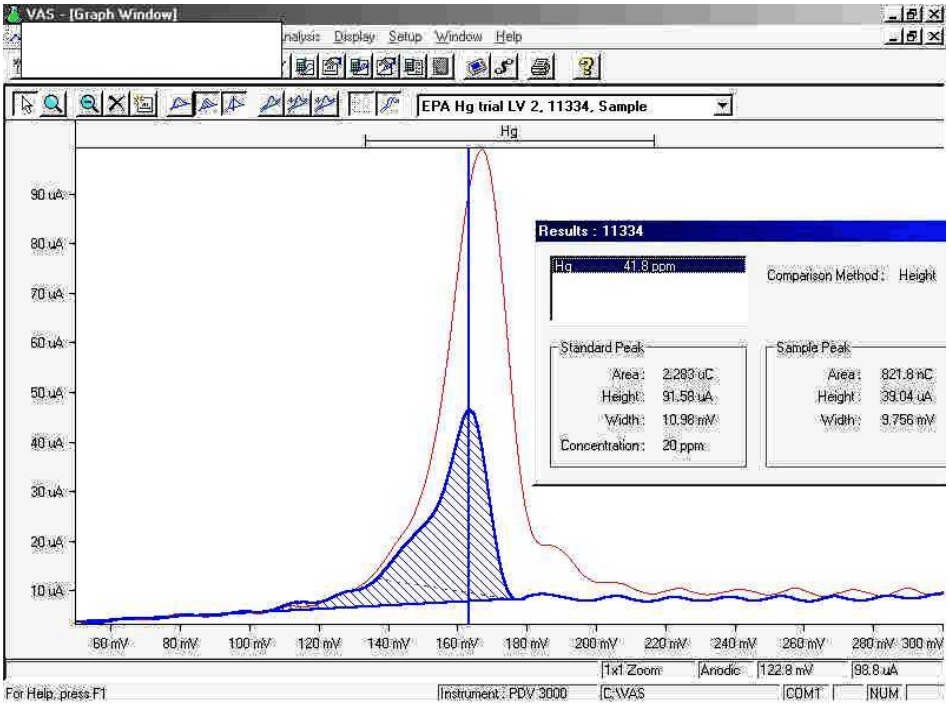


**Figure 6-5. PDV 6000 sample graph screen.**

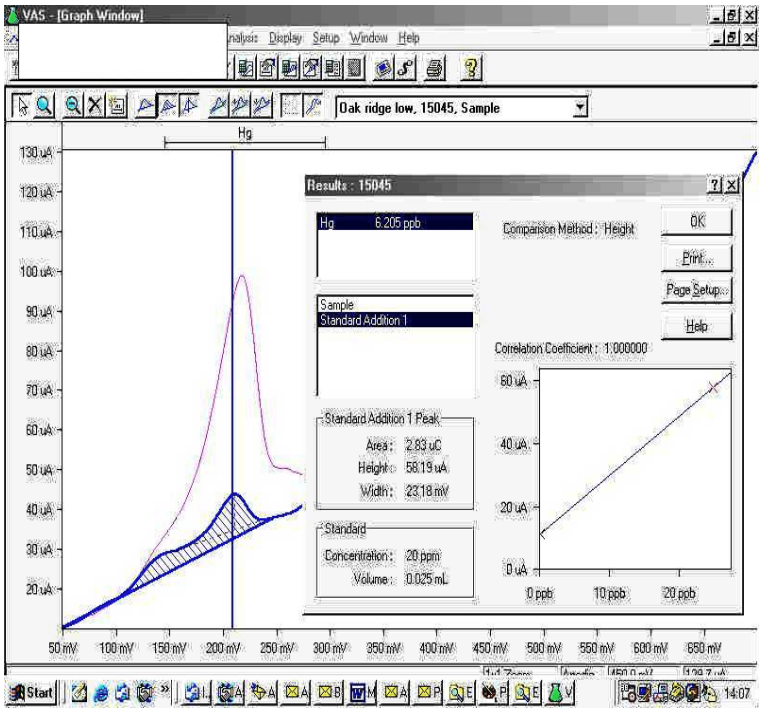


**Figure 6-6. PDV 6000 mercury graph for sample analyzed by method of standard additions.**

### 6.2.2 Health and Safety Concerns

**Documents potential health and safety concerns associated with operating the device.**

**The main health and safety concern observed during the demonstration was potential exposure to fumes resulting from vigorous reactions during sample preparation. This occurrence necessitates the use of appropriate PPE when conducting acid digestions.**

Health and safety concerns, including chemical hazards, radiation sources, electrical shock, explosion, and mechanical hazards were evaluated.

Chemicals were used in the preparation or processing of samples. These included the following:

- Nitric acid ($HNO_3$) (concentrated)
- Hydrogen peroxide ($H_2O_2$) (100%)
- An electrolyte solution containing sodium acetate, acetic acid, and trace metals
- Potassium chloride (KCl)
- Mercury standard

Of these chemicals, the two posing the greatest exposure risk are $HNO_3$ (a strong oxidizer) and $H_2O_2$ (a strong oxidant ). MTI does include Material Safety Data Sheets (MSDS) for $HNO_3$, $H_2O_2$, the electrolyte solution, and the mercury standard.

The main potential health and safety concern regarding MTI's process is, therefore, potential exposure to spilled chemicals or fumes caused by reactions of these chemicals with one another or with unknown sample constituents. Ampules of these chemicals were handled with gloves, and the operator wore safety glasses with side shields at all times. Such standard laboratory precautions mitigate the potential for dermal exposure. In addition, the MTI representative conducting the sample preparation wore a long-sleeved laboratory coat.

During the demonstration, a few samples reacted vigorously, releasing pungent reddish-yellow fumes from the digestion bottles, following the addition of $H_2O_2$ to the solution. In some instances, an effervescing solution frothed over the top of the digestion bottle and onto the table.

It should also be noted that the demonstration samples may pose a mercury inhalation hazard. During the original demonstration in Oak Ridge, TN, in May 2003, vapor measurements were recorded for the same samples that were analyzed by MTI in Las Vegas in June. The measurements were collected with a Jerome 431-x gold film mercury vapor analyzer, manufactured by Arizona Instruments Corporation. The instrument has a range from 0.000 to 0.999 $mg/m^3$. In all cases, readings were 0.000 $mg/m^3$ in the breathing zone of the operator, indicating no inhalation hazard.

In evaluating electrical shock potential, two factors were evaluated: 1) obvious areas where electrical wires are exposed and 2) safety certifications. No exposed wires were noted during the demonstration. All connections between equipment were made using standard electrical lines, interface cables, and 8-pin cords. The power cord was grounded with a ground fault interrupter.

No obvious explosion hazards were noted. The PDV 6000 has a CE electrical certification, which is the European equivalent of the Underwriters Laboratory (UL) electrical certification in the United States. The unit also has a N4266 electrical certification (Australia's equivalent to UL), but it does not have UL certification.

No serious mechanical hazards were noted during the demonstration. All equipment edges were smooth, minimizing any chance of cuts or scrapes. If an electrical cord is used to provide power to the PDV 6000, it needs to be installed in a manner designed to prevent trip hazard (e.g., taped down).

### 6.2.3 Portability of the Device

**Documents the portability of the device.**

**The PDV 6000 is a handheld device that is transported in a carrying case along with its main components. Due to its packaging and compact size and weight, the unit can be taken anywhere that is accessible by foot and can be operated on a small-level surface.**

The PDV 6000 display unit measured approximately 20 cm (L) by 10 cm (W) by 4 cm (H) when lying flat. The weight of the control unit was estimated at less than 1 kg. Also included as standard with the PDV 6000 were the cell assembly, stand for the cell assembly with integral stirrer, a set of electrodes, connecting cables, a NiMH battery and

battery charger, and the accompanying VAS software installation disk.

All of these accessories are lightweight and easily portable, and fit into a pelican-style case measuring approximately 35 cm (L) by 25 cm (W) by 15 cm high. As a result, the PDV 6000 is practical for field applications, including use in remote areas accessible only by foot.

The sample digestion required a flat, stable surface, which would also be suitable for a laptop computer. A table was supplied during the demonstration for preparing and staging samples. The majority of materials and supplies required for conducting sample preparation come in a kit that is the approximate size of a shoe box. Each kit comes with enough supplies to prepare 10 samples. Additionally, a small portable scale and pipettes are needed to properly prepare samples for analysis. These additional items, along with the kits, could be transported in a heavy duty bag or cardboard box.

The PDV 6000 is equipped with a NiMH battery for operation in the absence of electrical power. The battery powers the unit for about 4 hours and would allow for analyzing 10-20 samples. Line operation of the instrument requires a standard electrical source of 110 volts.

For the demonstration, the vendor was supplied with a folding table, two chairs, and a tent to provide shelter from inclement weather. In addition, two 1-gallon containers were provided for waste soil and for decontamination residual extract waste. A 2-gallon zip-lock bag was furnished for disposal of used gloves, wipes, and other wastes which were contaminated during the demonstration. Finally, a large trash bag was supplied for disposal of non-contaminated wastes.

### *6.2.4 Instrument Durability*

**Evaluates the durability of the device based on its materials of construction and engineering design.**

**The PDV 6000 is well designed and constructed for durability. A conformal coating on the device's electronics allows for use in humid climates.**

The outside of the PDV 6000 is constructed of sturdy plastic. The main display unit was secured with four screws. No environmental (e.g., corrosion) or mechanical (e.g., shear stress or impact) tests were performed. However, the outer shell of the instrument display unit appears to be well designed and constructed, indicating that the device should be durable under most field conditions. No evaluation could be made regarding the long-term durability of the cell assembly, or display circuitry. Visual inspection did not indicate that any problems were likely.

