



**EPA**

# Innovative Technology Verification Report

## Field Measurement Technology for Mercury in Soil and Sediment

### NITON's XLi/XLt 700 Series X-Ray Fluorescence Analyzers



EPA/600/R-03/148  
May 2004

# **Innovative Technology Verification Report**

## **NITON's XLi/XLt 700 Series X-Ray Fluorescence Analyzers**

Prepared by

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## **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.

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**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: NITON's® XLi/XLt 700™ Series Environmental Analyzers**

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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 the demonstrations of two XLi/XLt 700 Series X-ray Fluorescence Analyzers developed by NITON Inc.

**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 XLi/XLt 700 Series Analyzers XLi 702 (isotope) and XLt 792 (X-ray tube) and four other field measurement devices for mercury in soil and sediment. This verification statement focuses on these two analyzers; a similar statement has been prepared for each of the other four devices. The performance of each of these two X-ray fluorescence analyzers 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;

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- (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 the skills and training required to properly operate the devices;
- (2) Documenting potential health and safety concerns associated with operating the devices;
- (3) Documenting the portability of the devices;
- (4) Evaluating the devices durability based on their materials of construction and engineering design; and
- (5) Documenting the availability of the devices and associated spare parts.

The XLi/XLt 700 Series Analyzers analyzed 62 field soil samples, 23 field sediment samples, 42 spiked field samples, and 70 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 XLi/XLt 700 Series Analyzers. 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—NITON's XLi/XLt 700 Series X-Ray Fluorescence Analyzers" (EPA/600/R-03/148).

#### **TECHNOLOGY DESCRIPTION**

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

Detection of the characteristic mercury X-rays is achieved using a highly-efficient, therm o-electrically cooled, solid-state detector. Signals from this detector are amplified, digitized, and then quantified via integral multichannel analysis and data processing units. Results are displayed in ppm (mg/kg) of total elemental mercury.

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

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

#### **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.

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## 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 range of the MDL for the NITON X-ray tube instrument is between 13.9 and 69.8 mg/kg. It is likely that the MDL is closer to the lower end of this range based upon the results for sample lot 62 (referee laboratory value = 14.6 mg/kg) and sample lot 47 (SRM value = 32.4 mg/kg) which both had one of the seven results reported as below the NITON detection level indicating that these values are on the edge of the instruments detection capability. The lowest calculated MDL for the NITON Isotope instrument is 39.3 mg/kg. Based upon results presented in the report, the MDL for the NITON Isotope field instrument is close to 32 mg/kg. The equivalent calculated MDL for the referee laboratory is 0.0026 mg/kg.

**Practical Quantitation Limit** - The NITON X-ray PQL is somewhere between 62.9 mg/kg and 99.8 mg/kg. The %D for the 99.8 mg/kg SRM is 8.2%. The NITON Isotope PQL is also between 62.9 mg/kg and 99.8 mg/kg. The %D for the 99.8 mg/kg SRM is 9.2%. The referee laboratory PQL confirmed during the demonstration is 0.005mg/kg, with a %D <10%.

**Accuracy:** The results from the XLi/XLt 700 Series Analyzers were compared to the 95% prediction interval for the SRM materials and to the referee laboratory results (Method 7471B). NITON X-ray data were within SRM 95% prediction intervals 93% of the time, which suggests significant equivalence to certified standards. NITON Isotope data were within SRM 95% prediction intervals 91% of the time, which also suggest significant equivalence to certified standards.

The statistical comparison between the NITON X-ray field data and the referee laboratory results suggest that the two data sets are not the same. The statistical comparison between the NITON Isotope field data and the referee laboratory results also suggest that these two data sets are not the same. Because the NITON data compare favorably to the SRM values, the differences between NITON and the referee laboratory are likely the result of matrix interferences for field sample analysis. The number of NITON X-ray average values less than 30% different from the referee laboratory results or SRM reference values; however, was 14 of 26 different sample lots. Only 1 of 26 NITON average results have relative percent differences greater than 100% for this same group of samples. The number of NITON Isotope average values less than 30% different from the referee laboratory results or SRM reference values was 14 of 24 different sample lots. Zero of 24 NITON Isotope average results have relative percent differences greater than 100% for this same group of samples. Both NITON X-ray and NITON Isotope results; therefore, can provide a reasonable estimate of accuracy for field determination.

**Precision:** The precision of the NITON X-ray and NITON Isotope field instruments is better than the referee laboratory precision. The overall average RSD is 20.0% for the referee laboratory, compared to the NITON X-ray overall average RSD of 13.1% and the NITON Isotope overall average RSD of 14.4%. Both the laboratory and NITON precision goals are within the predicted 25% RSD objective for precision expected from both analytical and sampling variance.

**Measurement Time:** From the time of sample receipt, NITON required 17.5 hours (35 man hours) to prepare a draft data package of mercury results for 197 samples for both devices. Two technicians performed all setup, sample preparation and analysis, and equipment demobilization. Individual measurements took approximately 120 seconds each (after sample preparation), but the total time per analysis averaged 5.3 minutes when all field activities and data package preparation were included and only one technician per device is included in the calculation.

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**Measurement Costs:** The cost per analysis based upon 197 samples, when renting the XLi 702, is \$39.52 per sample. The cost per analysis for the 197 samples, excluding rental fee, is \$13.18 per sample. Based on the 3-day field demonstration, the total cost for equipment rental and necessary supplies is estimated at \$7,786. The cost breakout by category is: capital costs, 66.7%; supplies, 3.6%; support equipment, 3.5%; labor, 7.7%; and IDW, 18.5%.

The cost per analysis based upon 197 samples, when renting the XLt 792, is \$47.69 per sample. The cost per analysis for the 197 samples, excluding rental fee, is \$13.18 per sample. Based on the 3-day field demonstration, the total cost for equipment rental and necessary supplies is estimated at \$9,396. The cost breakout by category is: capital costs, 72.4%; supplies, 3.0%; support equipment, 2.9%; labor, 6.4%; and IDW, 15.3%.

Key demonstration findings are summarized below for the secondary objectives.

**Ease of Use:** Based on observations made during the demonstration, the XLi/XLt 700 Series Analyzers are very easy to operate, requiring one field technician with a high school education. A free 8-hour training course on instrument operation and radiation safety is mandatory prior to operating the instruments. The analyzers contain an integrated touch-screen display with an advanced and intuitive user interface.

**Potential Health and Safety Concerns:** No significant health and safety concerns were noted during the demonstration. Potential exposure to radiation from the excitation sources (Cd-109, Am-241, Fe-55 and X-ray tube) was the only health and safety concern during the demonstration. The analyzers should never be pointed at anyone while the sources are exposed. No solvents or acids are used for sample preparation. According to NITON, the sources are designed to remain secure even under extreme conditions, so that even if the instrument is broken, crushed or burned there should be no leakage of radioactive material.

**Portability:** The XLi/XLt 700 Series Analyzers are handheld portable single piece units weigh only 0.8 kg (XLi 702) and 1.4 kg (XLt 792). There are no cables and no separate processing units. The analyzers have an attractive ergonomic form. During the demonstration, the analyzers each operated on 1 battery pack that lasted for 4-8 hours.

**Durability:** Based on observations during the demonstration, the analyzers were well constructed, field-rugged and durable. They are constructed of high-strength injection molded plastic. During the three days in which the instrument was observed, there was no downtime, maintenance or repairs. The equipment apparently was not affected by the almost continuous rain.

**Availability of the Devices:** The XLi/XLt 700 Series Analyzers are readily available for lease or purchase. During most of the year, NITON is typically able to rent an analyzer to a customer in 10-14 days (10 isotope rentals and 3 X-ray tube rentals). There are also radiation licensing requirements for these devices. NITON offers over 100 user/radiation training classes to help expedite the process. Supplies not provided by NITON are readily available from supply firms.

## PERFORMANCE SUMMARY

In summary, during the demonstration, the XLi 702 and XLt 792 exhibited the following desirable characteristics of a field mercury measurement device: (1) good accuracy compared to standard reference materials, (2) good precision, (3) high sample throughput, (4) low measurement costs, and (5) ease of use. During the demonstration the XLi 702 and XLt 792 were found to have the following limitations: (1) a PQL that exceeds the residential soil PRG action limit. The XLi/XLt 700 Series Analyzers are handheld devices for rapid field measurements of mercury in soil and sediment.

**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.

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## 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  
Office of Research and Development

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## Abstract

NITON's XLi/XLt 700 Series X-ray fluorescence analyzers were demonstrated under the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation Program in May 2003 at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN. The purpose of the demonstration was to collect reliable performance and cost data for the XLi 702 and XLt 792 and four other field measurement devices for mercury in soil and sediment. 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 using field samples and standard reference materials (SRMs); 3) evaluate the precision of vendor field measurements; 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 for both instruments. Results with the XLi 702 were found to be very precise and accurate when compared to standard reference materials. During the demonstration, NITON required 17.5 hours (assumes one technician) for analysis of 197 samples. The measurement costs were estimated to be \$7,786 for NITON's XLi 702 rental option, or \$39.52 per sample; \$13.18 per sample excluding rental costs.

Results for the XLt 792 was found to be very precise and accurate when compared to standard reference materials. During the demonstration, NITON required 17.5 hours (assumes one technician) for analysis of 197 samples. The measurement costs were estimated to be \$9,396 for NITON's XLi 792 rental option, or \$47.69 per sample; \$13.18 per sample excluding rental costs.

The XLi/XLt 700 Series Analyzers exhibited good ease of use and durability, as well as no major health and safety concerns. The analyzers are hand-held single units and extremely portable. The demonstration findings collectively indicated that the XLi/XLt 700 Series Analyzers are rapid, lightweight, hand-held portable field measurement devices for mercury in soil.

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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
AAS	Atomic absorption spectrometry
ALSI	Analytical Laboratory Services, Inc.
bgs	Below ground surface
cm	Centimeter
CFR	Code of Federal Regulations
CI	Confidence Interval
COC	Chain of Custody
DOE	Department of Energy
EDXRF	Energy Dispersive X-ray Fluorescence
EPA	United States Environmental Protection Agency
FPXRF	Field Portable X-ray Fluorescence
g	Gram
H&S	Health and Safety
Hg	Mercury
HgCl <sub>2</sub>	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
MMT	Monitoring and Measurement Technology
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NERL	National Exposure Research Laboratory
ng	Nanogram
ORD	Office of Research and Development
ORNL	Oak Ridge National Laboratory

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## Abbreviations, Acronyms, and Symbols (Continued)

ORR	Oak Ridge Reservation
OSWER	Office of Solid Waste and Emergency Response
PPE	Personal protective equipment
ppm	Parts per million
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

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

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# 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 NITON's XLi/XLt 700 Series X-ray fluorescence instruments, designated as XLi 702 and XLt 792. 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 ( $\text{HgCl}_2$ ) 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

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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.

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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<sub>2</sub> 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 ( $\text{Hg}^{2+}$ ), mercurous form ( $\text{Hg}_2^{2+}$ ), elemental form ( $\text{Hg}^0$ ), and alkylated form (e.g., methyl or ethyl mercury).  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  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  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ . Mercury (II) also forms complexes with inorganic ligands such as fluoride ( $\text{F}^-$ ), bromide ( $\text{Br}^-$ ), iodide ( $\text{I}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), sulfide ( $\text{S}^{2-}$ ), and phosphate ( $\text{PO}_4^{3-}$ ) and forms strong complexes with organic ligands, such as sulfhydryl groups, amino acids, and humic and fulvic acids. The insoluble  $\text{HgS}$  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	<ul style="list-style-type: none"> <li>• inorganic mercury</li> <li>• organo-mercury</li> </ul>	10-2,000 ppb	Manual cold vapor technique widely used for total mercury determinations
SW-7472	ASV	<ul style="list-style-type: none"> <li>• inorganic mercury</li> <li>• organo-mercury</li> </ul>	0.1-10,000 ppb	Newer, less widely accepted method
SW-7473	TD, amalgamation, and AAS	<ul style="list-style-type: none"> <li>• inorganic mercury</li> <li>• organo-mercury</li> </ul>	0.2 - 400 ppb	Allows for total decomposition analysis
SW-7474	AFS	<ul style="list-style-type: none"> <li>• inorganic mercury</li> <li>• organo-mercury</li> </ul>	1 ppb - ppm	Allows for total decomposition analysis; less widely used/reference
EPA 1631	CVAFS	<ul style="list-style-type: none"> <li>• inorganic mercury</li> <li>• organo-mercury</li> </ul>	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	<ul style="list-style-type: none"> <li>• inorganic mercury</li> <li>• organo-mercury</li> </ul>	0.5 - 200 ppt	Requires "trace" analysis procedures; written for aqueous matrices; will require dilutions of high-concentration mercury samples
EPA 6200	FPXRF	<ul style="list-style-type: none"> <li>• inorganic mercury</li> </ul>	>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 contains general information on field portable X-ray fluorescence (FPXRF) analyzers, including the theory of operation, system components, radioisotope sources, and mode of operation. The chapter also provides a detailed description of the NITON XLi/XLt 700 Series Analyzers.

### 2.1 Description of X-Ray Fluorescence

Energy dispersive X-ray fluorescence (EDXRF) is a method of detecting metals and non-metallic elements in soil and sediment. Some of the elements that EDXRF can identify are arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, silver and zinc. Field-portable X-ray fluorescence units that operate on battery power and use a radioactive source were first developed for use in analysis of lead-based paint. FPXRF analyzers are being used in the field to identify and characterize metal-contaminated sites, and to guide remedial work.