MTI indicated that a conformal coating on the device electronics allows for operation in an unlimited humidity range (i.e., other than the unit being submersed in water, no damage should result due to moisture). The PDV 6000 was observed in both wet and dry conditions (the instrument was operated at both the Oak Ridge, TN, and Las Vegas, NV, demonstration locations.

### *6.2.5 Availability of Vendor Instruments and Supplies*

**Documents the availability of the device and spare parts.**

**The MTI PDV 6000 units are stocked and available for purchase, rent, or lease. They are available within one week of order placement through the new MTI US operations. Spare parts and consumable supplies can be added to the original PDV 6000 order. Supplies not typically provided by MTI (pipetters and a scale) are readily available from laboratory supply firms.**

EPA representatives contacted MTI regarding the availability of the PDV 6000 and supplies. MTI indicated that approximately 90% of its current business is purchase, but that units are stocked and available for purchase, rent, or lease. According to MTI, such systems are available within one week of order placement through the new MTI U.S. operations.

The instrument comes standard with the following items:

- PDV 6000 handheld control unit
- Analytical cell assembly
- Analytical cell stand
- Ag/AgCl reference electrode
- Platinum counter electrode
- Glassy carbon working electrode
- Cable to link analytical cell to control unit

- DB9 serial cable to link PDV 6000 to a computer
- Reference electrode plating accessory
- Main powered 12 VDC supply (plug pack)
- NiMH rechargeable battery pack
- NiMH battery pack charger
- PDV 6000 operation manual
- VAS software installation disks
- Printed VAS User's Guide
- Warranty and contact sheet

Consumable supplies that are required for sample preparation are provided by MTI as kits and can be ordered with the PDV 6000 equipment. The kits contain the following items:

- Digestion bottles (10)
- Electrolyte medium (one 500-mL bottle)
- Electrolyte ingredients
- Hydrogen peroxide (two 30-mL bottles)
- Deionized water (one 250-mL bottle)
- Mercury standard (one 30-mL bottle)
- Waste container (one 500-mL bottle with kitty litter)
- Analysis cups (15)
- PVC gloves (2 pair)
- 5-ml soil grabber samplers (10)
- 10-100 µL pipette tips (14)
- 100-1,000 µL pipette tips (15)
- 5,000 µL pipette tips (14)
- Part I - Electrode polishing kit - dry cloth
- Part II - Electrode polish mixture

Common laboratory equipment also needed for sample preparation include air displacement pipettes, a repeating pipette, and a portable balance. This equipment can be purchased from MTI as part of an accessory kit but also is readily available from laboratory supply companies.

# Chapter 7
# Economic Analysis

The purpose of the economic analysis was to estimate the total cost of mercury measurement at a hypothetical site. The cost per analysis was estimated; however, because the cost per analysis would decrease as the number of samples increased, the total capital cost was also estimated and reported. Because unit analytical costs are dependent upon the total number of analyses, no attempt was made to compare the cost of field analysis using the PDV 6000 to the analytical costs associated with the referee laboratory. "Typical" unit cost results, gathered from analytical laboratories, were reported to provide a context in which to review the PDV 6000 costs. No attempt was made to make a direct comparison between these costs for different methods because of differences in sample throughput, overhead factors, total equipment utilization factors, and other issues that make a head-to-head comparison impractical.

This chapter describes the issues and assumptions involved in the economic analysis, presents the costs associated with field use of the PDV 6000, and presents a cost summary for a "typical" laboratory performing sample analyses using the reference method.

## 7.1 Issues and Assumptions

Several factors can affect mercury measurement costs. Wherever possible in this chapter, these factors are identified in such a way that decision-makers can independently complete a project-specific economic analysis. MTI offers purchase, rental, and lease options for potential PDV 6000 users. Rentals have a 1-month minimum and MTI has a variation of the rental option which allows a 50% credit for rental fees toward 50% of the instrument purchase price. Lease agreements are for three months, in which the 3-month lease equals the purchase price. Because site and user requirements vary significantly, each of these three options is discussed to provide each user with the information to make a case-by-case decision.

A more detailed cost analysis was performed on the instrument purchase option because MTI has indicated that instrument purchase comprises approximately 90% of company orders. The results of that cost analysis are provided in Section 7.2.

### *7.1.1 Capital Equipment Cost*

The PDV 6000 (the analytical instrument) is marketed as a standard package that includes all necessary equipment needed to operate the PDV 6000. The instrument and its accessories are regarded as capital equipment since they represent a relatively significant capital expenditure that typically is depreciated. Other equipment is required for sample preparation; however, these are typically non-depreciable items of lower cost and are better categorized as supplies (see Section 7.1.2).

It should be noted upfront that the PDV 6000 can be used as a stand-alone unit (without the VAS software). For stand-alone use, the controller unit is programmed to analyze 10 metals in the concentration range of 10 ppb to 30 ppm. According to MTI, the stand-alone unit is more appropriately used for field screening, and it does not provide the accuracy of laboratory analysis. MTI has indicated that the stand-alone unit should only be used for determining whether a sample may be above or below a particular threshold.

During the demonstration, MTI utilized the VAS software in conjunction with the PDV 6000. Because this software incorporates features such as standard addition calibration, simultaneous multi-element analysis, and storage of data,

it allows for more flexible and accurate analysis. The cost of the software adds less than 3% to the total cost of the PDV 6000 unit (i.e., the PDV 6000 costs $7,900 as a stand-alone unit and $8,100 with the VAS software). For this reason, an assumption was made that the user will utilize the VAS software with the PDV 6000 unit, whether purchased or rented. Costing the unit with the software reflects the instrumentation configuration used during the demonstration.

The VAS software requires a computer that has a minimum specification of 300 Mhz 586 processor (Pentium or equivalent), 64 MB RAM, 10 MB of free hard disk space, and runs on Windows 98, ME, NT, 2000, or XP. The cost of a computer is not included. For this economic analysis, an assumption was made that the user will supply a laptop computer that meets those specifications.

The instrument cost quoted by MTI does not include any packaging or freight costs to ship the instrument to the user location. For rental and lease agreements, the first month rental or lease cost is required up front. A user manual is provided with the unit at no cost. An 8-hour training session is available for up to eight individuals, at an additional fee of $950.

### 7.1.2 Cost of Supplies

The cost of supplies was estimated based on the supplies required to analyze demonstration samples and on discussions with MTI. For purposes of this cost estimate, the supplies required to analyze solid samples were factored into the cost estimate. Supplies utilized by MTI during the demonstration consisted of both consumable and non-consumable items. The consumable supplies were contained within "sample processing kits" and consisted of the following items:

- Digestion bottles
- Electrolyte medium
- Electrolyte ingredients
- Nitric acid ampules
- Hydrogen peroxide
- Deionized water
- Mercury standard
- Waste electrolyte jar
- Analysis cups
- PVC gloves
- 5-mL soil samplers
- 10-100 µL pipetter tips
- 100-1000 µL pipetter tips
- 5000 µL pipetter tips
- Electrode polishing kit
- Electrode polish mixture

These consumable items contained in the kits are readily available from MTI. Because the user cannot return unused portions of the kit contents, no salvage value is included in the cost of supplies. Personal protective equipment (PPE) supplies are assumed to be part of the overall site investigation or remediation costs; therefore, no PPE costs are included as supplies.

Non-consumable supplies utilized by MTI consisted of reusable items that were not included in the kits. These items were necessary to conduct the sample digestion procedure. These items included a portable laboratory scale required to measure out the correct mass of sample to digest; a set of air displacement pipetters (5-50 µL, 100-1,000 µL, and 200-1,000 µL); and a repeating pipetter (0.5 -50 mL). It should be noted that this type of equipment may or may not be already owned by a potential PDV 6000 user; however, for this economic analysis, an assumption was made that the user does not possess these items.

### 7.1.3 Support Equipment Cost

During the demonstration, the PDV 6000, control unit, cell assembly, and laptop computer that ran the VAS software were operated using AC power. The costs associated with providing the power supply and electrical energy were not included in the economic analysis; the demonstration site provided AC power at no cost. None of the items mentioned above can operate on DC power; however, the PDV 6000 can run on a NiMH rechargeable battery. The laptop computer can also run on a rechargeable battery.

Because of the large number of samples expected to be analyzed during the demonstration, EPA provided support equipment, including tables and chairs for the two field technician's comfort. In addition, EPA provided a tent to ensure that there were no delays in the project due to inclement weather. These costs may not be incurred in all cases; however, such equipment is frequently needed in field situations, so these costs were included in the overall cost analysis.

### 7.1.4 Labor Cost

The labor cost was estimated based on the time required for PDV 6000 and sample preparation equipment setup, sample preparation, summary data preparation, and instrument packaging at the end of the day. Setup time covered the time required to unpack the instrument, set up all components, and ready the device for operation. Sample preparation is somewhat labor intensive, albeit a routine operation. Sample preparation involved the following steps:

1. 2.0 grams of sample is weighed out and placed into a digestion bottle,
2. 4.0 mL of $HNO_3$ is pipetted into the bottle,

3. 4.0 mL of $H_2O_2$ is pipetted into the bottle, 1 mL at a time.
4. 12 mL of deionized (DI) water is added to quench the sample, and
5. 20 mL of electrolyte medium is added to the bottle (thus, a total 40 mL solution is created).