#### 2.1.1 Theory of EDXRF Analysis

EDXRF analysis detects and measures many elements simultaneously. Generally, EDXRF units can detect and quantify elements from atomic number 19 (potassium) through 94 (plutonium). There are two types of EDXRF units. They can use either an X-ray tube or a radioisotope as a source of X-rays. Both types of EDXRF analyzers were evaluated during the demonstration.

In XRF analysis, a process known as photoelectric effect is used in analyzing samples. Fluorescent X-rays are produced by exposing a sample to an X-ray source that has an excitation energy similar to, but greater than, the binding energy of the inner-shell electrons of the elements in the sample. Some of the source X-rays will be scattered, but a portion will be absorbed by the elements in the

sample. Because of their higher energy level, they will cause ejection of the inner shell electrons. The electron vacancies that result will be filled by electrons cascading in from outer shells. However, since electrons in the outer shells have higher energy states than the inner-shell electrons they are replacing, the outer shell electrons must give off energy as they cascade down. The energy is given off in the form of X-rays, and the phenomenon is referred to as X-ray fluorescence (Figure 2-1). Because every element has a different electron shell configuration, each element emits a unique X-ray at a set energy level or wavelength that is characteristic of that element. The elements present in a sample can be identified by observing the energy level of the characteristic X-rays, while the intensity of the X-rays is proportional to the concentration and can be used to perform quantitative analysis.

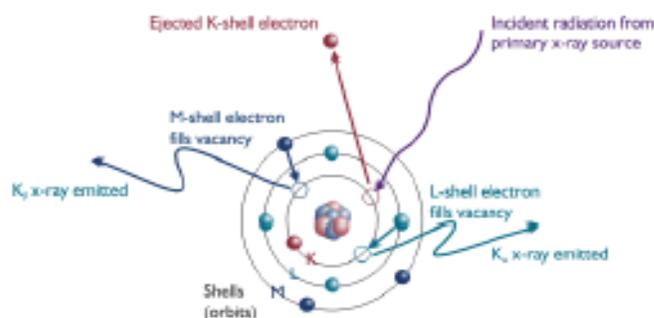


Figure 2-1. Basic X-ray fluorescence process.

## 2.1.2 System Components

A FPXRF system has two basic components: the radioisotope source and the detector. The source irradiates the sample to produce characteristic X-rays. The detector measures both the energy and the characteristic X-rays that are emitted and their intensity to identify and quantify the elements present in the sample.

The radioisotope sources currently being used are Fe-55, Cd-109, and Am-241. FPXRF units have been developed that use more than one source, which allows them to analyze a greater number and range of elements. Typical arrangements of such multi-source instruments include Cd-109 and Am-241 or Fe-55, Cd-109, and Am-241.

FPXRF units use either gas-filled or solid-state detectors. Solid state detectors include Si(Li), HgI<sub>2</sub>, and silicon-PIN diode. The Si(Li) is capable of the highest resolution, but is quite temperature sensitive. The Si(Li) has a resolution of 170 electron volts (eV) if cooled to at least -90 °C, either with liquid nitrogen or by thermoelectric cooling that uses the Peltier effect. The HgI<sub>2</sub> detector can operate at a moderately subambient temperature, is cooled by use of the Peltier effect, and has a resolution of 270 to 300 eV. The silicon-PIN diode detector is cooled only slightly by the Peltier effect, and has a resolution of 250 eV.

## 2.2 NITON XLi/XLt 700 Series Technology Description

The NITON XLi/XLt 700 Series sample analyzers are energy dispersive X-ray fluorescence (EDXRF) spectrometers that use either a radioactive isotope (XLi model 702) or a low powered miniature X-ray tube with a silver target (XLt model 792) to excite characteristic X-rays of a test sample's constituent elements (Figure 2-2). These characteristic X-rays are continuously detected, identified, and quantified by the spectrometer during sample analysis. The energy of each X-ray detected identifies a particular element present in the sample, and the rate at which X-rays of a given energy are counted provides a determination of the quantity of that element that is present in the sample.

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

The NITON XLt 700 Series Analyzer with X-ray tube excitation provides the user with the speed and efficiency of X-ray tube excitation, while reducing the regulatory demands typically encountered with isotope-based systems. In most cases, the X-ray tube can be shipped from state to state and country to country with minimal paperwork and expense.



Figure 2-2. Photograph of the NITON XLi/XLt 700 Series instruments during the field demonstration.

**Applications and Specifications** - The XLi and XLt 700 Series analyzers offer testing modes for soil and other bulk samples; filters, wipes and other thin samples; and lead-based paint. Testing applications include management of remediation projects, site assessments, and compliance testing. They provide simultaneous analysis of up to 25 elements, including all eight of the characteristic metals listed under the Resource Conservation and Recovery Act (RCRA). XRF analysis is non-destructive, so screened samples can be sent to an accredited laboratory for confirmation of results obtained on-site.

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

**Operation** - For in-situ analysis, the analyzer is placed directly on the ground or on bagged soil samples. Because contamination patterns tend to be heterogeneous, a large number of data points can be produced using in-situ testing to delineate contamination patterns. In-situ testing with either the XLi 702 or XLt 792 is in full compliance with U.S.

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EPA Method 6200. In-situ testing allows for testing many locations in a short time, and is ideal for rapid site-profiling, locating sources of contamination, and monitoring and fine-tuning remediation efforts on-the-spot. In-situ analysis is not appropriate for wet sediment samples. In that case, sediments must be dried, and can then be measured either bagged or in sample cups.

For intrusive testing, the XLi/XLt 700 Series can test prepared (dried, ground, sifted, homogenized), representative soil samples for laboratory grade analysis whenever analytical-grade data quality is required. Both the XLi and XLt 700 Series Soil Analyzers come with sample-preparation protocols. During the demonstration, all samples were tested intrusively.

The NITON instruments are factory-calibrated. NITON's Compton normalization software automatically corrects for any differences in sample density and matrix, so site-specific calibration standards are never required. The units also analyze for zinc, arsenic, and lead since these elements may cause interference at certain concentrations. The vendor states that total analysis time usually does not exceed 120 seconds (after sample preparation).

Depending on the data quality needed for a project, longer count times can be employed. As count times increase, the detector collects a larger number of X-rays from the sample, including more X-rays from interfering elements

that are present at comparable lower concentrations. The longer the count time, the lower the detection limit.

Sample preparation, for those samples not analyzed directly in-situ, may include grinding and/or sieving dried samples, using either mortar and pestle or electric grinder. Wet samples, at a minimum are filtered to remove standing water, then dried. Although EPA Method 6200 specifies that mercury samples should not be oven-dried due to the potential volatilization loss of mercury, NITON has oven-dried sample material without negative impact. During the demonstration, some samples which contained free-standing water were dried in a toaster oven for about 2 hours.

## **2.3 Developer Contact Information**

Additional information about NITON's XLi/XLt 700 Series Analyzers can be obtained from the following source:

NITON Corporation  
Jonathan J. Shein  
900 Middlesex Turnpike Building 8  
Billerica, MA. 01821  
Telephone: (800) 875-1578  
Fax: (978) 670-7430  
Email: [sales@niton.com](mailto:sales@niton.com)  
Internet: [www.niton.com](http://www.niton.com)

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## 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

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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

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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.

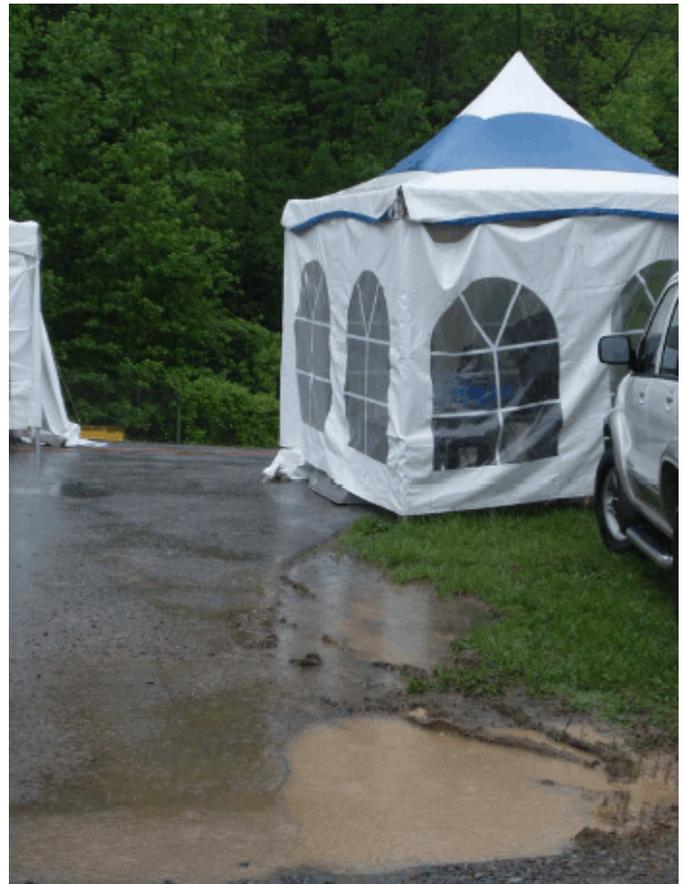
The percent sediment recovery was determined by dividing the length of material recovered by the depth of core penetration below the mud line. If the sample was deemed acceptable, overlying water was siphoned from the top of the core tube and each end of the tube capped and sealed with duct tape. Following 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.**

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### **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. 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, so that potential technology users have adequate information to make sound judgements regarding an innovative technology's applicability to a specific site, and 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
<b>Primary Objectives</b>		
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.	
<b>Secondary Objectives</b>		
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.	Post-demonstration investigation.
Secondary Objective # 5	Document the availability of the device and its spare parts.	

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

#### 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 the true value. The true value is considered the value reported by the referee laboratory for field samples or spiked field samples, or, in the case of SRMs, the certified value provided by the supplier. The equation used for the %D calculation is:

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

where:  $C_{\text{true}}$  = true concentration as determined by the referee laboratory or SRM reference value  
 $C_{\text{calculated}}$  = 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 NITON field instruments. Samples representing field samples and spiked field samples 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 on-going 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<sup>th</sup> percentile of the t-distribution with n-1 degrees of freedom  
 $n$  = number of measurements  
 $s$  = standard deviation of replicate measurements

The 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

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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, not all vendors analyzed the same samples.

During the demonstration, the vendor's instrumentation 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 were calculated individually, using the following equation:

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

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

H&S = Health and Safety

PPE = Personal Protective Equipment

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#### **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-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 6 Sediment	Tailings Piles (Six Mile Canyon) River Bank Sediments	4 L each for soil 12 L each for sediment
Y-12	10 Sediment 6 Soil	Poplar Creek Sediments Old Mercury Recovery Bldg. Soils	12 L each for sediment 4 L each for soil
Manufacturing Site	12 Soil	Subsurface Soils	4 L each
Puget Sound	4 Sediment	High-Level Mercury (below cap) 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.

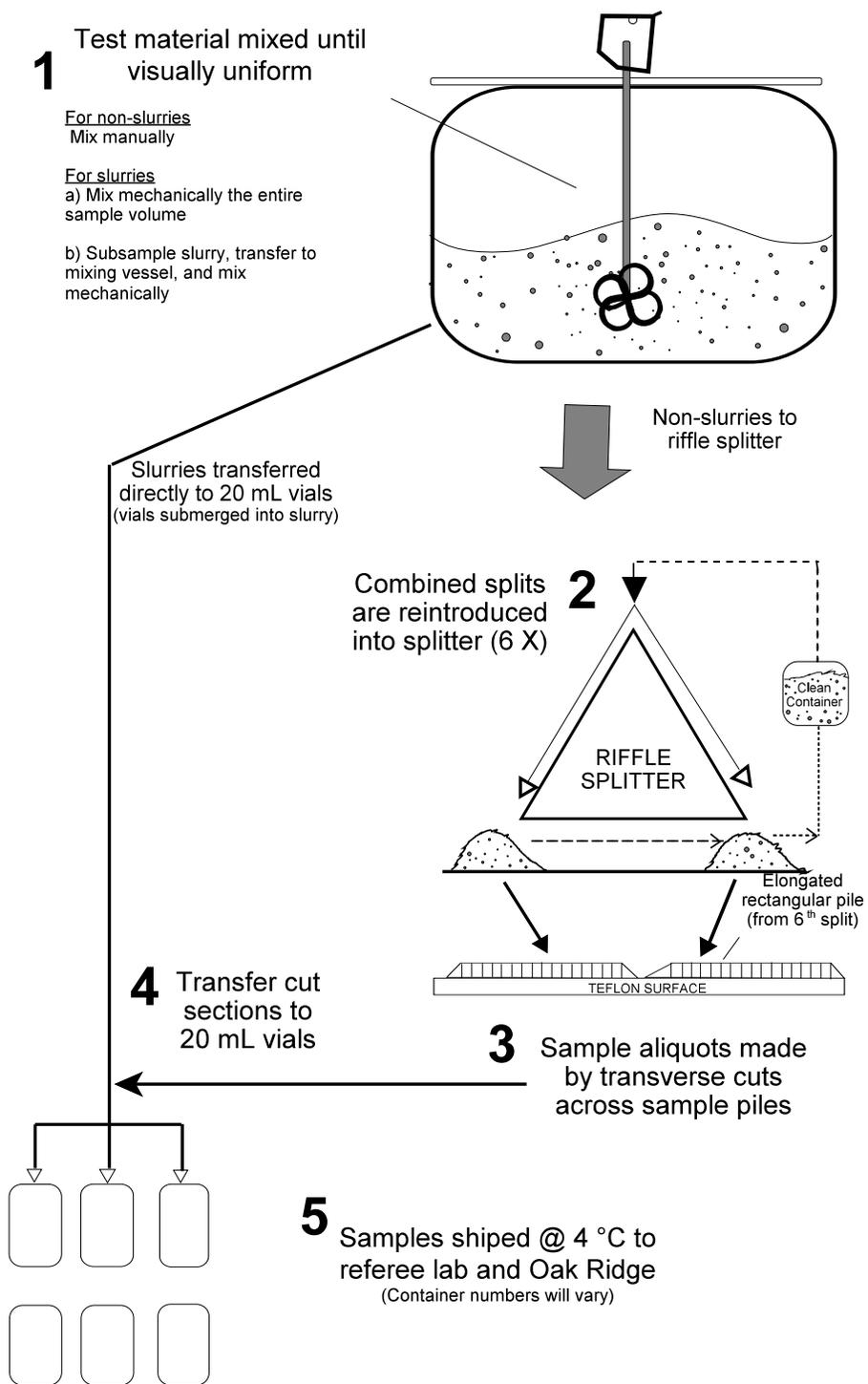


Figure 4-1. Test sample preparation at the SAIC GeoMechanics Laboratory.