Due to the large number of samples to be prepared and analyzed, MTI had decided to utilize two individuals, one to conduct sample preparation and the other to conduct sample analysis. Sample preparation was the faster component of the entire procedure. As a result, sample digestion of all 197 demonstration samples was completed near the end of the second day of operation. Sample analysis was the time required to analyze all samples and submit a data summary. The data summary was strictly a tabulation of results in whatever form the vendor chose to provide. In this case, the MTI analyst electronically transferred the results of all 197 samples from the computer database at the end of the demonstration.

The time required to perform all tasks was rounded to the nearest 5 minutes; however, for the economic analysis, times were rounded to the nearest hour and it was assumed that a field technician who had worked for a fraction of a day would be paid for an entire 8-hour day. Based on this assumption, a daily rate for a field technician was used in the analysis.

During the demonstration, EPA representatives evaluated the skill level required for 1) conducting the field sample preparation and 2) to analyze the samples with the PDV 6000 utilizing the VAS software and report the results for mercury samples. Based on these field observations, a field technician with basic chemistry skills acquired on the job or in a university setting was considered qualified to conduct the sample preparation procedure. If this individual also possessed basic computer skills and completed a 1-day training course specific to the PDV 6000, and for the VAS software, that individual was also considered qualified to operate the instrument.

Analysis with the PDV 6000 can be performed with either one or two operators, depending upon the number of samples expected to be analyzed on a daily basis. For analyzing 15 or fewer samples per day, MTI advises that 1 person would be sufficient. For analyzing more than 15 samples per day MTI advises using 2 people. One also has to consider that in remote areas, where the instrument could be used, a minimum of two field staff are typically required as a health and safety precaution. (In the case of the demonstration, where over 50 samples were analyzed daily, 2 people were deemed necessary by MTI to efficiently process the samples.)

The use of two individuals may increase costs if travel and per diem were required; however, these cost are not considered, as explained in Section 7.1.6. For this economic analysis, an assumption was made that one technician will be able to conduct both sample preparation and sample analysis, with the understanding that there are ongoing activities at the site, allowing the technician to be in constant communication with other individuals.

An hourly rate of $15 was used for the field technician. A multiplication factor of 2.5 was applied to labor costs to account for overhead costs. Based on this hourly rate and multiplication factor, and an 8-hour day, a daily rate of $300 was used for the economic analysis. Monthly labor rates are based on the assumption of an average of 21 work days per month. This assumes 365 days per year, and non work days totaling 113 days per year (104 weekend days and 9 holidays; vacation days are discounted assuming vacations will be scheduled around short-term work or staff will be rotated during long projects). Therefore, 252 total annual work days are assumed.

### *7.1.5 Investigation-Derived Waste Disposal Cost*

MTI was instructed to segregate its waste into three categories during the demonstration: 1) general trash; 2) lightly contaminated PPE and wipes; and 3) excess contaminated soil (both analyzed and unanalyzed) and other highly contaminated wastes such as the digestion liquid. General trash was not included as investigation-derived waste (IDW) and is not discussed in this document. A separate container was provided for each waste category.

Lightly contaminated wastes consisted primarily of used surgical gloves and wipes. The surgical gloves were discarded for one of three reasons: 1) they posed a risk of cross contamination (noticeably soiled), 2) they posed a potential health and safety risk (holes or tears), or 3) the operator needed to leave the analysis area to perform other tasks (e.g., using a cell phone, etc.). The rate of waste PPE generation was in excess of what would be expected in a typical application of this instrument since EPA evaluators occasionally contributed used gloves to this waste accumulation point.

The specific wastes that were generated by MTI's measurement process consisted of the following:

- Empty $HNO_3$ ampules
- Waste PPE (nitrile gloves) and wipes
- Spent 70-mL digestion bottles containing a mixture of residual contaminated soil, $HNO_3$, and $H_2O_2$
- Empty analysis cups
- Spent electrolyte solution, containing a small concentration of mercury and other metals

The empty $HNO_3$ ampules were considered general trash, the PPE and wipes were considered lightly contaminated material, and the remaining items were considered hazardous wastes for purposes of this cost analysis.

### *7.1.6 Costs Not Included*

Items for which costs were not included in the economic analysis are discussed in the following subsections, along with the rationale for exclusion of each.

**Oversight of Sample Analysis Activities.** A typical user of the PDV 6000 would not be required to pay for customer oversight of sample analysis. EPA representatives observed and documented all activities associated with sample analysis during the demonstration. Costs for this oversight were not included in the economic analysis because they were project specific. For the same reason, costs for EPA oversight of the referee laboratory were also not included in the analysis.

**Travel and Per Diem for Field Technician.** Field technicians may be available locally. Because the availability of field technicians is primarily a function of the location of the project site, travel and per diem costs for field technicians were not included in the economic analysis.

**Sample Collection and Management.** Costs for sample collection and management activities, including sample homogenization and labeling, are site specific and, therefore, were not included in the economic analysis. Furthermore, these activities were not dependent upon the selected reference method or field analytical tool. Likewise, sample shipping, COC activities, preservation of samples, and distribution of samples were specific requirements of this project that applied to all vendor technologies and may vary from site to site. None of these costs were included in the economic analysis.

**Items Costing Less than $10.** The costs of inexpensive items, such as paper towels, were not included in the economic analysis.

**Documentation Supplies.** The costs for digital cameras used to document field activities were not included in project costs. These were considered project-specific costs that would not be needed in all cases. In addition, these items can be used for multiple projects. Similarly, the cost of supplies (logbooks, copies, etc.), used to document field activities, was not included in the analysis because they are project specific.

**Health and Safety Equipment.** Costs for rental of the mercury vapor analyzer and the purchase of PPE were considered site specific and, therefore, not included as costs in the economic analysis. Safety glasses and disposable gloves were required for sample handlers and would likely be required in most cases. However, these costs are not specific to any one vendor or technology. As a result, these costs were not included in the economic analysis.

**Mobilization and Demobilization.** Costs for mobilization and demobilization were considered site specific, and not factored into the economic analysis. Mobilization and demobilization costs actually impact laboratory analysis more than field analysis. When a field economic analysis is performed, it may be possible to perform a single mobilization and demobilization. During cleanup or remediation activities, several mobilizations, demobilizations, and associated downtime costs may be necessary when an off-site laboratory is used because of the wait for analytical results.

## 7.2 PDV 6000 Costs

This section presents information on the individual costs of capital equipment, supplies, support equipment, labor, and IDW disposal for the PDV 6000.

### *7.2.1 Capital Equipment*

The PDV 6000 sells for $7,900 as a stand-alone unit, and for $8,100 with the VAS software. Whether purchased or rented, the unit comes with the following components and items:

- Handheld control unit
- Analytical cell assembly
- Analytical cell stand
- Reference electrode
- Counter electrode
- Working electrode
- Cable to link unit/cell
- Cable to link unit/laptop
- Plating accessory
- 12 VDC supply
- NiMH battery
- NiMH battery charger
- Operation manual
- VAS installation discs
- VAS User's Guide
- Warranty/contact sheet

During the demonstration, the PDV 6000 was operated for approximately 3 days and was used to analyze 197 samples. Table 7-1 summarizes the PDV 6000 capital cost for four procurement options: purchase, rental, lease, and rental with an option to purchase. These scenarios cover only capital cost, not the cost of optional or user-supplied equipment, supplies, support equipment, labor, and IDW disposal.

**Table 7-1. Capital Cost Summary for the PDV 6000**

| Item | Quantity | Unit Cost ($) | Total Cost for Selected Project Duration | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1-Month | 3-Month | 6-Month | 12-Month | 24-Month |
| Purchase PDV 6000/VAS | 1 | $8,100 | $8,100 | $8,100 | $8,100 | $8,100 | $8,100 |
| Monthly Rental of PDV 6000 [a] | 1 | $2,200 | $2,200 | $6,600 | $13,200 | $26,400 | $52,800 |
| Lease PDV 6000/VAS | 1 | $2,700 | $2,700 | $8,100 | $8,100 | $8,100 | $8,100 |
| Rental with purchase option [b] | 1 | $2,200 | $2,200 | $6,600 | $12,850 [c] | $12,850 [c] | $12,850 [c] |

a The standard rental period is generally a minimum of 1-month; however, the PDV 6000 can be rented for a 1-week period for $600 (with pipettes) or $800 (without pipettes).
b 50% of monthly rental fee is credited to 50% of the purchase price.
c After 4 months of renting the unit, $8,800 of rentals fees are incurred. Up to $4,050 can be credited toward purchase. Therefore, a balance of $4,050 would be owed to purchase the instrument and the total cost would be $12,850.

Figure 7-1 shows the relative costs for the basic capital equipment for the purchase, rental, and rental/purchase option (PO) scenarios. The lease arrangement is not shown since it is very similar to direct purchase for the time scales presented. These costs reflect the basic PDV 6000 unit and accessories (with VAS software included). No options (e.g., laboratory scale or multi-volume dispensing pipetters) and no supply or shipping costs are included.

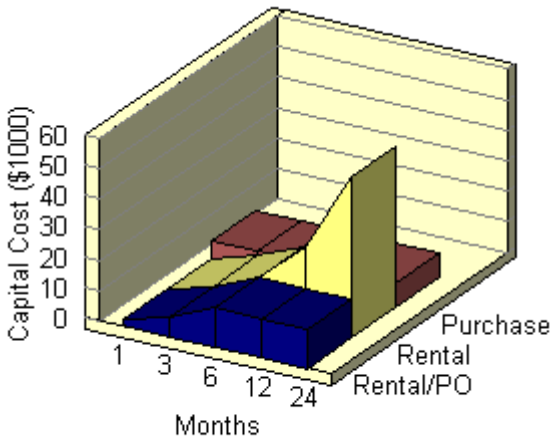


**Figure 7-1. Capital equipment costs.**

As would be expected, this chart shows that purchase is the most cost-effective option (in terms of capital costs) for long-term use, and the rental with a purchase option may be desirable for product trial. Rental is shown to be a logical choice only for short-term projects (i.e., three months or less).