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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 known concentrations 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 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

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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 these 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.

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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 used to analyzing such "dirty" samples. Both laboratories have been longtime participants in this program.

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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 have 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
TOC	SW-846 9060	Carbonaceous analyzer
Total Solids	EPA 2540G	Gravimetric

## 4.5 Deviations from the Demonstration Plan

There were no deviations to the demonstration plan.

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## 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

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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 XLi/XLt 700 Series Analyzers

NITON analyzed 197 samples from May 5-7, 2003 in Oak Ridge, TN. Results for these samples were reported by NITON, and a statistical evaluation was performed by SAIC. Since X-ray is non-destructive for soil samples, NITON prepared each sample once and analyzed the sample on both the XLt and XLi instruments. Additionally, the observations made during the demonstration were reviewed, and the remaining primary and secondary objectives were completed. The results of the studies for the primary and secondary objectives, identified in Chapter 1, are discussed in Sections 6.1 and 6.2, respectively.

Samples with high amounts of water (based upon visual examination) were dried in a toaster oven. Those samples identified as “dried” by NITON were compared to the laboratory “dry weight” result. All other samples were compared to the laboratory “as received” result.

The distribution of the samples prepared for NITON and the referee laboratory is presented in Table 6-1. From the four sites, NITON received samples at 35 different concentrations for a total of 197 samples. These 197 samples consisted of 23 concentrations in replicates of 7 and 12 concentrations of 3.

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

Site	Concentration Range	Sample Type			
		Soil	Sediment	Spiked Soil	SRM
Carson River (Subtotal = 31)	Low (1-500 ppb)	0	0	0	0
	Mid (0.5-50 ppm)	7	0	0	0
	High (50->1,000 ppm)	3	0	7	14
Puget Sound (Subtotal = 34)	Low (1 ppb - 10 ppm)	3	0	0	0
	High (10-500 ppm)	0	10	7	14
Oak Ridge (Subtotal = 54)	Low (0.1-10 ppm)	0	3	0	0
	High (10-800 ppm)	13	10	14	14
Manufacturing (Subtotal = 78)	General (5-1,000 ppm)	36	0	14	28
Subtotal (Total = 197)		62	23	42	70

## 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 both of NITON’s field instruments (XLi 702 and XLt 792). Any sample analyzed by NITON and subsequently reported as below their level of detection, was not used as part of any additional evaluations. This was done because the expectation that values below the lower limit of instrument sensitivity would not reflect the true instrument accuracy and precision.

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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 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. Because the NITON field instruments do not use a calibration curve for the analysis of samples, but instead depend upon instrument counts and an associated standard deviation to determine the lower level of quantitation, our approach was to let the vendor provide the lower limits of quantitation as determined by their particular standard operating procedure, and then test these limits by comparing the results to referee laboratory results, or comparing the results to results for a standard reference material, if available. Comparison of these data are, therefore, presented for the lowest level 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, that sample (or samples) 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 99th 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 similar 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 provided or implied.

Several blind standards and field samples were provided to NITON at their estimated lower limit of sensitivity. The

NITON lower limit of sensitivity for both instruments was previously estimated at 20 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 NITON 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.

### **NITON XLt (X-ray) Evaluation**

A field sample with an average concentration of 14.6 mg/kg as reported by the referee laboratory (sample lot 62 from the Puget Sound site) was run by NITON 7 times. One result was reported as below their detection limit and the other 6 results had a reported average concentration of 27.4 mg/kg and a standard deviation of 4.14 mg/kg. Calculation of the respective MDL is 13.9 mg/kg. Because Niton reported a result below their detection limit additional samples were selected for calculating the MDL.

Seven replicates were run by NITON for an SRM with a reference value of 32.6 mg/kg (sample lot 47). The average concentration reported by NITON for this sample was 78 mg/kg and the standard deviation was 6.4 mg/kg. This particular sample lot was not used in the general calculations because of problems noted with reported results from all the vendors who analyzed this SRM and the laboratory reported result. Specifically this sample lot was thrown out because all vendor results and the referee laboratory results were outside acceptable SRM reported values. It was therefore determined that there was likely a problem with this SRM. Nonetheless this was considered an accuracy problem and because MDL calculations are determined using precision results (standard deviation calculations) and because this SRM has a reported concentration of 32.6 it would likely still be an acceptable value for determining an MDL. There are only six valid results reported by NITON as one result was reported as below their detection limit. The MDL calculation using this sample is 21.5 mg/kg.

It should be noted that if the SRM value of 32.6 mg/kg were correct (there is evidence to suggest that this may be incorrect for the sample lot received but it is likely close to this value) then this concentration would likely be close to

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the NITON MDL, as they reported one of the seven tested samples below their limit of detection.

Seven replicates were run by NITON for an SRM that had a reference value of 99.8 mg/kg (sample lot 49). The average concentration reported by NITON for this sample was 108 mg/kg and the standard deviation was 22.2 mg/kg. Calculation of the MDL for this sample is 69.8 mg/kg.

The average of all three of these values (if an average were used) is 35.1 mg/kg. It is probably more accurate, however, to report that the range of the MDL, as determined statistically by 40 CFR part 136 is between 13.9 and 69.8 mg/kg. It is likely that the MDL is closer to the lower end of this range based upon the results for sample lot 62 (referee laboratory value = 14.6 mg/kg) and sample lot 47 (SRM value = 32.4 mg/kg) which both had 1 of the 7 results reported as below the NITON detection level indicating that these values are on the edge of the instruments detection capability. It is also more likely to conclude that the MDL is closer to the lower end of this range because MDLs calculated for the lower concentration samples are also at the lower end of the calculated range of results.

As a further check of the MDL, sample lot 18 had a reported average concentration by the referee laboratory of 10.1 mg/kg. This was consistently reported by NITON as below their MDL thereby confirming that the calculated MDL, noted previously was above this value.

Based upon the results presented above, the three different MDL calculations for this instrument have reported values of 13.9, 21.5, and 69.8 mg/kg. It appears that the MDL for this instrument is close to the lower end of this range. The equivalent MDL for the referee laboratory based upon analysis of a low standard analyzed 7 times is 0.0026 mg/kg. The calculated result is only intended as a statistical estimation and not a true test of instrument sensitivity.

**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. For the NITON field instruments, there is no calibration curve, and therefore the low standard from a calibration curve is not a valid estimation of the PQL. 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 NITON and subsequent %Ds were calculated.

The lower limit of sensitivity previously provided by the vendor (20 mg/kg) appears to be below their calculated MDL and below the vendor PQL. The PQL should have a precision and accuracy that matches the instrument capabilities within a certain operating range of analysis. The relationship between sensitivity and precision is such that the lower the concentration, the higher the variation in reported sample results. Five times the estimated MDL (estimated PQL) would result in a value of 69.5 to 349 mg/kg. The average calculated PQL would be 209 mg/kg; however, based upon sample results, this is clearly above the PQL noted during the demonstration. Therefore, values closer to 69.5 mg/kg were chosen for estimating the PQL and associated %D between the NITON 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.

Sample lot 65 had a reported average value by the referee laboratory of 62.9 mg/kg. The average value reported by NITON for this sample was 84.6 mg/kg with a standard deviation of 35.0 mg/kg. The 95% CI for this sample is 52.2 to 117 mg/kg. The %D for this sample is 34.5%.

The result for the 32.6 mg/kg SRM noted above (sample lot 47) had a reported average concentration of 77.5 mg/kg. The standard deviation was 6.44 mg/kg and the 95% CI is 71.5 to 83.5 mg/kg. The %D for this sample is 137%, and therefore, this concentration appears to be below the instrument PQL.

The result for the 99.8 mg/kg SRM (sample lot 49) had a reported average concentration of 108 mg/kg. The standard deviation was 22.2 mg/kg and the 95% CI is 79.3 to 120 mg/kg. The %D for this sample is 8.2%.

It could be inferred that the NITON XLt field instrument PQL may be somewhere between 62.9 and 99.8 mg/kg. The SRM with a reference value of 32.6 mg/kg had a reported %D of 137% and therefore was lower than the PQL.

#### **NITON XLi (Isotope) Evaluation**

Seven replicates were analyzed by NITON for an SRM that had a reference value of 99.8 mg/kg (sample lot 49). The average concentration reported by NITON for this sample was 109 mg/kg and the standard deviation was 35.6 mg/kg. Another SRM that had a reference value of 32.6 mg/kg (sample lot 47) had an average concentration from

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seven separate replicates reported by NITON as 92.7 mg/kg and a standard deviation of 12.5 mg/kg. A field sample with an average concentration of 14.6 mg/kg as reported by the referee laboratory (sample lot 62 from the Puget Sound site) was analyzed by NITON seven times. All but one result was reported as below their detection limit. This suggests that this sample is below the NITON XLi MDL. Calculations of the respective MDLs, based upon 2 of the 3 samples/standards noted above, are 112 and 39.3 mg/kg. The average of these two values is 75.6 mg/kg.

As a further check of the MDL, sample lot 18 (Carson River) had a reported average concentration by the referee laboratory of 10.1 mg/kg. This was consistently reported by NITON as below their MDL, thereby confirming that the calculated MDL noted previously was above this value. Sample lot 47 (SRM) had a reference value of 32.6 mg/kg (noted previously) and the average result reported by NITON was 92.7 mg/kg. The %D for this sample is 184%. This would suggest that NITON's MDL is below the average calculated above.

Based upon these results, the MDL for this instrument is close to 32 mg/kg, however, this is not the average of the MDL calculations, but close to the lower calculated value of 39.3 mg/kg. The estimated sensitivity provided by NITON of 20 mg/kg is probably close to the observed MDL value. In fact, sample lot 46 (SRM with a reference value of 21.4 mg/kg) was analyzed 7 times and reported an average value of 121 mg/kg for 5 of 7 analyses. The other two analyses were reported as non-detect, suggesting that this is close to or below the instrument's capability. The equivalent calculated MDL for the referee laboratory is 0.0026 mg/kg. The calculated result is only intended as a statistical estimation, and not a true test of instrument sensitivity.

**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 NITON and %Ds were calculated from the results.

The lower limit of sensitivity previously provided by the vendor (20 mg/kg) appears to be close to their MDL and below the vendor PQL. The PQL should have a precision and accuracy that matches the instrument capabilities

within a certain operating range of analysis. The relationship between sensitivity and precision is such that the lower the concentration, the higher the variation in reported sample results. Five times the estimated MDL (estimated PQL) would result in values of 196.5 and 560 mg/kg. The average calculated PQL would be 378 mg/kg, however, based upon sample results this is clearly far above the PQL noted during the demonstration. Therefore, values closer to 32 mg/kg were chosen for estimating the PQL and associated %D between the NITON reported average and the reference value if it is an SRM, or the average value reported by the referee laboratory. The 95% CIs are also compared for additional descriptive information.

Sample lot 65 had a reported average value by the referee laboratory of 62.9 mg/kg. The average value reported by NITON for this sample was 80.3 mg/kg with a standard deviation of 26.9 mg/kg. The 95% CI for this sample is 55.4 to 105 mg/kg. The %D for this sample is 27.7%.

The result for the 32.6 mg/kg SRM noted above (sample lot 47) had a reported average concentration of 92.7 mg/kg. The standard deviation is 12.5 mg/kg and the 95% CI is 81.1 to 104 mg/kg. The %D for this sample is 184% and therefore, this concentration appears to be below the instrument PQL.

The result for the 99.8 mg/kg SRM (sample lot 49) had a reported average concentration of 109 mg/kg. The standard deviation is 35.6 mg/kg and the 95% CI is 76.1 to 132 mg/kg. The %D for this sample is 9.2%.

It can be inferred that the NITON XLi field instrument PQL is between 62.9 and 99.8 mg/kg. The SRM with a reference value of 32.6 mg/kg had a reported %D of 184% and therefore, was lower than the PQL.