MTI's policy of applying a portion of rental costs toward instrument purchase would be a consideration in instances where the project duration is unknown, or when the user's acceptability and reliance on the instrument increase with usage. As noted in Table 7-1, after 4 months of renting the PDV 6000, $4,050 of the $8,800 expended for rental fees can be credited toward instrument purchase. Therefore, a balance of $4,050 would be owed to purchase the instrument, and the total cost of the rent-to-own option would be $12,850.

### *7.2.2 Cost of Supplies*

During the demonstration, there were two types of supplies used by MTI. The first type was consumable items that were contained within "sample preparation kits." One kit contained enough supplies for 10 sample measurements, which correlated to approximately $10 per analysis. Based on the assumed 10-hour workday and 21-day work month (estimated in Section 7.1.4), and MTI's sample measurement rate of roughly 50 samples per day (as calculated in Section 6.1.4), a total of 5 "sample preparation kits" would be required per day. MTI prices

these kits at $99 each and offers a 15% discount on orders of 20 kits or more. Therefore, using a discounted price of $84 per kit cost, a 21-day (i.e., 1 month) supply would total approximately $8,800.

In addition to the consumable items contained within the sample preparation kits, there was reusable sample preparation equipment used during the demonstration. These items included a portable laboratory scale used to measure out the proper mass of sample and a set of variable-sized pipetters used to dispense accurate and precise volumes of reagents and standards.

The scale used by MTI was an Aculab portable scale. A compact electronic scale manufactured by Ohaus is priced at about $110 (www.Fishersci.com, 2003). This comparable scale would be sufficient for the sample mass measurements in the field.

MTI was equipped with four pipetters during the demonstration. Three of the instruments were air displacement pipetters with a 50-1000 µL dispensing capacity, and one of the instruments was a repeating pipetter with a 0.5-50 mL dispensing capacity. The disposable pipetter tips used for the demonstration were provided in the kits which prevented cross contamination between samples.

The microliter range air displacement pipetters are priced at $230 each (www.Fishersci.com, 2003); therefore, a set of three air displacement pipetters would cost $690. For dispensing set amounts of larger liquid volume, MTI used a 0.5-50 mL HandyStep repeating pipetter. This type of pipetter prices at $320 (www.Fishersci.com, 2003). The lifetime of these pipetters could vary significantly, but it is assumed that the pipetters would last several years. The total annual costs for these supplies (i.e., kits, scale, and pipetters) would total roughly $10,000.

Table 7-2 summarizes the costs for the supplies, assuming that the same number of samples are run per day during each 3-month period. As indicated, for continuous daily measurements the sample preparation kits dominate the cost of supplies. For 1 month of continuous sampling, the kits comprise about 89% of total supply costs. This percentage escalates with duration until the kits comprise nearly the entire supply cost percentage. Table 7-3 indicates the costs associated with analysis when the user prepares their reagents and purchases disposable supplies as opposed to purchasing preparation kits. The 1-month column is indicated as not applicable (NA) because it is not advantageous to prepare reagents for short periods of time. In addition to the chemical and supply costs, $1,000 per month amount is added to the cost to account for preparation time and reagent analysis. Based on this observation, the instrument supplies (i.e., scale and pipetters) should be considered negligible costs, especially after the first few months of daily measurements.

**Table 7-2. Supplies Cost Summary, Using Preparation Kits**

| Item | Months [a,b] | | | | |
|---|---|---|---|---|---|
| | 1 | 3 | 6 | 12 | 24 |
| Prep. Kits | $8,800 | $26,000 | $53,000 | $110,000 | $210,000 |
| Scale | $110 | $110 | $110 | $110 | $110 |
| µL Pipetters | $690 | $690 | $690 | $690 | $690 |
| mL Pipetter | $320 | $320 | $320 | $320 | $320 |
| Total Cost | $9,900 | $27,000 | $54,000 | $110,000 | $210,000 |

a Cost values are rounded to two significant digits.
b MTI can arrange to make bulk kits available with electrolyte and water in 25 L reusable drums, the standard as the small 20-mL vials, the acid and peroxide in reusable 5 L containers with accurate dispenser and plasticware in a big bag (no packaging) for $4,000 for 1,000 samples, subject to a minimum of order of $12,000. The 24-month cost for bulk supplies would be $96,000.

**Table 7-3. Supplies Cost Summary, Preparing Reagents**

| Item | Months [a] | | | | |
|---|---|---|---|---|---|
| | 1 | 3 | 6 | 12 | 24 |
| Reagents [b] | NA | $8,900 | $16,000 | $31,000 | $62,000 |
| Scale | NA | $110 | $110 | $110 | $110 |
| µL Pipetters | NA | $690 | $690 | $690 | $690 |
| mL Pipetter | NA | $320 | $320 | $320 | $320 |
| Total Cost | NA | $10,000 | $17,000 | $32,000 | $63,000 |

a Cost values are rounded to two significant digits.
b The "reagents" cost includes disposable supplies and preparation labor.

### *7.2.3 Support Equipment*

MTI was provided with a 10x10 foot tent for protection from inclement weather during the demonstration. It was also provided with one table and two chairs for use during sample preparation and analytical activities. The rental cost for the tent (including detachable sides, ropes, poles, and pegs) was $270 per week. The rental cost for the table and two chairs for one week totaled $6. Total support equipment costs were $276 per week for rental.

For longer projects, purchase of support equipment should be considered. Two folding chairs would cost approximately $40. A 10x10 foot tent would cost between $260 and $1,000, depending on the construction materials and the need for sidewalls and other accessories (e.g., sand stakes, counter weights, storage bag, etc.). A cost of $800 was used for this cost analysis. A folding table would cost between $80 and $250, depending on the supplier. For purposes of this cost analysis, $160 was used. Total purchase costs for support equipment are estimated at $1,000.

### 7.2.4 Labor Cost

MTI utilized two people to analyze 197 samples; a sample preparation person spent almost two days performing sample digestions and an instrument analyst spent three days analyzing and reporting data results. Combined, the total operational time was 2,280 minutes. Including instrument setup and disassembly, the total labor time expended during the demonstration was roughly 3,000 minutes. This time correlates to 50 hours, or five 10-hour days for one individual. Based on a labor rate of $300 per day, total labor cost for using the PDV 6000 during the demonstration was $1,500.

Labor costs for the hypothetical site assume qualified technicians are available locally (i.e., no lodging or per diem costs are apply). Table 7-4 summarizes labor costs for various operational periods, assuming 21 work days per month (on average) and 252 work days per year. The costs presented do not separate supervision and quality control because these would be associated with use of any analytical instrument and are a portion of the overhead multiplier built into the labor rate.

**Table 7-4. Labor Costs**

| Item | Months | | | | |
|---|---|---|---|---|---|
| | 1 | 3 | 6 | 12 | 24 |
| Technician | $6,300 | $18,900 | $37,800 | $75,600 | $151,200 |
| Supervisor | NA | NA | NA | NA | NA |
| Quality Control | NA | NA | NA | NA | NA |
| Total | $6,300 | $18,900 | $37,800 | $75,600 | $151,200 |

NA = Not applicable.

### 7.2.5 Investigation-Derived Waste Disposal Cost

MTI generated PPE waste, digestate solution with excess soil waste, and waste electrolyte solution. The PPE waste was charged to the overall project due to project constraints. The minimum waste volume is a 5-gallon container. Mobilization and container drop-off fees were $1,040; a 5-gallon soil waste drum was $400, and a 5-gallon liquid waste drum was $400. (These costs were based on a listed waste stream with hazardous waste number U151.)

The total demonstration IDW disposal cost was $1,840. These costs may vary significantly from site to site, depending on whether the waste is classified as hazardous or nonhazardous and whether excess sample material is generated that requires disposal. Table 7-5 presents IDW costs for various operational periods, assuming that waste generation rates were similar to those encountered during the demonstration.

It should be noted that when a large amount of digestion samples are conducted for using the PDV 6000, the waste digestion liquid would be poured out of each digestion bottle and into a liquid waste container (as opposed to just discarding the 70 mL digestion bottle containing the liquid, as was done during the demonstration). The empty digestion bottles could then be thrown away as non-hazardous waste. Since there is 40 mL of digestion liquid generated per sample analyzed, there would be approximately 42 liters, or 11 gallons, of digestion liquid generated per month (40 mL x 50 samples x 21 days).

**Table 7-5. IDW Costs**

| Item | Months | | | | |
|---|---|---|---|---|---|
| | 1 | 3 | 6 | 12 | 24 |
| Drop Fee | $1,040 | $3,120 | $6,240 | $12,480 | $24,960 |
| Disposal [a] | $1,400 | $2,000 | $3,400 | $6,000 | $10,000 |
| Total | $2,440 | $5,120 | $9,640 | $18,480 | $34,960 |

a Disposal costs are estimated at $1,400 for a 20-gallon container and $2,000 for 55-gallon drum. The most economical combination of containers is used for disposal cost estimates.