### **Sensitivity Summary**

The low standard calculations suggest that the MDL for the NITON XLi field instrument is 42 mg/kg (average of MDL calculations). Based upon the results presented above, the MDL for the NITON XLi field instrument is close to 32 mg/kg. The lowest calculated MDL, however, is 39.3 mg/kg. The equivalent calculated 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.

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The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg. The %D is <10%. The NITON XLt field instrument PQL is between 62.9 and 99.8 mg/kg. The %D for the 99.8 mg/kg SRM is 8.2%. The NITON XLi field instrument PQL is between 62.9 and 99.8 mg/kg. The %D for the 99.8 mg/kg SRM is 9.2%.

### **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 concentrations 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 57 data points by the vendor and 62 data points by the laboratory. One specially prepared SRM (sample lot 55) was not included because analyses performed by the vendor and the laboratory suggested that

the SRM value was in question. Because this was a specially prepared SRM and had less documentation in regards to the reference value, and because both the referee laboratory and vendor results while statistically equivalent were statistically different from the SRM value, this SRM was not included in the evaluation.

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 by the 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 there is evidence of a laboratory bias. 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 24 sample lots for the NITON XLi field instrument and on 26 sample lots for the NITON XLt field instrument. (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 the same 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. The percentage of total results within the prediction interval for the vendor are reported in Tables 6-2 and 6-3, and the laboratory in Table 6-4. 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).

**Table 6-2. NITON SRM Comparison (XLt )**

Sample Lot No.	SRM Value/ 95% CI	NITON Avg./ 95% CI	CI Overlap (yes/no)	No. of Samples Analyzed	95% Prediction Interval	NITON No. w/in Prediction Interval
51	405/ 365 - 445 <sup>a</sup>	312/ 301 - 323	no	7	194 - 615	7
48	77.78/ 71.53 - 84.03	128/ 89.4 - 167	no	4	45.58 - 109.97	1
50	203/ 183 - 223 <sup>a</sup>	195/ 183 - 207	yes	7	97.4 - 308	7
53	910/ 821 - 999 <sup>a</sup>	712/ 664 - 760	no	7	437 - 1380	7
54	1120/ 1010 - 1230 <sup>a</sup>	896/ 863 - 929	no	7	582 - 1701	7
49	99.8/ 81.9 - 118	108/ 87.5 - 128	yes	7	31.3 - 168	7
52	608/ 490 - 726 <sup>a</sup>	496/ 475 - 517	yes	7	292 - 924	7
Total Samples				46		43
% of samples w/in prediction interval						93%

a 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. NITON SRM Comparison (XLi )**

Sample Lot No.	SRM Value/ 95% CI	NITON Avg./ 95% CI	CI Overlap (yes/no)	No. of Samples Analyzed	95% Prediction Interval	NITON No. w/in Prediction Interval
51	405/ 365 - 445 <sup>a</sup>	305/ 269 - 343	no	7	194 - 615	7
48	77.78/ 71.53 - 84.03	171/ 100 - 242	no	4	45.58 - 109.97	0
50	203/ 183 - 223 <sup>a</sup>	217/ 164 - 270	yes	7	97.4 - 308	7
53	910/ 821 - 999 <sup>a</sup>	720/ 673 - 767	no	7	437 - 1380	7
54	1120/ 1010 - 1230 <sup>a</sup>	917/ 837 - 997	no	7	582 - 1701	7
49	99.8/ 81.9 - 118	109/ 76.1 - 142	yes	7	31.3 - 168	7
52	608/ 490 - 726 <sup>a</sup>	504/ 465 - 543	yes	7	292 - 924	7
Total Samples				46		42
% of samples w/in prediction interval						91%

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

**Table 6-4. 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
51	405/ 365 - 445 <sup>a</sup>	291/ 254 - 328	no	7	194 - 615	7
48	77.78/ 71.53 - 84.03	87.1/ 60.6 - 114	yes	7	45.58 - 109.97	6
50	203/ 183 - 223 <sup>a</sup>	167/ 140 - 194	yes	7	97.4 - 308	7
53	910/ 821 - 999 <sup>a</sup>	484/ 325 - 643	no	7	437 - 1380	4
54	1120/ 1010 - 1230 <sup>a</sup>	711/ 573 - 849	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 <sup>a</sup>	424/ 338 - 510	yes	7	292 - 924	7
Total Samples				49		43
% of samples w/in prediction interval						88%

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

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Evaluation of vendor and laboratory analysis of SRMs was 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 information 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.

#### **SRM Analysis for NITON XLt (X-ray)**

The single most important number from these tables is the percentage of samples within the 95% prediction interval. As noted for the NITON XLt data, this percentage is 93% with  $n = 46$ . This suggests that the NITON data are within expected accuracy, accounting for statistical variation. For 5 of the 7 determinations, NITON average results are below the reference value. This would suggest that there is a possible bias associated with the NITON data; however, this is not necessarily significant based upon the minimum number of sample lots evaluated. There were fewer SRMs than expected because NITON's detection limit was much lower than predicted (see Section 6.1.1). This resulted in three SRM results that could not be used.

The percentage of samples within the 95% prediction interval for the laboratory data is 88%. For 6 of the 7 determinations, ALSI average results are below the reference value. This suggests that the ALSI data are potentially 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 (49) 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 6-5), 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.

#### **SRM Analysis for NITON XLi (Isotope)**

The single most important number from these tables is the percentage of samples within the 95% prediction interval. As noted for the NITON XLi data, this percentage is 91%, with  $n = 46$ . This suggests that the NITON data are within expected accuracy, accounting for statistical variation. For 5 of the 7 determinations, NITON average results are

below the reference value. This would suggest that there is a possible bias associated with the NITON data, however, as noted above this is not necessarily significant based upon the minimum number of sample lots evaluated. There were fewer SRMs than expected because NITON's detection limit was much lower than predicted (see Section 6.1.1). This resulted in three SRM results that could not be used.

The percentage of samples within the 95% prediction interval for the laboratory data is 88%. For 6 of the 7 determinations, ALSI average results are below the reference value. This suggests that the ALSI data are potentially 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 (49) 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 6-6), 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.

#### **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 (per instrument) 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 test does not separate precision from bias, if NITON's or ALSI's computed standard deviation was large due to a highly variable result (indication of poor precision), the two CIs could overlap. Conversely, if the variance is small then relatively small differences between the two sample means could be significant. The fact that there was no significant difference between the two results could be due to high sample variability or could be a result of the small variance (i.e. high precision) for that particular sample lot.

Accordingly, associated RSDs have also been reported in Tables 6-5 and 6-6 along with results of the hypothesis testing for each sample lot. Results of these analyses

should therefore be considered accordingly; based upon the minimum number of samples tested for each different sample lot for each instrument.

**Table 6-5. Accuracy Evaluation by Hypothesis Testing (NITON XLt)**

Sample Lot No./ Site	Avg. Conc. mg/kg	RSD or CV	Number of Measurements	Significantly Different at Alpha = 0.01	Relative Percent Difference (NITON to ALSI)
22/ Oak Ridge				yes	34.8%
NITON	116	7.9%	3		
ALSI	81.6	9.4%	3		
24/ Oak Ridge				yes	67.3%
NITON	417	9.6%	7		
ALSI	207	48.4%	7		
26/ Oak Ridge				yes	23.7%
NITON	156	12.4%	7		
ALSI	123	13.5%	7		
31/ Oak Ridge				no	35.8%
NITON	1360	3.3%	3		
ALSI	947	13.2%	3		
51/ Oak Ridge				no	7.0%
NITON	312	3.9%	7		
ALSI	291	13.4%	7		
65/ Oak Ridge				no	28.7%
NITON	84.6	35.0%	7		
ALSI	62.9	8.5%	7		
67/ Oak Ridge				yes	45.7%
NITON	1330	4.5%	7		
ALSI	835	14.8%	7		
25/ Puget Sound				no	4.6%
NITON	43.7	11.5%	3		
ALSI	39.1	10.7%	3		
27/ Puget Sound				no	-7.6%
NITON	126	13.3%	7		
ALSI	136	16.9%	7		
48/ Puget Sound				no	38.0%
NITON	128	18.9%	4		
ALSI	87.1	32.9%	6		
50/ Puget Sound				no	15.5%
NITON	195	6.6%	7		
ALSI	167	17.2%	7		
23/ Carson River				no	39.2%
NITON	174	22.2%	3		
ALSI	117	5.7%	3		
53/ Carson River				no	38.1%
NITON	712	7.3%	7		
ALSI	484	35.5%	7		
54/ Carson River				no	23.0%
NITON	896	4.0%	7		
ALSI	711	21.0%	7		
63/ Carson River				yes	17.8%
NITON	202	9.2%	7		
ALSI	169	6.5%	7		
19/ Manufacturing Site				no	45.3%
NITON	45.5	19.5%	4		
ALSI	28.7	32.2%	7		
20/ Manufacturing Site				no	-16.2%
NITON	54.3	19.2%	3		
ALSI	63.9	25.4%	7		

**Table 6-5. Continued**

Sample Lot No./ Site	Avg. Conc. mg/kg	RSD or CV	Number of Measurements	Significantly Different at Alpha = 0.01	Relative Percent Difference (NITON to ALSI)
28/ Manufacturing Site					
NITON	318	8.2%	3	no	23.6%
ALSI	251	15.6%	3		
29/ Manufacturing Site					
NITON	335	27.8%	3	no	-11.0%
ALSI	374	17.4%	7		
30/ Manufacturing Site					
NITON	376	13.8%	3	no	-18.1%
ALSI	451	11.4%	3		
32/ Manufacturing Site					
NITON	300	7.8%	7	yes	-65.5%
ALSI	592	12.7%	7		
33/ Manufacturing Site					
NITON	379	10.8%	6	yes	-104%
ALSI	1204	13.3%	7		
49/ Manufacturing Site					
NITON	108	20.5%	7	no	24.8%
ALSI	84.2	12.5%	7		
52/ Manufacturing Site					
NITON	496	4.7%	7	no	15.7%
ALSI	424	21.9%	7		
64/ Manufacturing Site					
NITON	404	8.7%	7	yes	34.5%
ALSI	285	8.9%	7		
66/ Manufacturing Site					
NITON	985	3.8%	7	no	34.5%
ALSI	892	11.2%	7		

CV = Coefficient of variance

**Table 6-6. Accuracy Evaluation by Hypothesis Testing (NITON XLi )**

Sample Lot No./ Site	Avg. Conc. mg/kg	RSD or CV	Number of Measurements	Significantly Different at Alpha = 0.01	Relative Percent Difference (NITON to ALSI)
22/ Oak Ridge					
NITON	141	15.8%	3	no	53.4%
ALSI	81.6	9.4%	3		
24/ Oak Ridge					
NITON	438	23.7%	7	yes	71.6%
ALSI	207	48.4%	7		
26/ Oak Ridge					
NITON	157	15.8%	7	no	23.7%
ALSI	123	13.5%	7		
31/ Oak Ridge					
NITON	1279	6.4%	3	no	29.8%
ALSI	947	13.2%	3		
51/ Oak Ridge					
NITON	305	13.1%	7	no	4.7%
ALSI	291	13.4%	7		
65/ Oak Ridge					
NITON	80.3	33.5%	7	no	24.3%
ALSI	62.9	62.9%	7		
67/ Oak Ridge					
NITON	1296	5.0%	7	no	43.3%
ALSI	835	14.8%	7		

**Table 6-6. Continued**

Sample Lot No./ Site	Avg. Conc. mg/kg	RSD or CV	Number of Measurements	Significantly Different at Alpha = 0.01	Relative Percent Difference (NITON to ALSI)
27/ Puget Sound					
NITON	97.0	21.1%	7	yes	33.5%
ALSI	136	16.9%	7		
48/ Puget Sound					
NITON	171	25.9%	4	no	65.0%
ALSI	87.1	32.9%	6		
50/ Puget Sound					
NITON	217	10.0%	7	yes	26.0%
ALSI	167	17.2 %	7		
23/ Carson River					
NITON	153	11.7%	3	no	26.7%
ALSI	117	5.7%	3		
53/ Carson River					
NITON	720	7.0%	7	no	39.2%
ALSI	484	35.5%	7		
54/ Carson River					
NITON	917	9.4%	7	no	25.3%
ALSI	711	21.0%	7		
63/ Carson River					
NITON	223	11.2%	7	yes	27.6%
ALSI	169	6.5%	7		
20/ Manufacturing Site					
NITON	73.4	18.3%	3	no	13.8%
ALSI	63.9	25.4%	7		
28/ Manufacturing Site					
NITON	370	8.6%	3	yes	38.3%
ALSI	251	15.6%	3		
29/ Manufacturing Site					
NITON	319	16.2%	3	no	-15.9%
ALSI	374	17.4%	7		
30/ Manufacturing Site					
NITON	362	17.5%	3	no	-21.9%
ALSI	451	11.4%	3		
32/ Manufacturing Site					
NITON	309	3.9%	7	yes	-62.8%
ALSI	592	12.7%	7		
33/ Manufacturing Site					
NITON	416	9.5%	6	yes	-97.3%
ALSI	1204	13.3%	7		
49/ Manufacturing Site					
NITON	109	32.8%	7	no	25.7%
ALSI	84.2	12.5%	7		
52/ Manufacturing Site					
NITON	504	8.3%	7	no	17.2%
ALSI	424	21.9%	7		
64/ Manufacturing Site					
NITON	400	7.1%	7	yes	33.6%
ALSI	285	8.9%	7		
66/ Manufacturing Site					
NITON	974	3.6%	6	no	8.8%
ALSI	892	11.2%	7		

CV = Coefficient of variance

**NITON XLt (X-ray) Evaluation**

Of the 26 sample lots, 8 results are significantly different, based upon the hypothesis test noted above. Most of the

relative percent differences are positive which indicates that the NITON 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 NITON results that are less than the laboratory result, therefore, no overall NITON high or low bias is apparent. It appears that NITON data are subject to more random variability.

In determining the number of results significantly above or below the value reported by the referee laboratory, 14 of 26 NITON average results were found to have relative percent differences less than 30% for sample concentrations above the estimated PQL. Only 1 of 26 NITON average results have relative percent differences greater than 100% for this same group of samples (see Table 6-7). Interferences

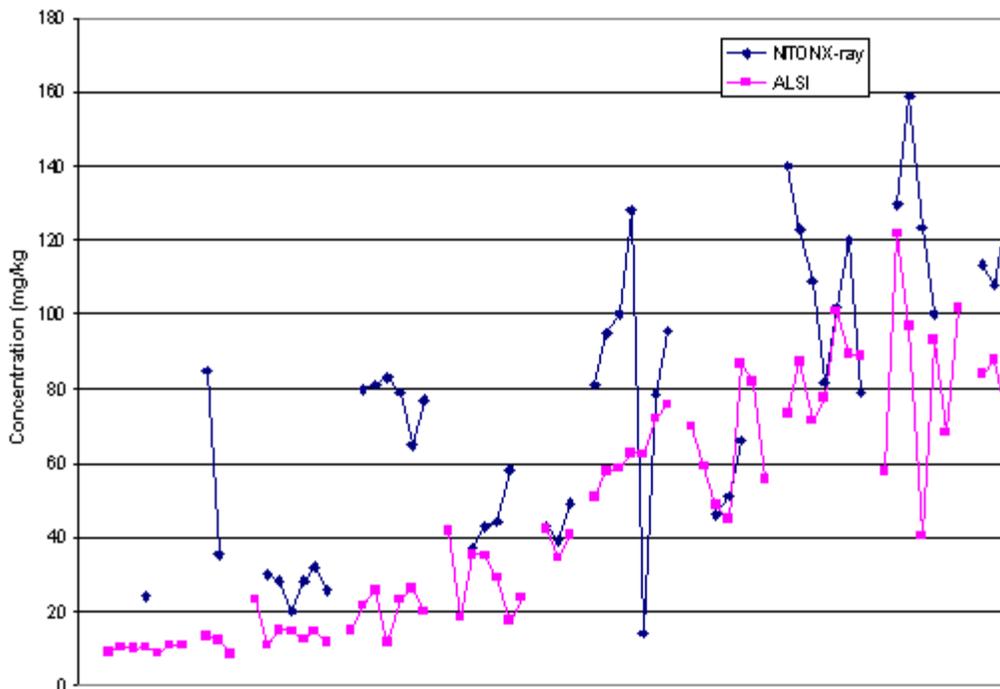
may be a problem but, because of the random variability associated with the data, no interferences are specifically apparent.

In addition to the statistical summary presented above, data plots (Figures 6-1 and 6-2) are included in order to present a visual interpretation of the accuracy. Two separate plots have been included for the NITON X-ray data. These two plots are divided based upon sample concentration in order to provide a more detailed presentation.

**Table 6-7. Number of Sample Lots Within Each %D Range (NITON XLt )**

	<30%	>30%, <50%	>50%, <100%	>100%	Total
Positive %D	10	9	1	0	20
Negative %D	4	0	1	1	6
Total	14	9	2	1	26

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



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

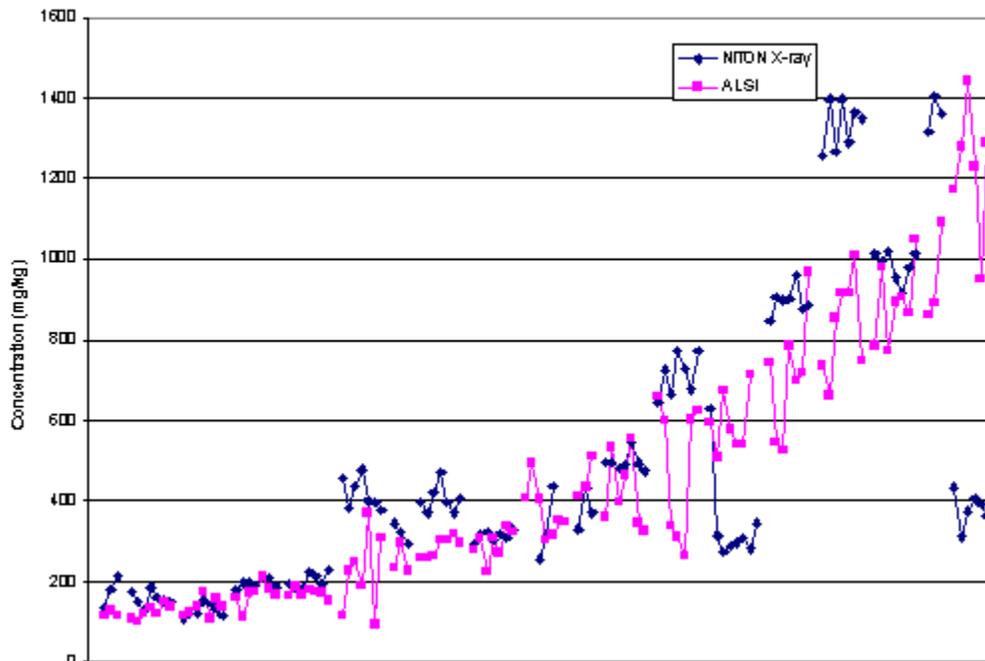


Figure 6-2. Data plot for the NITON XLt high concentration sample results.

Concentrations of samples analyzed by NITON ranged approximately from 10 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 NITON X-ray field instrument. This graphical presentation presents all data points. It shows NITON X-ray 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 NITON below about 100 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.

#### NITON XLi (Isotope) Evaluation

Of the 24 sample lots, 8 results are significantly different based upon the hypothesis test noted above. Most of the relative percent differences are positive which indicates that the NITON XLi 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 NITON results that are less than the laboratory result; therefore, no overall NITON high or low bias is apparent. It appears that NITON data are subject to more random variability.

In determining the number of results significantly above or below the value reported by the referee laboratory, 14 of 24 NITON average results were found to have relative percent differences less than 30% for sample concentrations above the estimated PQL. Zero of 24 NITON average results have relative percent differences greater than 100% for this same group of samples (see Table 6-8). Interferences may be a problem but, because of the random variability associated with the data, no interferences are specifically apparent.

**Table 6-8. Number of Sample Lots Within Each %D Range (NITON XLi )**

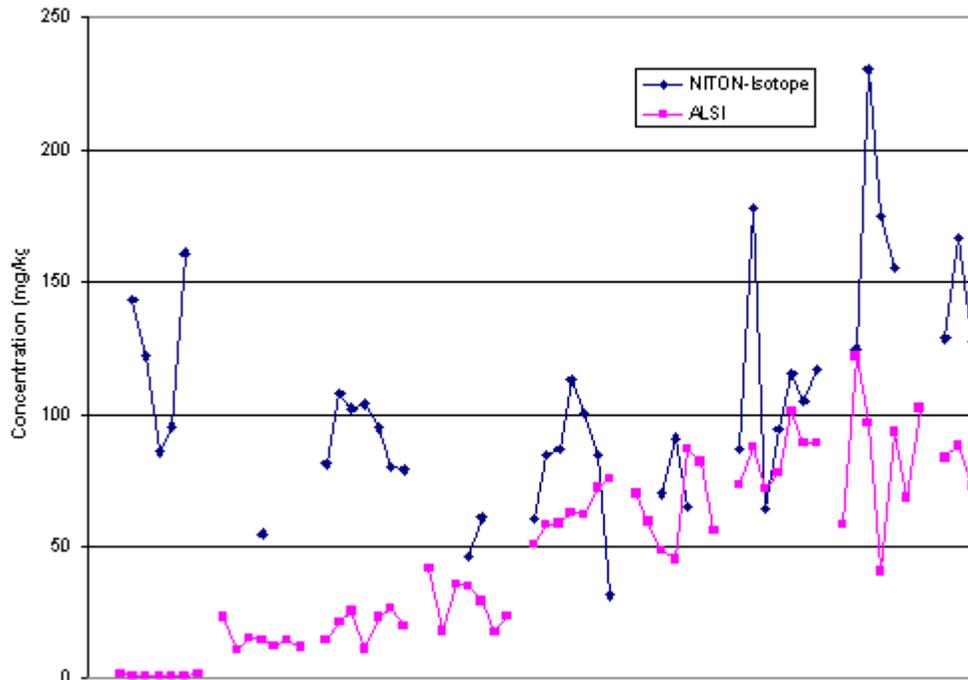
	<30%	>30%, <50%	>50%, <100%	>100%	Total
Positive %D	12	5	3	0	20
Negative %D	2	0	2	0	4
Total	14	5	5	0	24

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

In addition to the statistical summary presented above, data plots (Figures 6-3 and 6-4) are included in order to present a visual interpretation of the accuracy. Two separate plots have been included for the NITON Isotope data. These two plots are divided based upon sample concentration in order to provide a more detailed presentation. Concentrations of samples analyzed by NITON ranged approximately from 1 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 NITON Isotope field instrument. This graphical presentation presents all data points. It shows NITON Isotope 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 NITON below about 100 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.



**Figure 6-3. Data plot for the NITON XLi low concentration sample results.**

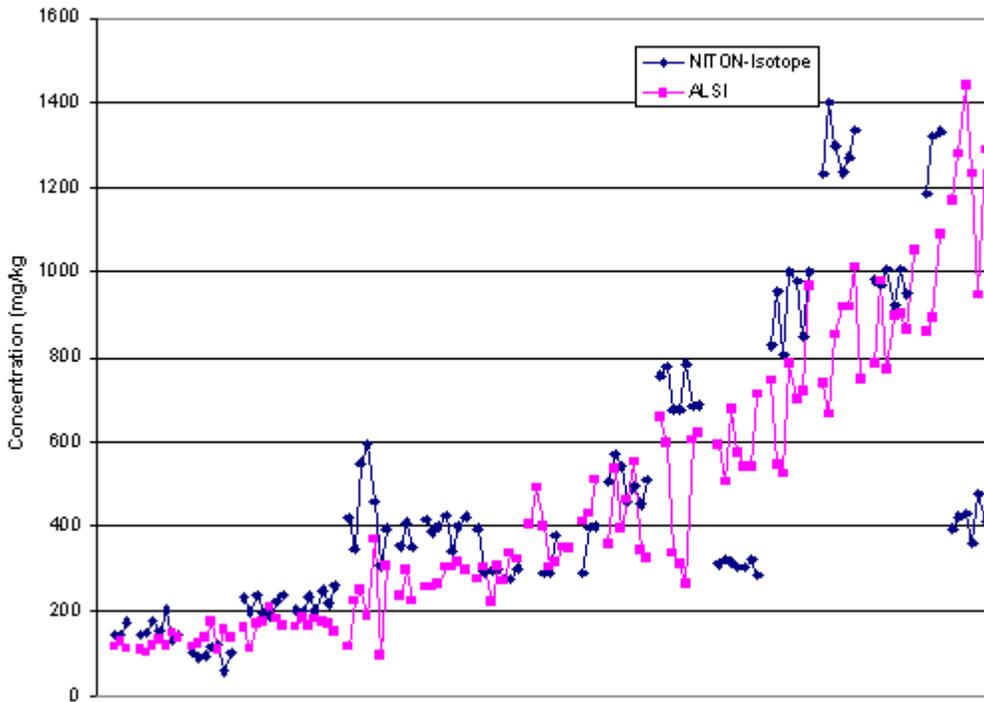


Figure 6-4. Data plot for the NITON XLi high concentration sample results.

### **Discussion of Interferences**

RSDs for the NITON XLt and XLi instruments are small, suggesting that precision is good. (This will be discussed in more detail in Section 6.1.3) As noted previously, it would therefore, appear that interferences may be the cause of the inaccurate analyses for field samples, but it is not apparent as to the specific interferent causing the problem. There is no apparent significant difference between reported values and associated sites from which the samples were collected. Table 6-9 shows additional, non-target analyses for each of the collected samples and associated sampling sites.

### **Unified Hypothesis Test**

SAIC performed a unified hypothesis test analysis to assess the comparability of analytical results provided by NITON and those provided by ALSI. (See appendix B for

a detailed description of this test.) NITON and ALSI both supplied multiple assays on replicates derived from a total of 24 different sample lots for the NITON XLi field instrument and 26 different sample lots for the NITON XLt field instrument, be they field materials or reference materials. The NITON 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 for both the NITON XLi and XLt instruments. The null hypothesis tested was that, on average, NITON and ALSI produce the same results within a given sample lot. The null hypothesis is rejected in part because NITON 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.