### 7.2.6 Summary of PDV 6000 Costs

The total cost for performing mercury analysis is summarized in Table 7-6. This table reflects costs for project durations of from 1 to 24 months. The purchase option was used for estimating the equipment cost. For the first month of use, the total cost is primarily the instrument purchase and labor. As time progresses, supplies and labor become dominant cost categories, the sample

preparation kits being the dominant supplies cost. When operating the PDV 6000 for periods in excess of three months, it may be more economical to prepare the reagents and purchase the disposable items, as opposed to purchasing the sample extraction kits.

**Table 7-6. Summary of Purchase Costs for the PDV 6000**

| Item | Quantity | Unit | Unit Cost ($) | Total Cost for Selected Project Duration | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1-Month | 3-Month | 6-Month | 12-Month | 24-Month |
| Capital Equipment [a] | | | | | | | | |
| Purchase | 1 | NA | $8,100 | $8,100 | $8,100 | $8,100 | $8,100 | $8,100 |
| Supplies [b] | | | | | | | | |
| Reagents and Disposable | 1 | each | $84 | $8,800 | $8,900 | $16,000 | $31,000 | $62,000 |
| Micro Pipetters (set of 3) | 1 | set | $690 | $690 | $690 | $690 | $690 | $690 |
| Repeating Pipetter | 1 | each | $320 | $320 | $320 | $320 | $320 | $320 |
| Portable Scale | 1 | each | $110 | $110 | $110 | $110 | $110 | $100 |
| Total Supply Cost | – | ------- | -------- | $9,900 | $10,000 | $17,000 | $32,000 | $63,000 |
| Support Equipment [a, c] | | | | | | | | |
| Table (optional) - weekly | 1 | each | $5 | $20 | $60 | $120 | $160 | $160 |
| Chairs (optional) - weekly | 2 | each | $1 | $10 | $25 | $40 | $40 | $40 |
| Tent (for inclement | 1 | each | $270 | $800 | $800 | $800 | $800 | $800 |
| Total Support Equip. Cost | -- | ------- | ------- | $830 | $885 | $960 | $1,000 | $1,000 |
| Labor | | | | | | | | |
| Field Technician | 1 | hour | $38 | $6,300 | $18,900 | $37,800 | $75,600 | $151,000 |
| IDW | | | | | | | | |
| Drop Fee | NA | | $1,040 | $1,040 | $3,120 | $6,240 | $12,480 | $24,960 |
| Disposal | NA | week | $400 | $1,400 | $2,000 | $3,400 | $6,000 | $10,000 |
| Total IDW Costs | – | ------- | --------- | $2,440 | $5,120 | $9,640 | $18,480 | $34,960 |
| Total Cost [d] | | | | $28,000 | $43,000 | $74,000 | $136,000 | $260,000 |

a Costs are rounded to a maximum of three significant digits.
b The number of sample preparation kits (or reagents) provides sufficient supplies to analyze 50 samples per day. Significant cost savings are achieved if reagents are purchased in bulk. The 1-month cost uses sample preparation kits, all other months are based upon preparing reagents and purchasing disposable supplies (e.g., beakers, pipette tips).
c Rental costs were used through the 3-month period for chairs and the 6-month period for the table. Purchase costs were used for longer periods. Purchase costs for the tent were used for all periods.
d Totals are rounded to two significant digits.

From these data, it is apparent that the cost to purchase the PDV 6000 instrument and accompanying software becomes relatively insignificant after 6 months of continual use. This may imply that the instrument purchase option is the most cost-effective in many instances; however, the decision on which procurement option to utilize should be made on a case-by-case basis.

An alternative to the vendor-supplied kits may be desirable due to the relatively high cost of the kits when used over an extended period of time. MTI will supply the reagent concentrations to anyone interested is preparing their own extraction reagents.

Table 7-7 summarizes costs for the actual demonstration. Note that the 1-month rental cost of the PDV 6000 was used for capital costs.

The cost per analysis based on 197 samples when renting the PDV 6000 is $43.74 per sample. The cost per analysis for the 197 samples, excluding instrument cost, is $32.57 per sample.

**Table 7-7. PDV 6000 Costs by Category**

| Category | Category Cost | Percentage of Total Costs [a] |
|---|---|---|
| Instrument | $2,200 | 25.5% |
| Supplies [b] | $2,800 | 32.5% |
| Support Equipment | $276 | 3.2% |
| Labor | $1,500 | 17.4% |
| IDW Disposal | $1,840 | 21.4% |
| Total | $8,616 | 100.0% |

a The percentages are rounded to one decimal place; the total percentage is 100%.

b Includes 20 sample preparation kits, a portable scale, 3-µL capacity pipetters, and a milliliter capacity pipetter.

## 7.3 Typical Reference Method Costs

This section presents costs associated with the reference method used to analyze the demonstration samples for mercury. Costs for other project analyses are not covered. The referee laboratory utilized SW-846 Method 7471B for all soil and sediment samples. The referee laboratory performed 421 analysis over a 21-day time period.

A typical mercury analysis cost, along with percent moisture for dry-weight calculation, is approximately $35. This cost covers sample management and preparation, analysis, quality assurance, and preparation of a data package. The total cost for 197 samples at $35 would be approximately $6,895. This is based on a standard turnaround time of 21 calendar days. The sample turnaround time from the laboratory can be reduced to 14, 7, or even fewer calendar days, with a cost multiplier between 125% to 300%, depending upon project needs and laboratory availability. This results in an approximate cost range from $6,895 to $20,685. The laboratory cost does not include sample packaging, shipping, or downtime caused to the project while awaiting sample results.

# Chapter 8
# Summary of Demonstration Results

As discussed previously in this ITVR, the MTI PDV 6000 was evaluated by having the vendor analyze 197 soil and sediment samples. These 197 samples included high-, medium-, and low-concentration field samples from four sites, SRMs, and spiked field samples. Table 8-1 provides a breakdown of the numbers of these samples for each sample type and concentration range or source. Collectively, these samples provided different matrices, concentrations, and types of mercury needed to perform a comprehensive evaluation of the PDV 6000.

## 8.1 Primary Objectives

The primary objectives of the demonstration were centered on evaluation of the field instrument and performance in relation to sensitivity, accuracy, precision, time for analysis, and cost. Each of these objectives was discussed in detail in previous chapters and is summarized in the following paragraphs. The overall demonstration results suggest that the experimental design was successful for evaluation of the MTI PDV 6000. Quantitative results were reviewed. The results from this instrument were found not to be comparable to standard analyses performed by the laboratory in terms of precision and accuracy, and the collected data provide evidence to support this statement.

The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Following procedures established in 40 CFR Part 136, the MDL is between 1.67 and 3.67 mg/kg. The equivalent MDL for the referee laboratory is 0.0026 mg/kg. Examples from analyzed samples, however, suggest that the MTI MDL may be closer to 0.811 mg/kg or lower. Values detected at these lower levels; however, would likely be highly inaccurate and should only be considered as a “positive hit” without any implied accuracy or precision. The calculated MDL is only intended as a statical estimation and not a true test of instrument sensitivity.

The low standard calculations suggest that a PQL for the MTI field instrument is 4-8 mg/kg. The %D for the average MTI result for a sample concentration of 4.75 mg/kg is 46%. The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg with a %D of 10% or less, based upon a lower calibration standard. Both the MDL and PQL were determined for soils and sediments.

Accuracy was evaluated by comparison to SRMs and comparison to the referee laboratory analysis for field samples. This included spiked field samples for evaluation of additional concentrations not otherwise available. In summary, MTI data were within the SRM 95% prediction intervals about 50% of the time. ALSI data compared to SRM values were within the 95% prediction interval 89% of the time. The comparison between the MTI field data and the ALSI results suggests that the two data sets are not different, but the similarity for individual samples is often the result of high variability associated with the MTI reported values.

In determining the number of results significantly above or below the value reported by the referee laboratory, the number of MTI average values greater than 50% different from the referee laboratory results or SRM reference values was only 6 for 21 different sample lots and those greater than 100% different were only 2 for 21 different sample lots. MTI results, therefore, appear to provide a rough estimate of accuracy for field determination, and may be affected by interferences not identified by this demonstration. It should be concluded, however, that the MTI PDV 6000 did not compare well to laboratory Method 7471B in terms of obtaining accurate analyses of mercury in soil.

Precision was determined by analysis of replicate samples. The precision of the MTI field instrument did not compare well to the measured laboratory precision. The overall RSD for MTI is 35.1% which is above the 25% RSD objective set for the laboratory. The overall laboratory RSD is 22.3%.

Time measurements were based on the length of time the operator spent performing all phases of the analyses, including setup, calibration, and sample analyses (including all reanalyses). MTI analyzed 197 samples in 2,280 minutes over three days, which averaged to 11.6 minutes per sample result. Based on this, an operator could be expected to analyze 41 samples (8 hours x 60 minutes ÷ 11.6 minutes/sample) in an 8-hour day.

Cost of the MTI sample analyses included capital, supplies, labor, support equipment, and waste disposal. The cost per sample was calculated both with and without the cost of the instrument included. This was performed because the first sample requires that the instrument is either purchased or rented, and as the sample number increases, the cost per sample would decrease. A comparison of the field MTI cost to off-site laboratory cost was not made. To compare the field and laboratory costs correctly, it would be necessary to include the expense incurred to the project due to waiting for analysis results to return from the laboratory (potentially several mobilizations and demobilizations, stand-by fees, and other aspects associated with field activities).

Table 8-2 summarizes the results of the primary objectives.

## 8.2 Secondary Objectives

Table 8-3 summarizes the results of the secondary objectives.

**Table 8-1. Distribution of Samples Prepared for MTI and the Referee Laboratory**

| Site | Concentration Range | Sample Type | | | |
|---|---|---|---|---|---|
| | | Soil | Sediment | Spiked Soil | SRM |
| Carson River | Low (1-500 ppb) | 3 | 10 | 7 | 0 |
| (Subtotal = 48) | Mid (0.5-50 ppm) | 0 | 0 | 0 | 7 |
| | High (50->1,000 ppm) | 0 | 0 | 7 | 14 |
| Puget Sound | Low (1 ppb - 10 ppm) | 13 | 0 | 7 | 3 |
| (Subtotal = 51) | High (10-500 ppm) | 0 | 10 | 7 | 11 |
| Oak Ridge | Low (0.1-10 ppm) | 0 | 3 | 0 | 14 |
| (Subtotal = 54) | High (10-800 ppm) | 13 | 10 | 0 | 14 |
| Manufacturing | General (5-1,000 ppm) | 23 | 0 | 7 | 14 |
| (Subtotal = 44) | | | | | |
| Subtotal | | 52 | 33 | 35 | 77 |

**Table 8-2. Summary of PDV 6000 Results for the Primary Objectives**

| Demonstration Objective | Evaluation Basis | Performance Results PDV 6000 | Reference Method |
|---|---|---|---|
| Instrument Sensitivity | MDL. Method from 40 CFR Part 136 | Between 1.67 and 3.67 mg/kg | 0.0026 mg/kg |
| | PQL. Low concentration SRMs and samples. | Approximately 4-8 mg/kg | 0.005 mg/kg |
| Accuracy | Comparison to SRMs, field, and spiked samples covering the entire range of the instrument calibration. | MTI's PDV 6000 is not within expected accuracy for laboratory analyses. MTI's field instrument was only within the SRM 95% prediction intervals about 50% of the time. The comparison between the MTI field data and the ALSI results suggests that the two data sets are not different but similarity for individual samples is often the result of high variability associated with the MTI reported values. The MTI PDV does, however, appear to provide a rough estimate of mercury concentrations in soil and sediment. | |
| Precision | Determined by analysis of replicate samples at several concentrations. | Overall RSD for the MTI PDV 6000 was computed to be 35.1% compared to the referee laboratory RSD of 22.3%. This is a combined measure of precision which includes sampling and aliquoting variations. | |
| Time per Analysis | Timed daily operations for 3 days and divided the total time by the total number of analyses. | Two MTI representatives performed all setup, calibration checks, sample preparation, sample analysis, and equipment disassembly. Individual analyses took 7.5 minutes each, but the total time for preparation and analysis averaged approximately 11.6 minutes per sample. | |
| Cost | Costs were provided by MTI and independent suppliers of support equipment and supplies. Labor costs were estimated based on a salary survey. IDW costs were estimated from the actual costs encountered at the Oak Ridge demonstration. | The cost per analysis, based on measurement of 197 samples, when incurring a minimum 1-month rental fee for the PDV 6000, is $43.74 per sample. Excluding the instrument rental cost, the cost for analyzing the 197 samples is $32.57 per sample. The total cost for equipment rental and necessary supplies during the demonstration is estimated at $8,600. The cost breakout for the demonstration by category is: capital costs, 25.5%; supplies, 32.5%; support equipment, 3.2%; labor, 17.4%; and IDW disposal, 21.4%. | |

**Table 8-3. Summary of PDV 6000 Results for the Secondary Objectives**

| Demonstration Objective | Evaluation Basis | Performance Results |
|---|---|---|
| Ease of Use | Field observations during the demonstration. | The instrument appears to be easy to operate as a stand-alone unit or in conjunction with the VAS software. Training on the unit and the VAS software would be recommended for first-time users. A laboratory or field technician with a basic knowledge of chemistry and basic computer skills could operate the equipment after a 1-day training course. |
| Health and Safety Concerns | Observation of the equipment, operating procedures, and any equipment certifications during the demonstration. | No significant health and safety concerns were noted for the PDV 6000. The main potential health and safety concern observed during the demonstration was potential exposure to fumes resulting from the reactions that occurred during sample preparation. This observation emphasizes the need for PPE such as safety glasses, gloves, and possibly a laboratory apron when conducting acid digestions. |
| Portability of the Device | Review of device specifications, measurement of key components, and observation of equipment setup and tear down before, during, and after the demonstration. | The PDV 6000 was easily portable due to its compact size and weight, and by the method by which it is transported (i.e., the unit and instrument accessories are transported within a briefcase size carrying case. The unit was easily set up by MTI and was easily carried while walking. The instrument can be characterized as truly field portable. |
| Instrument Durability | Observation of the equipment design and construction, and evaluation of any necessary repairs or instrument downtime during the demonstration. | The PDV 6000 control unit is well designed and constructed for durability. The hard shell carrying case used to transport the unit and ancillary equipment provides adequate protection of electrodes and other sensitive components. |
| Availability of the Vendor Instruments and Supplies | Review of vendor website and telephone calls to the vendor after the demonstration. | Per MTI, the PDV 6000 units are stocked in the U.S. and available for purchase, rent, or lease within one week of order placement through the new MTI U.S. operations. Spare parts and consumable supplies can be added to the original PDV 6000 order. Supplies not typically provided by MTI (pipetters and laboratory scale) are readily available from laboratory supply firms. |

# Chapter 9
# Bibliography


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.

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

Monitoring Technologies International Pty. Ltd. 2002a. PDV 6000 - Portable Heavy Metals Analyzer, Operation Manual, version 2.2.

Monitoring Technologies International Pty. Ltd. 2002b. Voltammetric Analysis System - VAS User's Guide, version 2.1.

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

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

U.S. Environmental Protection Agency. 1995. *Contaminants and Remedial Options at Selected Metal-Contaminated Sites*. July 1995. Washington D.C. EPA/540/R-95/512.

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. 1998. Unpublished. *Quality Assurance Project Plan Requirements for Applied Research Projects*, August 1998.

U.S. Department of Energy. 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, TN. DOE/OR/01-1641&D2.

U.S. Environmental Protection Agency. 2002a. Region 9 Internet Web Site, www.epa.gov/region9/index.html.

U.S. Environmental Protection Agency. 2002b. *Guidance on Data Quality Indicators.* EPA G-5i, Washington D.C., July 2002.

U.S. Environmental Protection Agency. 2003. *Field Demonstration and Quality Assurance Project Plan - Field Analysis of Mercury in Soil and Sediment*. August 2003. Washington D.C., EPA/600/R-05/053.

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.

www.Fishersci.com, 2003.

www.monitoring-technologies.com, 2003.

www.mti.com.au, 2003.

# Appendix A
# MTI Comments

**Site Demonstration Comments**

The ITVR demonstration showed that the PDV 6000 can produce data in the field that can confidently be used to effectively manage on site investigations and remediation projects. MTI is a small company and values the opportunity to compare its method to a fully validated reference method. MTI would like to thank the teams at SAIC and the EPA for setting up the program and looking after the vendors in such a professional way.

MTI completed all 197 samples in a 3-day working period, 2 days using 2 technicians and the third day using just 1. This time would have been significantly reduced had the PDV 6000 method been used to classify soil samples into set concentration bands as against a more quantitative analysis.

The PDV 6000 when used in the field is designed to provide screening data and is not expected to generate laboratory quality data over a wide concentration range. The instrument is calibrated using a single point calibration, either by the method of curve comparison or standard addition. The concentration selected to calibrate the PDV 6000 is equivalent to the pollutant action level for that site. This concentration is simply achieved by varying the volume of standard added to the analysis cup. The amount of sample extract analysed can also be varied to reflect the expected concentration range in the soil. This approach has two benefits:

1. It is very easy to change the calibration range to reflect changing pollutant concentrations in the soil.
2. It gives the best accuracy around the important action concentration without the need to generate multipoint calibration curves and therefore allows for significantly faster sample throughput.

The PDV 6000 field analysis procedure has been designed to give the best accuracy around the site specific pollutant concentration that drives the investigation or remediation. For example, if the threshold for contamination is 5 mg/kg the standard concentration and analysis procedure sets 5mg/kg as the midpoint of the calibration. This will provide accurate results within a 1-10 mg/kg range (x10 range) for the samples analysed. The PDV calibration curve is linear over 2 orders of magnitude and therefore a single point calibration is sufficient to cover 1 order of magnitude.

Table A-1 shows the volumes and analysis methods recommended for the commonly encountered contamination ranges.

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**Table A-1. Calibration Standard and Analysis Information**

| Target Soil Concentration (mg/kg) | Volume of sample extract (ml) to add to analysis cup | Volume of Hg Electrolyte (ml) to add to analysis cup | Deposit time (seconds) | Hg calibration concentration (mg/ml) |
|---|---|---|---|---|
| 0.5 - 5 | 5 | 15 | 200 | 0.025 – 0.075 |
| 2 - 20 | 2 | 20 | 100 | 0.01 – 0.1 |
| 10 - 100 | 1 | 20 | 60 | 0.025 – 0.25 |
| 100 -1000 | 0.1 | 20 | 30 - 60 | 0.025 – 0.25 |

The above procedure could not be adopted for this ITVR evaluation, as a quantitative result was wanted across a very wide concentration range. The concentration ranges encountered were:

Carson River: low x500 (0.001 – 0.5 ppm), mid x100 (0.5 – 50 ppm), high x200 (50 – >1000 ppm)
Puget Sound: low x10,000 (0.001 - 10 ppm, high x50 (10 – 500 ppm)
Manufacturing Site: x200 (5 - 1000 ppm)
Oak Ridge: low x100 0.1 – 10 ppm), high x80 (10 – 800 ppm)

This meant that the procedure used to analyze the sample deviated from the standard operating procedure for the PDV 6000. The data generated however clearly shows that the PDV 6000 method has similar precision and accuracy to the laboratory method when the calibration is close to the actual concentration of mercury in the sample. This makes the PDV 6000 perfectly acceptable for managing site investigations and remediations.