**Table 6-9. Concentration (in mg/kg) of Non-Target Analytes**

Lot #	Site	TOC	O&G	Ag	As	Ba	Cd	Cr	Cu	Pb	Se	Sn	Zn	Hg
11	Puget Sound	3800	130	<0.5	4	20	<0.5	18	8	1	<2	<5	24	0.63
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
18	Carson River	1900	70	26	17	46	2	6	62	200	<2	<5	390	9.3
19	Manufacturing Site	630	60	<0.5	<2	410	<0.5	5.7	30	4	<2	<5	140	36
20	Manufacturing Site	2000	<50	<0.5	<2	150	<0.5	35	52	5	2	<5	68	83
21	Manufacturing Site	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
23	Carson River	5700	100	37	11	280	0.9	25	170	140	<2	<5	170	120
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
28	Manufacturing Site	2000	50	0.86	<2	160	<0.5	28	55	4	<2	<5	74	250
29	Manufacturing Site	900	110	<0.5	<2	210	<0.4	16	37	6	<2	<4	88	440
30	Manufacturing Site	1400	70	<0.5	<2	230	<0.5	15	32	6	<2	<5	83	460
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
45	SRM CRM 033	NR	NR	0.78	130	220	89	100	96	61	89	390	230	6.4
46	SRM CRM 032	NR	NR	81	370	120	130	15	590	4600	170	1300	2600	21
47	SRM NIST 2710	NR	NR	35	630	700	22	39	3000	5500	NR	NR	7000	33
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
51	SRM RTC spec.	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	400
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
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
64	Spiked Lot 19	630	60	<0.5	<2	410	<0.5	5.7	30	4	<2	<5	140	320
65	Spiked Lot 14	7800	180	0.32	2	41	0.4	16	9	11	<2	<4	74	51
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

**Accuracy Summary**

In summary, NITON XLt data were within SRM 95% prediction intervals 93% of the time, which suggests significant equivalence to certified standards. NITON XLi data were within SRM 95% prediction intervals 91% of the time, which also suggests significant equivalence to certified standards. ALSI data compared favorably to SRM values and were within the 95% prediction interval 88% of the time, indicating statistical parity found to be biased low.

The comparison between the NITON XLt field data and the ALSI results suggest that the two data sets are not the same. The comparison between the NITON XLi field data and the ALSI results also suggest that these two data sets are not the same. When a unified hypothesis test is performed, these conclusions are confirmed. NITON data are found to be both above and below referee laboratory concentrations. The number of NITON XLt average values less than 30% different from the referee laboratory results

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or SRM reference values was 14 of 26 different sample lots. The number of NITON XLI average values less than 30% different from the referee laboratory results or SRM reference values was also 14 of 24 different sample lots. Both NITON XLt and XLI results; therefore, often provide a reasonable estimate of accuracy for field determination, and may be affected by interferences not identified by this demonstration. Because the NITON data compare favorably to the SRM values, the differences between NITON and the referee laboratory are likely the result of matrix interferences for field sample analysis.

Initially, there were more sample lots tested for both instruments, however, several of the samples were below the estimated detection limit. Many samples were not used because they were reported as non-detect by NITON. The previously estimated detection limit was found to be too low for several of the analyses performed. More information on detection limits is provided in Section 6.1.1.

### **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 NITON and the referee laboratory. In some cases, samples may have been analyzed as few as three times and some NITON 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 differences between NITON RSDs and the referee laboratory RSDs was determined. In Tables 6-9 and 6-10, the RSD for each separate sample lot is shown for NITON compared to the referee laboratory. The average RSD was computed for all measurements made by NITON, 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 Tables 6-10 and 6-11 and shown for both NITON instruments 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.

Originally, it was anticipated that NITON detection limits would be lower, based upon information supplied by the developer. During the demonstration it was discovered that several lower concentration samples analyzed by NITON were reported as non-detect because the NITON detection limit was higher than expected. Therefore, there are fewer sample lots than originally anticipated for the evaluation because these non-detect samples could not be included.

Tables 6-10 and 6-11 show 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 Tables 6-10 and 6-11 and compared between NITON 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 NITON'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, and are included here for purposes of precision comparison. Sample concentrations were separated into approximate ranges: medium and high, as noted in Tables 6-10, 6-11, and 6-1. Sample results reported by NITON as below their approximated PQL were not included in Tables 6-10 and 6-11. There appears to be no correlation between concentration (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 NITON. This was used for purposes of precision comparison to NITON. RSD for the vendor and

the laboratory were calculated individually and shown in Tables 6-10 and 6-11.

**Table 6-10. Evaluation of Precision (NITON XLt)**

Sample Lot No. NITON and Lab	Avg. Conc. or Reference SRM Value	RSD	Number of Samples	w/in 25% RSD Goal?
<b>OAK RIDGE</b>				
Lot no. 22	81.6 (medium)			
NITON		7.9%	3	yes
ALSI		9.4%	3	yes
Lot no. 24	207 (high)			
NITON		9.5%	7	yes
ALSI		48.4%	7	no
Lot no. 26	123 (high)			
NITON		12.4%	7	yes
ALSI		13.5%	7	yes
Lot no. 31	947 (high)			
NITON		3.3%	3	yes
ALSI		13.2%	3	yes
Lot no. 51	405 (high)			
NITON		3.9%	7	yes
ALSI		13.4%	7	yes
Lot no. 65	62.9 (medium)			
NITON		41.3%	7	no
ALSI		13.5%	7	yes
Lot no. 67	835 (high)			
NITON		4.5%	7	yes
ALSI		14.8%	7	yes
Oak Ridge Avg. RSD				
NITON		19.6%		yes
ALSI		20.4%		yes
<b>PUGET SOUND</b>				
Lot no. 25	39.1 (medium)			
NITON		11.5%	3	yes
ALSI		10.7%	3	yes
Lot no. 27	136 (high)			
NITON		13.3%	7	yes
ALSI		16.9%	7	yes
Lot no. 48	77.8 (medium)			
NITON		18.9%	4	yes
ALSI		32.9%	6	no
Lot no. 50	203 (high)			
NITON		6.6%	7	yes
ALSI		17.7%	7	yes
Puget Sound/ Avg. RSD				
NITON		13.3%		yes
ALSI		22.1%		yes
<b>CARSON RIVER</b>				
Lot no. 23	117 (medium)			
NITON		22.2%	3	yes
ALSI		5.7%	3	yes
Lot no. 53	910 (high)			
NITON		7.3%	7	yes
ALSI		35.5%	7	no
Lot no. 54	1120 (high)			
NITON		4.0%	7	yes
ALSI		21.0%	7	yes

**Table 6-10. Continued**

Sample Lot No. NITON and Lab	Avg. Conc. or Reference SRM Value	RSD	Number of Samples	w/in 25% RSD Goal?
Lot no. 63	169 (high)			
NITON		9.2%	7	yes
ALSI		6.5%	7	yes
Carson River/ Avg. RSD				
NITON		15.7%		yes
ALSI		6.7%		yes
<b>MANUFACTURING SITE</b>				
Lot no. 19	28.7 (medium)			
NITON		19.5%	4	yes
ALSI		32.2%	7	no
Lot no. 20	63.9 (medium)			
NITON		19.2%	3	yes
ALSI		25.4%	7	yes
Lot no. 28	251 (high)			
NITON		8.2%	3	yes
ALSI		15.6%	3	yes
Lot no. 29	374 (high)			
NITON		27.8%	3	no
ALSI		17.4%	7	yes
Lot no. 30	451 (high)			
NITON		13.8%	3	no
ALSI		11.4%	3	no
Lot no. 32	592 (high)			
NITON		7.8%	7	yes
ALSI		12.7%	7	yes
Lot no. 33	379 (high)			
NITON		10.8%	6	yes
ALSI		13.3%	7	yes
Lot no. 49	99.8 (medium)			
NITON		20.5%	7	yes
ALSI		12.5%	7	yes
Lot no. 52	608 (high)			
NITON		4.7%	7	yes
ALSI		21.9%	7	yes
Lot no. 64	285 (high)			
NITON		8.7%	7	yes
ALSI		8.9%	7	yes
Lot no. 66	985 (high)			
NITON		3.8%	7	yes
ALSI		11.2%	7	yes
Manufacturing Site/ Avg. RSD				
NITON		3.8%		yes
ALSI		11.2%		yes
<b>SUMMARY STATISTICS</b>				
Overall Avg. RSD				
NITON		13.1%		yes
ALSI		20.0%		yes
Field Samples/ Avg. RSD				
NITON		16.9%		yes
ALSI		17.5%		yes
SRMs/ Avg. RSD				
NITON		9.3%		yes
ALSI		22.5%		yes

**Table 6-11. Evaluation of Precision (NITON XLi)**

Sample Lot No. NITON and Lab	Avg. Conc. or Reference SRM Value	RSD	Number of Samples	w/in 25% RSD Goal?
<b>OAK RIDGE</b>				
Lot no. 22	81.6 (medium)			
NITON		15.8%	3	yes
ALSI		9.4%	3	yes
Lot no. 24	207 (high)			
NITON		23.7%	7	yes
ALSI		48.4%	7	no
Lot no. 26	123 (high)			
NITON		15.8%	7	yes
ALSI		13.5%	7	yes
Lot no. 31	947 (high)			
NITON		6.4%	3	yes
ALSI		13.2%	3	yes
Lot no. 51	405 (high)			
NITON		13.1%	7	yes
ALSI		13.4%	7	yes
Lot no. 65	62.9 (medium)			
NITON		33.5%	7	no
ALSI		13.5%	7	yes
Lot no. 67	835 (high)			
NITON		5.0%	6	yes
ALSI		14.8%	7	yes
Oak Ridge Avg. RSD				
NITON		16.7%		yes
ALSI		20.4%		yes
<b>PUGET SOUND</b>				
Lot no. 27	136 (high)			
NITON		21.1%	7	yes
ALSI		16.9%	7	yes
Lot no. 48	77.8 (medium)			
NITON		25.9%	4	no
ALSI		32.9%	6	no
Lot no. 50	203 (high)			
NITON		10.0%	7	yes
ALSI		17.7%	7	yes
Puget Sound/ Avg. RSD				
NITON		21.1%		yes
ALSI		22.1%		yes
<b>CARSON RIVER</b>				
Lot no. 23	117 (medium)			
NITON		11.7%	3	yes
ALSI		5.7%	3	yes
Lot no. 53	910 (high)			
NITON		7.0%	7	yes
ALSI		35.5%	7	no
Lot no. 54	1120 (high)			
NITON		9.4%	7	yes
ALSI		21.0%	7	yes
Lot no. 63	169 (high)			
NITON		11.2%	7	yes
ALSI		6.5%	7	yes
Carson River/ Avg. RSD				
NITON		11.4%		yes
ALSI		6.7%		yes

**Table 6-11. Continued**

Sample Lot No. NITON and Lab	Avg. Conc. or Reference SRM Value	RSD	Number of Samples	w/in 25% RSD Goal?
<b>MANUFACTURING SITE</b>				
Lot no. 20	63.9 (medium)			
NITON		18.3%	3	yes
ALSI		25.0%	7	yes
Lot no. 28	251 (high)			
NITON		8.6%	3	yes
ALSI		15.6%	3	yes
Lot no. 29	374 (high)			
NITON		16.2%	3	yes
ALSI		17.4%	7	yes
Lot no. 30	451 (high)			
NITON		17.5%	3	yes
ALSI		11.4%	3	yes
Lot no. 32	592 (high)			
NITON		3.9%	7	yes
ALSI		12.7%	7	yes
Lot no. 33	379 (high)			
NITON		9.5%	6	yes
ALSI		13.3%	7	yes
Lot no. 49	99.8 (medium)			
NITON		32.8%	7	no
ALSI		12.5%	7	yes
Lot no. 52	608 (high)			
NITON		8.3%	7	yes
ALSI		21.9%	7	yes
Lot no. 64	285 (high)			
NITON		7.1%	7	yes
ALSI		8.9%	7	yes
Lot no. 66	985 (high)			
NITON		3.6%	6	yes
ALSI		11.2%	7	yes
Manufacturing Site/ Avg. RSD				
NITON		11.6%		yes
ALSI		16.3%		yes
<b>SUMMARY STATISTICS</b>				
Overall Avg. RSD				
NITON		14.4%		yes
ALSI		20.0%		yes
Field Samples/ Avg. RSD				
NITON		13.8%		yes
ALSI		17.5%		yes
SRMs/ Avg. RSD				
NITON		15.0%		yes
ALSI		22.5%		yes

**NITON XLt (X-ray) Evaluation**

As noted from Table 6-10, the NITON XLt precision is better than that of the referee laboratory. The single most important measure of precision provided in Table 6-10, overall average RSD, is 20.0% for the referee laboratory, compared to the NITON XLt average RSD of 16.1%. The laboratory and NITON RSD are both 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 17.5% for ALSI and 16.9% for NITON; SRM RSD is 22.5% for ALSI and 9.3% for NITON. This is similar to the results for

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the accuracy comparison. NITON appears to have better precision for the SRM analyses compared to the field samples. NITON's comparison for SRMs was statistically significant, and for the precision evaluation NITON had a narrower range for the RSD. 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 also confirm the pre-demonstration results, showing that sample homogenization procedures met their originally stated objectives.

There appears to be no significant site variation in precision between Oak Ridge, Puget Sound, Carson River, and the manufacturing site samples. (See Table 6-10 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 the other NITON instrument or other data sets and, therefore, may not be significant.

#### **NITON XLi (Isotope) Evaluation**

As noted from Table 6-11, the NITON XLi precision is better than that of the referee laboratory. The single most important measure of precision provided in Table 6-11, overall average RSD, is 20.0% for the referee laboratory, compared to the NITON XLi average RSD of 14.4%. The laboratory and NITON RSD are both within the predicted 25% RSD objective for precision expected from both analytical and sampling variance. Field sample precision compared to SRM precision shows no significant difference between these two sample lots; field sample RSD is 17.5% for ALSI and 13.8% for NITON; SRM RSD is 22.5% for ALSI and 15.0% for NITON.