It should also be noted that in this evaluation, all of the samples had been carefully prepared to ensure they were virtually identical for all the vendors. In the field, the issue of sample homogenization is critical. The PDV 6000 procedure uses a 2 g sample that can be prepared on site using a very quick mixing procedure from an initial 500 – 1000g sample. Two grams are considered to be the minimum amount of sample that can be used to get a representative field analysis for soil types that include, clays, chalks and large particles of other porous stones. The relevance of any field or laboratory analysis data will only be good if the sampling is statistically meaningful and sample size is an important factor in this. The smaller the sample analyzed on site, the more samples that must be analyzed to provide meaningful data.

**Comments on SRM Precision and Accuracy Interpretation**

As discussed above, quantifying over wide concentration ranges is not ideal for the PDV as a single calibration point cannot cover the entire range. The PDV operators in this situation therefore selected the mid point of the expected sample concentration range to set the calibration to, knowing that it would be less accurate at either end of the range. It was hoped to initially screen the samples and those that fell out of the calibration range could be re-analyzed during the course of the evaluation. The emergencies unfortunately prevented this from being done for all of these samples. The data generated was still submitted and MTI accepted that this would compromise the statistical analysis of the results at either end of the range.

Of the SRM sets analyzed, 57% of the target concentrations were at the extreme limit of the sample set and therefore out of the effective calibration range of the PDV. Where the SRMs were within the calibration range of the PDV, good agreement with the expected concentration was achieved, together with reasonable precision. (lot# 48 %RSD 26.8, lot# 49 %RSD 28.2, lot# 50 %RSD 38.2, lot# 62 %RSD 21.1, lot# 63 %RSD 34.8 and lot# 66 %RSD 26.6), which compares to an average 25% RSD for the laboratory analysis. Not shown in the report is the data for SRM lot# 46 (%RSD 20), which on extraction evolved large amounts of Bromine. The target value was 21 ppm and the PDV method averaged 18 ppm over 5 samples analyzed using the 10 to 100 ppm calibration range with a % RSD of 15.3. Sample lot# 44 also evolved bromine, but these were reported as below detection limits using the 1 – 10 ppm calibration range, even though the expected concentration was 4.7 ppm. For this sample lot 5 mL of sample extract were added to the electrolyte, compared to 1 mL for lot#

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46. The extra Bromine in the analysis cup could have allowed the formation of the relatively insoluble $HgBr_2$. It is suggested that the evolution of bromine on site would indicate that there was a serious problem with the soil in the area and further investigation of the site would be needed. The laboratory was unable to accurately detect mercury in either of these brominated SRMs.

Lot# 52 was within the calibration range, but both the laboratory and the PDV method reported significantly lower concentrations than expected.

The low concentration SRM results from the initial analysis using a 1–10 ppm calibration range did not detect any Mercury and only a trace for those samples with 0.6 ppm and higher. The exception was samples from lot#38 that showed good peaks. The analysis was then repeated using the very low level method. The mercury concentrations using the low level method were typically reported as up to 5 times the expected concentration. For these samples (Lot#35, 37 and 57) 10 mL of sample and 10 mL of electrolyte were used with a 120-180 second deposit time. These samples were run sequentially, using the same batch of electrolyte. The initial matrix blank indicated no mercury. The sample analysis however all showed a significant peak at the Mercury position. This shows mercury was in the analysis cup. The results for lot# 2 and 35 which are below the detection limits of the PDV indicate approximately 40 parts per billion of mercury was in the analysis cup. This is equivalent to 1.6 ppm in the soil. All of these samples stood in the extraction bottle for over 24 hours before analysis, which is not in the usual SOP, where analysis is required within a few hours of the extraction.

The better variability in %RSD between the SRMs and the field samples could be due to the chemical form of the mercury in the sample. The field samples have been in contact with the Mercury for several decades and as such the mercury can form tighter associations with the matrix. SRMs due to their method of production are often highly processed with very small particle sizes and rarely contain elemental Hg or Hg in amalgams. The PDV 6000 extraction procedure is less effective for these forms of Hg which were present in the field samples. Variability within the field sample matrix, even though some processing had occurred would also vary the extraction efficiency.

The results obtained from the SRMs shows that the PDV 6000 field method gives acceptable precision and accuracy when used in accordance with its designed operating parameters.

**Comments on the Precision and Accuracy Interpretation of Field samples**

The PDV 6000 field extraction is the main cause of variability between the results within each sample lot. This extraction method is not time or temperature controlled and cannot be expected to give absolutely consistent or 100% extraction efficiency. It is expected that approximately 85%-100% of the Mercury will be extracted during the initial acid digest and peroxide addition, where temperatures will reach 80 $^0$C. The addition of water and electrolyte does not completely neutralize the solution, as residual acidity is needed to keep any mercury extracted in solution. This means further extraction may occur over time. It was however decided to keep the soil in the extraction solution before analysis and not to decant sample to a separate container in order to reduce the waste generated in the field and reduce cross contamination of the low concentration range samples.

In some cases the samples were re-analyzed at the end of the day using the correct calibration range, which means that the sample remained in the extraction solution for over 5 hours. The combination of a more accurate calibration and longer extraction time will have given the much wider %RSD observed for many of the sample batches as the statistics will include results from both sets of analysis.

For example, lot# 13 from the Manufacturing Site gives an average of 15 ppm for 5 samples when the actual concentration is 5.5 ppm. However, 2 of those samples were re-analyzed using the lower concentration calibration range and gave an average of 5.15 ppm with a %RSD of 17.8. Sample lot# 32, also from the manufacturing site, gives an average concentration from 5 samples of 875.5 ppm with a %RSD of 40. If the one high value reported is removed from this set of results, the average value is 700 ppm with a %RSD of 3. The expected result was 650 ppm. It is likely that the high sample result was genuine because the laboratory also found one sample in this batch with more than twice the concentration of the other samples.

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For soil samples above 1,000 ppm, the extraction efficiency will be lower depending on the competing effects of other compounds in the matrix neutralizing the acid and the physical form of the Mercury. Elemental Mercury and amalgams are the most difficult to dissolve.

In practice however, soils containing over 310 ppm are usually considered highly contaminated and the PDV and laboratory methods both gave similar results for samples in this range.

The field samples that theoretically should have had less than 1 ppm in (Lot# 2, 5, 11) were detected as more than 1ppm by the PDV 6000 method. In every case the raw data shows a significant peak at the mercury position. These samples were again exposed to the extraction liquid for 24 hours and were also analyzed using the very low level method. Lot#1 was only analyzed at the 1–10 ppm range and showed no mercury present. Sample lot#4 was analyzed as part of a separate batch of samples, and gave an average concentration of 0.28 ppm compared to the laboratory 0.11 ppm average. Sample lot#6 out of 5 samples were analyzed in the same batch as lot#4 and showed less than 0.5 ppm in the sample. The raw data gives an average of 0.46 for 4 samples for the values above 0.25 ppm estimated and the laboratory estimated 0.23 ppm. The other 3 samples from the set gave an average concentration of 0.19 ppm. These results were not submitted in the data set as the standard run with these samples was accidentally deleted while calculating the results. The estimated concentrations are based on a comparison with a standard run using different analysis times.

The results from sample lots# 1, 4 and 6 indicate that the values obtained for the other low concentration samples may be contamination in the reagents, possibly the electrolyte used to dilute the initial extract.

**Comments on the Calculated MDL and PQL**

The lowest quantifiable concentration of mercury detected by the PDV 6000 is 2.5 micrograms per liter. The dilution effect of the soil extraction procedure and the volume of the extract added to the analysis cup would mean 2.5 ppb is equivalent to 0.1 mg/kg in the soil. At this level of sensitivity, sample or reagent contamination during extraction or handling may cause an erroneous result.

The very low concentration samples were analyzed using different calibration ranges. The reported results are from the 0.1–1 ppm calibration range. The initial results at the 1–10 ppm range did not detect Mercury above 1ppm, indicating all samples were below 1 ppm. The subsequent analysis for samples on lot# 2, 5, 11, 35, 37 and 57 using the same batch of extraction reagents gave results greater than 1 ppm. Unfortunately, no blank was analyzed for the extraction reagent and contamination from this part of the procedure cannot be ruled out due to the close proximity of samples and extraction reagents in this trial.

All of the low level samples showed Mercury peaks that are significantly higher than the 2.5 ppb peak. This does indicate that Mercury was present in the analysis solution, but the source is not clear. The end result is that in this trial the true MDL could not be determined from the data set. The PQL estimated in the report is also slightly high.

The sample lots analyzed in the low level range have concentrations that jump from 0.6 ppm to 4.75 ppm. This large jump makes it difficult to calculate a PQL from the data at anything less than 4 ppm. If the estimated contribution by contamination is removed from the results obtained and the results from sample lots# 4 and 6, a PQL of around 1 ppm is obtained. This is in line with MTI's reported field PQL of between 0.5 and 1 ppm.

**Comments on the Economic Analysis**

When evaluating the costs of an instrument it should also be taken into consideration any other analyses that can be carried out with it. The PDV 6000 can be used to analyze soil and water samples for many toxic heavy metals, including As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Sn, Tl, Te and Zn with low part per billion detection limits. In most cases the extraction procedure is the same for all metals. This means only a few extra reagents such as standards would be required in order to analyze a much wider suite of metals. For sites where several metals are present, the per sample cost of the PDV would be considerably reduced.

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**Method Improvements that Have Been Implemented**

The evaluation gave MTI a wonderful opportunity to compare its method against a fully approved method on samples that are genuine field samples. This information has highlighted some improvements that have now been incorporated into the product and analysis procedure.

The PDV instrument has had a software modification that allows greater sensitivity to be achieved. This gives an improved signal to noise ratio and will generate better peaks for quantification. This will improve the instrument repeatability.

For the very low detection limits, the longer analysis times will allow any Mercury coming from contamination to contribute to the total mercury result to a significantly greater extent. Due to the volumes of extract used, electrolyte blanks can only performed once on the bulk electrolyte and not for each sample. The analysis procedure has been modified to run bulk electrolyte blanks more frequently to exclude contamination in this reagent as a source of error.

The VAS software has been modified to automatically calculate the soil concentration directly. This removes the need to transfer data to another program for the final data generation and saves several hours of labor.

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# Appendix B
# Statistical Analysis

Two separate hypothesis tests were used to compare the referee laboratory samples to the vendor tested samples. This appendix details the equations and information for both of these statistical analyses. For purposes of this appendix, we have chosen to call the test comparing sample populations using a separate calculation for each sample lot the "hypothesis test," and the statistical comparison of the entire sample set (all 32 separate sample lots) analyzed by the vendor and the laboratory the "unified hypothesis test," also known as an "aggregate analysis" for all of the sample lots.

**Hypothesis Test**

A hypothesis test is used to determine if two sample populations are significantly different. The analysis is performed based on standard statistical calculations for hypothesis testing. This incorporates a comparison between the two sample populations assuming a specified level of significance. For establishing the hypothesis test, it was assumed that both sample sets are equal. Therefore, if the null hypothesis is rejected, then the sample sets are not considered equal. This test was performed on all sample lots analyzed by both MTI and the referee laboratory. $H_0$ and $H_a$, null and alternative hypothesis respectively, were tested with a 0.01 level of significance (LOS). The concern related to this test is that, if two sample populations have highly variable data (poor precision), then the null hypothesis may be accepted because of the test's inability to exclude poor precision as a mitigating factor. Highly variable data results in wider acceptance windows, and therefore, allows for acceptance of the null hypothesis. Conclusions regarding this analysis are presented in the main body of the report.

To determine if the two sample sets are significantly different, the absolute value of the difference between the laboratory average $\bar{x}_L$ and the vendor average $\bar{x}_V$ is compared to a calculated μ. When the absolute value of the difference is greater than μ, then the alternate hypothesis is accepted, and the two sets (laboratory and vendor) are concluded to be different.

To calculate μ, the variances for the laboratory data set and the vendor data set are calculated by dividing their standard deviations by the number of samples in their data set. The effective number of degrees of freedom is then calculated.

$$f = \frac{\left(V_L + V_V\right)^2}{\left(\frac{V_L 2}{n_L + 1}\right) + \left(\frac{V_V 2}{n_V + 1}\right)} - 2$$

Where:

| | |
|---|---|
| f | = effective number of degrees of freedom |
| $V_L$ | = variance for the laboratory results |
| $n_L$ | = number of samples for the laboratory data set |
| $V_V$ | = variance for the vendor results |
| $n_V$ | = number of samples for the vendor data set. |

The degrees of freedom (f) is used to determine the appropriate "t" value and used to calculate μ at the 0.01 level of significance using the following:

$$\mu = t_{1-(0.005/2)} \sqrt{V_L + V_V}$$

**Unified Hypothesis Test**

For a specified vendor, let $Y_{ij}$ be the measured Hg concentration for the $j^{th}$ replicate of the $i^{th}$ sample for $I$ =1,2,...,I and $j$ = 1,2,...,$J_i$. Let $X_{ij} = \log(Y_{ij})$, where log is the logarithm to the base 10. Define $\bar{x}_{i\log.}$ to be the average over all log replicates for the $i^{th}$ sample given by:

$$\bar{X}_{i\log} = J_i^{-1} \log \sum_{j=1}^{J_i} X_{ij}$$

Denote the estimate of the variance of the log replicates for the $i^{th}$ sample to be:

$$s^2 = \left( \sum_{i=1}^{I} (J_i - 1) \right)^{-1} \log \sum_{i=1}^{I} \sum_{j=1}^{J_i} \left( X_{ij} - \bar{X}_{i\log} \right)^2$$

Now for the reference laboratory, let $Y'_{ij}$ be the measured Hg concentration for the $j^{th}$ replicate of the $i^{th}$ sample for $I$ =1,2,...,I' and $j$ = 1,2,...,$J'_i$. Denote the reference laboratory quantities $X'_{ij}$, $\bar{x}_I'$, and $s'^2$ defined in a manner similar to the corresponding quantities for the vendor.

Assumptions: Assume that the vendor measurements, $Y_{ij}$, are independent and identically distributed according to a lognormal distribution with parameters $\mu_I$ and $\sigma^2$. That is, $X_{ij} = \log(Y_{ij})$ is distributed according to a normal distribution with expected value $\mu_I$ and variance $\sigma^2$. Further, assume that the reference laboratory measurements, $Y'_{ij}$, are independent and identically distributed according to a lognormal distribution with parameters $\mu'_I$ and $\sigma'^2$.

The null hypothesis to be tested is:

$$H_0 : \mu_i = \mu'_i + \delta, \ \ for\ some\ \delta\ and\ i = 1,\ldots,I$$

against the alternative hypothesis that the equality does not hold for at least one value of $I$.

The null hypothesis $H_o$ is rejected for large values of:

$$\chi^2_{I-1} = \frac{\sum_{i=1}^{I} \left( \bar{X}_{i\log} - \bar{X}'_{i\log} - \delta \right)^2 \div \left( J_i^{-1} + J'^{-1}_i \right)}{s^2_{pool}}$$

Where $x^2_{I-1}$ is approximately a chi-square random variable with (I-1) degrees of freedom:

$$\delta = I^{-1} \log \sum_{i=1}^{I} \left( \bar{X}_{i\log} - \bar{X}'_{i\log} \right)$$

and

$$s^2_{pool} = \frac{s^2 \log \sum_{i=1}^{I} (J_i - 1) + s'^2 \log \sum_{i=1}^{I'} (J'_i - 1)}{\sum_{i=1}^{I} (J_i - 1) + \sum_{i=1}^{I'} (J'_i - 1)}$$

Critical values for the hypothesis test are the upper percentile of the chi-square distribution with (I-1) degrees of freedom obtained from a chi-square table.

**Results of Unified Hypothesis Test for MTI**

SAIC performed a unified hypothesis test analysis to assess the comparability of analytical results provided by MTI and those provided by ALSI. MTI and ALSI both supplied multiple assays on replicates derived from a total of 31 different sample lots, be they field materials or reference materials. The MTI and ALSI data from these assays formed the basis of this assessment.

The statistical analysis is based on log-transformed (logarithm base 10) data and uses a chi-square test for equality of MTI and ALSI population means for given sample lot. Equality of variances is assumed.

Initially, the null hypothesis tested was that, on average, MTI and ALSI would produce the same results within a given sample lot. This hypothesis is stated as

$H_{1O}$: (MTI Lot log mean) = (ALSI Lot log mean)

$H_{1O}$ was strongly rejected in that the chi-square statistic was 941.12, which exceeds the upper 99th percentile of the chi-square distribution with 31 degrees of freedom having a value of 52.19.

The null hypothesis was rejected in part because MTI results tended to exceed those from ALSI for the same sample lot. To explore this effect, the null hypothesis was revised to included a bias term in the form of

$H_{2O}$: (MTI Lot log mean) = (ALSI Lot log mean) +(delta),

where delta is a single value that does not change from one sample lot to another, unlike the lot log means. $H_{2O}$ was rejected strongly in that the chi-square statistic was 699.19, which exceeded the upper 99$^{th}$ percentile of the chi-square distribution with 30 degrees of freedom with a value of 50.89. In this analysis, delta was estimated to be 0.355 in logarithmic (base 10) space, which indicates an average upward bias for MTI of $10^{0.355}$=12.265 or about 127%.

For both hypotheses, the large values of the chi-square test statistics summarize the disagreement between the MTI and ALSI analytical results. Furthermore, a review of the statistical analysis details indicates that the overall discordance between MTI and ALSI analytical results cannot be traced to the disagreement in results for one or two sample lots.

Summary information on these analyses is provided in Table B-1. The p-value can be considered as a significance level. This is a calculated value and usually when one sets a p-value (e.g., 95% confidence level which translates to a p-value of 0.05), this value is used to test the level of significance for comparison. As noted in Table B-1 the p-value is calculated from the test statistics and therefore it can be seen that because the p-value is so small (< 0.000000) the two sample populations are considered to be non-equivalent and hence the large chi-square value.

**Table B-1. Unified Hypothesis Test Summary Information**

| Hypothesis | Total Sample Lots | Excluded Lot | DF | $s^2_{pool}$ | Delta | Chi-square | P-value |
|---|---|---|---|---|---|---|---|
| $H_{1O}$ | 31 | None | 31 | 0.02645 | 0.0000 | 941.12 | 0.000000 |
| $H_{2O}$ | 31 | None | 30 | 0.02645 | 0.3546 | 699.19 | 0.000000 |