There appears to be no significant site variation between Oak Ridge, Puget Sound, Carson River, and the manufacturing site samples. (See Table 6-11 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 Carson River site had a lower average RSD for both the vendor and the laboratory but this difference was not significant in results from the other NITON instrument or other data sets and, therefore, may not be significant.

#### **Precision Summary**

The precision of the NITON XLt and XLi field instruments is better than the referee laboratory precision. The overall average RSD is 20.0% for the referee laboratory,

compared to the NITON XLt average RSD of 13.1% and the NITON XLi average RSD of 14.4%. Both the laboratory and NITON precision goals of 25% overall RSD were achieved.

#### **6.1.4 Time Required for Mercury Measurement**

The 700 Series Analyzers were evaluated over a 3-day period. The amount of time that was needed to setup, prepare and analyze 197 samples using 2 instruments, calibrate the analyzers, as well as the time necessary to demobilize was determined.

Two technicians performed all activities including sample preparation and analysis for four batches of mercury-contaminated soil. Setup involved taking the analyzers, test stands, battery packs and battery charger out of the carrying case, installing a battery pack and connecting the computers and keyboard (optional equipment) to the electric power source. This took approximately 2 minutes. After turning on the instruments, they were allowed to warm up for 10 minutes before the instruments were calibrated. The technician selected the Calibrate Detector icon to recalibrate either instrument. The instrument calibration screen was displayed until the calibration was complete. After the calibration finished, the calibration results were displayed. During the demonstration, calibration check samples were analyzed prior to analysis, in the middle of the day, and towards the end operation for the day. The check samples were analyzed for 240 seconds, the same time used when analyzing samples for the demonstration.

Total setup time including warm-up was about 20 minutes on the first day of the demonstration. The XL Series Analyzers were calibrated with a 230 mg/kg standard. The instruments recorded concentrations very close to the standard throughout the demonstration.

The time required for mercury measurements started with sample setup and ended when NITON disconnected the devices and placed them back into the padded carrying cases. After setup, sample preparation was carried out. Soil samples were provided to NITON in 20 mL amber VOA vials. Prior to filling the XRF sample cups, the NITON technicians prepared for the samples by placing a circle of Mylar film on top of the sample cup, and securing the film with a collar. The film was smooth and taut. NITON performed this step, which took 3 seconds per sample, ahead of time. (The observer watched the Mylar film placed on several sample cups during the demonstration.) Dry soil was transferred from the VOA vial to the sample cup using a metal spatula. A metal spatula was used to

lightly tamp the sample in the cup. A filter paper disc was then placed on the sample. The rest of the sample cup was stuffed with polyester filling to prevent the sample from moving during measurement. Finally a cap and sample label were placed on the cup. Sample preparation took about two minutes per sample. The cup was now ready for measurement. Sample analysis was done in approximately the top 2-5 mm of the sample.

Some sample batches had free standing water. One batch was moist and appeared tar-like. Some of these samples were placed in a toaster oven at 200 °F for 2-3 hours prior to analysis. Sample preparation and analysis continued while the moist samples were drying in the toaster oven.

Measurements taken with the 700 Series Analyzers required placing the test platform on a flat level surface. The technician then placed the nose cone adapter with the analyzer's window against the test stand's analysis window and the LCD screen towards the technician. The prepared sample was placed in the pocket on the test stand. The technician depressed the test platform lever and pushed the sample test drawer fully closed. The technician then selected the desired test procedure. There are four different methods of operation for taking sample measurements. During the demonstration, the trigger-and proximity-sensor method was used. With this method, the measurement window was placed against the sample to be analyzed to engage the proximity sensor on the front of the instrument and the trigger for sample analysis was then activated.

Measurement times from 30-600 seconds can be employed, depending on the data quality needs of the project. As the measurement time increases, the detector collects a larger number of X-rays from the sample. Based on years of experience and sound engineering practice, NITON determined the measurement times used during the demonstration. The measurement time selected was 120 seconds per sample. The measurement time shown on the screen was the total time that had elapsed. In some cases sample measurement times exceeded 120 seconds.

Sample results were transcribed from the computer screen to the Chain-of-Custody form and given to the EPA representative prior to leaving the site on day one. On days two and three, the results were given to the EPA representative shortly after returning to the hotel. Results were available on-site, however NITON wanted some additional time to look over the data.

### **Analysis Time Summary**

NITON required a total of 17.5 hours (35 man hours) for mercury measurements of 197 soil samples analyzed using 2 instruments during their 3-day demonstration. It should be noted that one technician performed sample preparation while the other technician simultaneously operated both analyzers. Table 6-12 indicates the time required to complete mercury measurements using the 700 Series Analyzers.

**Table 6-12. Mercury Measurement Times**

<u>Measurement Activity</u>	<u>Time Required</u>
System Setup	2 minutes
Battery Pack Installation	1 minute
Battery Pack Charge	120 minutes
Analyzer Warm Up	10 minutes
Analyzer Calibration	5 minutes
Sample Preparation	2 minutes per sample
Count Times	2 minutes per sample
Demobilization	2 minutes

### **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 XL-700 Series Analyzers in terms of secondary objectives described in Section 4.1. These secondary objectives were addressed based on observations of the XLi 702 and XLt 792 and information provided by NITON.

### **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, the 700 Series Analyzers are very easy to operate, requiring one field technician with a high school education. NITON requires any user to attend a free-of-charge, 8-hour training course prior to operating their analyzers. The instruments come equipped with customizable, PC-based reporting software that automatically corrects for variations in soil-sample chemistry and density. Internet-based diagnostics and troubleshooting are available.**

During the demonstration, one technician prepared most of the soil samples while the other technician performed sample analysis. However, both technicians did perform sample preparation and analysis during the three days in the field. One technician could easily perform both sample preparation and analysis for one instrument. Two technicians were used during the demonstration in order to increase sample throughput during the limited time on-site. Based on observations and conversations during the field demonstration, the instrument could be easily operated by a high school graduate, after attending NITON's 8-hour training course.

After the analyzer, test stand, computer, keyboard, and battery charger were unpacked from the carrying case, the technicians prepared the analyzers for use. The NITON devices are hand-held portable X-ray fluorescence analyzers. The on/off /escape button on the control panel was pressed for about 3 seconds to turn the instrument on. On start-up, the screen display was replaced by the re-start screen which counts down from 29 to 0, in increments of 1 second. When the restart was complete, it was replaced by the logon screen. The technician selected a 4-digit security code, followed by the enter key. After the technician completed the log-on procedure, the word "success" appeared on the screen. The technician checked the date/time on the screen. The NITON 700 Series main menu system allows the technician to take readings, view and move data with a minimum number of steps. Menus were presented as small pictures (Figure 6-5) which allowed the technician to do several things:

1. Toggle between two different functions or views, such as turning backlighting on or off.
2. Present a sub-menu which allowed access to more choices.
3. Present a screen which allowed the technician to view data, edit data or control the instrument.

The standard soil testing mode was available from the bulk mode menu. The standard soil testing menu allowed the technician to perform tests on soil without adjusting for a particular matrix. The standard soil testing mode uses Compton Normalization to automatically adjust for the effects of the matrix. Sample spectra are viewed on the screen (Figure 6-6).

The results were displayed throughout the duration of the reading, and updated every 3 seconds. When the reading was complete, a final screen on the analyzer displayed the final measurements which have just been completed. XL-700 Series downloads include precision data and X-ray

spectra, name of data collector, test location, sample-identification, and sample results (Figure 6-7).



Figure 6-5. Main menu screen shot.

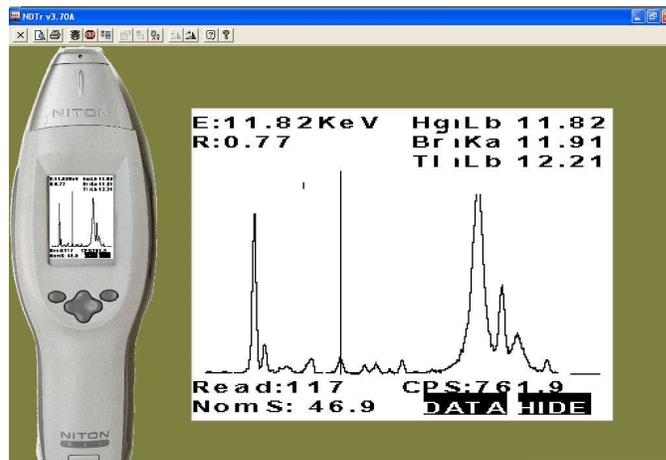


Figure 6-6. Screen shot of sample spectra.

Index	Time	Type	Duration	Mo	Pb	Se	As	Hg	Zn	Cu
1	2002-05-10 20:50	SHUTTER_CAL	50.56	8.59 ± 0.00	Properties ± 0.00	16.20 ± 0.00	12.40 ± 0.00	72.52 ± 0.00	141.75 ± 0.00	100.00 ± 0.00
2	2002-05-10 20:55	BULK	124.00	20.48 ± 12.59	81.08 ± 14.54	5.92 ± 4.95	23.17 ± 10.03	261.20 ± 22.06	296.34 ± 21.65	102.12 ± 22.71
3	2002-05-10 21:12	BULK	151.32	-0.50 ± 10.48	10.20 ± 9.52	6.03 ± 3.82	5.54 ± 6.20	81.06 ± 13.56	107.18 ± 13.86	29.36 ± 16.11
4	2002-05-10 21:16	BULK	190.87	0.54 ± 12.74	39.24 ± 13.98	5.64 ± 5.25	5.93 ± 9.67	478.41 ± 27.20	207.72 ± 20.32	24.18 ± 22.25
5	2002-05-10 21:23	BULK	156.60	6.67 ± 14.09	42.55 ± 15.21	-1.57 ± 5.37	12.77 ± 10.57	398.29 ± 28.12	247.13 ± 23.13	64.71 ± 25.12
6	2002-05-10 21:28	BULK	212.91	20.01 ± 10.50	84.80 ± 11.82	6.26 ± 3.81	4.12 ± 7.49	23.18 ± 12.18	437.73 ± 19.86	69.40 ± 18.58
7	2002-05-10 21:32	BULK	123.97	2.08 ± 15.65	35.79 ± 20.34	-2.14 ± 6.81	-12.17 ± 12.67	319.95 ± 29.86	21.43 ± 20.55	48.22 ± 27.86
8	2002-05-10 21:35	BULK	160.49	14.13 ± 11.42	131.13 ± 15.15	-8.25 ± 5.03	22.42 ± 11.53	1288.71 ± 36.04	433.53 ± 22.08	159.80 ± 21.67
9	2002-05-10 21:38	BULK	141.43	77.50 ± 18.58	4800.41 ± 88.55	198.27 ± 15.40	455.95 ± 58.71	-1.38 ± 30.50	3072.85 ± 71.77	691.65 ± 54.06
10	2002-05-10 21:44	BULK	208.36	-10.99 ± 11.12	29.09 ± 10.52	-2.01 ± 3.67	11.93 ± 6.96	107.82 ± 14.56	191.02 ± 16.23	51.41 ± 18.36
11	2002-05-10 21:48	BULK	177.98	51.18 ± 11.05	133.65 ± 14.59	0.26 ± 5.11	24.00 ± 11.14	1395.14 ± 35.22	440.67 ± 21.00	149.33 ± 20.42
12	2002-05-10 21:53	BULK	263.14	7.26 ± 10.77	5.41 ± 13.34	6.78 ± 4.91	-0.87 ± 8.44	315.90 ± 20.40	16.01 ± 13.94	23.61 ± 18.65
13	2002-05-10 21:58	BULK	139.92	-8.26 ± 14.84	39.36 ± 19.51	4.43 ± 6.73	-6.42 ± 12.23	303.31 ± 28.01	29.88 ± 19.55	-34.96 ± 24.32
14	2002-05-10 22:02	BULK	205.31	-6.98 ± 12.09	-4.09 ± 14.92	6.01 ± 5.56	5.93 ± 9.56	315.53 ± 23.17	26.45 ± 15.95	-18.13 ± 20.31
15	2002-05-10 22:06	BULK	156.62	55.25 ± 18.37	5301.90 ± 91.97	206.38 ± 15.64	434.16 ± 60.64	20.36 ± 31.77	3046.40 ± 71.25	626.79 ± 53.61
16	2002-05-10 22:10	BULK	156.67	4.99 ± 13.92	-53.23 ± 15.20	6.72 ± 6.30	22.57 ± 10.12	306.05 ± 26.08	-0.27 ± 17.46	-10.83 ± 23.30
17	2002-05-10 22:13	BULK	133.79	32.66 ± 12.00	103.15 ± 15.31	1.05 ± 5.61	14.40 ± 11.73	1348.98 ± 38.55	344.73 ± 21.61	134.10 ± 21.73
18	2002-05-10 22:18	BULK	203.79	-10.80 ± 11.55	32.10 ± 11.03	-0.06 ± 3.91	15.58 ± 7.39	125.82 ± 15.55	190.79 ± 16.87	80.30 ± 19.52
19	2002-05-10 22:22	BULK	214.43	1.69 ± 8.65	27.66 ± 8.24	-1.90 ± 2.89	4.45 ± 5.36	95.63 ± 11.48	124.66 ± 11.58	17.72 ± 12.82
20	2002-05-10 22:25	BULK	149.82	-3.11 ± 10.33	35.12 ± 10.11	-1.30 ± 3.49	-1.88 ± 6.45	100.10 ± 13.83	108.63 ± 13.48	16.94 ± 15.32
21	2002-05-10 22:29	BULK	158.93	28.14 ± 11.33	103.13 ± 13.62	9.86 ± 4.53	9.13 ± 9.03	227.46 ± 18.92	296.72 ± 19.25	76.56 ± 19.81
22	2002-05-10 22:32	BULK	153.62	52.88 ± 18.52	5036.29 ± 90.62	211.32 ± 15.91	610.45 ± 60.82	38.59 ± 32.74	3261.41 ± 73.92	596.07 ± 53.65
23	2002-05-10 22:35	BULK	149.07	-19.96 ± 13.99	-14.55 ± 17.07	3.02 ± 6.39	17.80 ± 11.20	329.55 ± 27.38	44.08 ± 19.09	7.39 ± 24.30
24	2002-05-10 22:38	BULK	176.40	-13.49 ± 13.09	58.96 ± 15.06	2.39 ± 5.29	-6.26 ± 10.09	456.02 ± 27.79	165.29 ± 20.11	39.28 ± 22.85
25	2002-05-10 22:42	BULK	207.60	49.90 ± 16.70	4843.25 ± 79.23	220.76 ± 14.32	619.13 ± 53.30	21.99 ± 28.77	3100.59 ± 64.82	665.46 ± 49.41
26	2002-05-10 22:46	BULK	205.29	-3.67 ± 10.68	47.32 ± 12.85	-1.53 ± 5.07	-3.79 ± 9.88	1360.30 ± 35.38	126.94 ± 16.66	54.67 ± 19.16
27	2002-05-10 22:51	BULK	174.93	17.08 ± 11.05	152.51 ± 15.27	-0.07 ± 5.17	16.58 ± 11.45	1363.06 ± 35.54	396.96 ± 20.92	214.31 ± 21.77
28	2002-05-10 22:59	BULK	150.56	8.27 ± 14.35	35.05 ± 15.40	5.28 ± 5.83	17.28 ± 10.86	435.06 ± 29.49	177.72 ± 22.14	67.17 ± 25.70
29	2002-05-10 23:03	BULK	146.79	-6.33 ± 10.28	18.22 ± 9.57	-1.40 ± 3.49	6.64 ± 6.32	111.00 ± 14.19	92.95 ± 13.21	26.87 ± 15.48
30	2002-05-10 23:07	BULK	238.77	-2.95 ± 8.28	20.01 ± 7.77	4.04 ± 2.96	6.27 ± 5.06	78.61 ± 10.68	108.91 ± 10.98	35.00 ± 12.83
31	2002-05-10 23:11	BULK	166.48	23.72 ± 13.84	17.44 ± 13.84	-6.00 ± 5.00	22.57 ± 9.95	393.59 ± 27.25	150.83 ± 20.36	8.46 ± 23.20
32	2002-05-10 23:14	BULK	170.33	41.22 ± 17.35	4985.95 ± 85.19	198.44 ± 14.67	458.06 ± 56.44	50.06 ± 30.71	2795.34 ± 65.52	585.24 ± 50.11
33	2002-05-10 23:18	BULK	171.06	-0.03 ± 13.53	14.91 ± 13.72	1.77 ± 5.26	10.70 ± 9.54	380.87 ± 26.62	129.31 ± 19.68	58.67 ± 23.76
34	2002-05-10 23:21	BULK	160.47	-9.44 ± 12.56	40.86 ± 12.24	-4.26 ± 4.06	12.26 ± 8.11	113.58 ± 16.66	213.68 ± 18.85	88.17 ± 21.50
35	2002-05-10 23:24	BULK	169.62	-5.24 ± 11.84	15.36 ± 13.34	5.06 ± 5.77	1.46 ± 10.48	1315.09 ± 38.58	110.95 ± 18.14	65.19 ± 21.67
36	2002-05-10 23:28	BULK	222.79	-0.79 ± 8.56	22.14 ± 8.00	-1.83 ± 2.85	8.39 ± 5.27	94.36 ± 11.30	123.49 ± 11.45	37.12 ± 13.10
37	2002-05-10 23:33	BULK	236.50	31.94 ± 9.60	129.21 ± 12.66	1.00 ± 4.39	19.18 ± 9.51	1254.63 ± 29.55	424.63 ± 18.21	145.21 ± 17.83
38	2002-05-10 23:37	BULK	209.13	-2.13 ± 10.68	76.85 ± 12.06	5.06 ± 3.91	6.86 ± 7.71	35.51 ± 13.10	604.27 ± 22.85	67.05 ± 19.77
39	2002-05-10 23:40	BULK	136.86	-3.42 ± 15.27	38.07 ± 16.54	3.64 ± 6.06	0.83 ± 11.13	375.44 ± 30.06	148.33 ± 22.74	10.64 ± 25.92
40	2002-05-10 23:42	BULK	136.83	6.48 ± 14.88	2.98 ± 18.30	5.82 ± 6.73	11.64 ± 11.80	293.13 ± 27.63	42.23 ± 19.96	44.75 ± 26.13
41	2002-05-10 23:46	BULK	190.82	89.43 ± 16.06	4762.06 ± 76.05	195.63 ± 13.21	423.20 ± 50.27	35.91 ± 27.15	2955.67 ± 60.82	676.56 ± 46.04
42	2002-05-10 23:54	BULK	147.57	49.50 ± 12.26	160.66 ± 16.78	-4.17 ± 5.53	12.22 ± 12.54	1395.51 ± 39.13	437.76 ± 23.41	184.01 ± 23.45
43	2002-05-10 23:58	BULK	168.08	41.04 ± 16.87	5068.77 ± 84.24	180.56 ± 13.96	349.82 ± 55.22	24.24 ± 29.16	3016.04 ± 66.17	681.75 ± 50.44

Figure 6-7. Multi-element data report.

## 6.2.2 Health and Safety Concerns

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

No significant health and safety concerns were noted during the demonstration. The XLi 702 contains radioisotope sources, and should never be pointed at any person when the shutter is open. With the safety shutter(s) open while testing samples, the exposure to the user's hand is <.05 mR/hr. During setup and operation, both analyzers are password protected.

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

Potential exposure to radiation from the excitation sources (Cd-109, Am-241, Fe-55 and the X-ray tube) was the primary health and safety concern during the demonstration. The XLi 702 used during the demonstration contained a three radioactive source configuration of a 10 millicurie (mCi) Cd-109 source, a 14 mCi Am-241 source and a 20 mCi Fe-55 source. The Cd-109 source was the only source used during the demonstration. The XLi 702 instrument is distributed under a specific Massachusetts license and a general license, and it is expected that under normal use an operator would not accumulate a radiation

dose higher than that from naturally occurring radiation. A health physicist from the Tennessee Department of Environment and Conservation used a gamma-ray detector to monitor radiation for half an hour during one day of the demonstration. Background radiation at the site was 5 microrems per hour ( $\mu\text{rem/hr}$ ). During sample analysis 20  $\mu\text{rem/hr}$  was obtained on contact with the sample tray, and 50  $\mu\text{rem/hr}$  was obtained on contact with the window port. The sources are sealed and locked in place in a tungsten alloy source holder. According to NITON, the sources are designed to remain secure even under extreme conditions, so that even if the instrument is broken, crushed or burned there should be no leakage of radioactive material.

The cadmium source used was originally 10 mCi, and has a half life of about 15 months. The cadmium source would have to be replaced every 15 months and disposed of in accordance with Nuclear Regulatory Commission (NRC) regulations. The replacement of the source and its disposal would have to be done by the manufacturer or their authorized representative.

During the demonstration, the operators wore nitrile gloves and safety glasses while transferring about 15 grams of mercury-contaminated soil per sample from the VOA vials into the sample cups. SAIC continuously monitored ambient air for mercury, using a mercury vapor analyzer. Mercury was not detected ( $0.000 \text{ mg/m}^3$ ) in the air or breathing zones during the course of the demonstration.

### **6.2.3 Portability of the Device**

*Documents the portability of the device.*

**The NITON 700 Series Analyzers are single piece units weighing only 0.8 kg (XLi 702) and 1.4 kg (XLt 792). There are no cables, no separate processing units. They were easy to set up and can be carried in a waist belt holder. High strength injection molding plastic housing enables them to withstand harsh environments. Quick-swap batteries allow up to 6-12 hours of continued use. Samples can be analyzed in less than five minutes.**

The NITON 700 Series Analyzers are single units that are hand-held. Polyethylene sample cups, Mylar film, filter discs, polyester filling and a small metal spatula are required during sample preparation activities. These items can be purchased separately from NITON, or directly from

the manufacturer. One hundred small (approximately 40 mm) sample cups, one roll of Mylar film, filter discs, polyester filling and a small sample tool can fit easily into a small box. The analyzers, test stands and accessories are housed in a padded carrying case. The XLi 702 weighs 0.8 kilograms (kg) and is 292 mm by 89 mm by 76 mm. The XLt 792 weighs 1.8 kg and is 248 mm by 273 mm by 95 mm. The test stand for both units is 278 mm by 63 mm by 139 mm. During the demonstration, a fully charged battery pack lasted for almost 8 hours. The instruments can also operate off a 115 volt electric line.

According to NITON the analyzers will operate between  $-7$  and  $49$   $^{\circ}\text{C}$ . In addition, the analyzers can operate at a humidity range of 0-95% relative humidity. During the demonstration, relative humidity as high as 98.3% was recorded.

During the demonstration, NITON performed sample preparation and analysis under a tent. The instruments were setup in two minutes on a six-foot long folding table. The small, lightweight battery-operated analyzers could be easily carried by hand to another sample location and operated for about 4-8 hours on one battery pack.

No solvents or acids were used for sample preparation. The only additional waste generated were the sample cups, Mylar film, filter discs and polyester filling which were used during analysis of intrusive samples. Finally, even though the XLi contains radioisotopes, in most cases no notification is required if transporting within state boundaries. This may not be the case when entering federal properties. The NITON XLi 702 conforms to the conditions and limitations specified in 49 CFR 173.421 for excepted radioactive material. (Excepted package instruments and articles, N.O.S. UN-2911.) In most countries, the analyzers can be transported in a fully padded carrying case by plane or car, or shipped as an ordinary package. For most courier services, no special labels are required on the outside of the NITON carrying case or on additional packaging. In the U.S., the XLt 792 can be carried, shipped or transported in the carrying case without exterior labeling.

### **6.2.4 Instrument Durability**

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

**NITON introduced the first ever hand-held XRF analyzer in 1994. They are well designed and constructed for durability.**

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The NITON analyzers were designed so that virtually no measurable radiation can escape when the shutter is closed. According to NITON, even if the instrument is broken, crushed or burned there should be no leakage of radioactive material.

Each sealed isotope source is locked in place in a solid tungsten alloy source holder. The source is secure in its housing because the aperture at the end of housing is smaller than the source and completely sealed. The source assembly is secured in the instruments case, which is fitted with tamper-proof screws. Finally, the high strength plastic housing should withstand harsh environments. Based on observations during the demonstration, the analyzers were well constructed and durable. During the three days in which the instruments were observed, there was no downtime, maintenance, or repairs. The equipment was not apparently affected by the three days of almost continuous rain, and relative humidity as high as 98.3%. The instruments were, however, operated under a tent.

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

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

**The NITON 700 Series Analyzers are readily available for rental, lease, or purchase. Another analyzer if needed, can be received within 2-6 weeks of order placement. Sample cups, Mylar film, spatulas, filter-discs and polyester filling are readily available from NITON or several supply firms.**

During the demonstration, NITON 700 Series Analyzers and disposable supplies did not have to be replaced. If a replacement analyzer or test stand were required, NITON claimed it could have been shipped by express courier and held for pick-up the next day. There are currently 10 XLi 702 units available for rental. At the time of the demonstration, the NITON XLt Analyzer was a prototype and replacement parts may have been difficult to obtain. NITON now has 3 XLt 792 units available for rental. The instruments must be held for pick-up at the local express courier office, and can not be delivered to any location because the instruments contain radioisotopes or an X-ray tube. The express courier office was located twenty minutes away from the site. In general, no time would be lost picking up another unit at a local express courier office rather than having it delivered the next day to the site by 10:30 a.m. Many express courier offices are open as early as 8 a.m.

In general, the 700 Series Analyzers are available within 2-6 weeks of order placement. The disposable supplies (sample cups, Mylar film, spatulas, filter discs) if needed for intrusive analysis could be obtained from the manufacturers, and shipped directly to the site by overnight courier. NITON claims the 700 Series Analyzers never need site-specific calibrations.

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## 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 analyzed increased, the total capital cost was also estimated and reported separately. Because unit analytical costs are dependent upon the total number of analyses, no attempt was made to compare the cost of field analyses with the NITON 700 Series Analyzers XLi 702 (isotope) and XLt 792 (X-ray tube) to the costs associated with the referee laboratory. "Typical" unit cost results, gathered from analytical laboratories, were reported to provide a context in which to review NITON XLi/XLt 700 Series Analyzer 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 NITON XLi/XLt 700 Series Analyzers, 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. NITON offers three options for potential users: 1) purchase of the analyzers, 2) monthly rental and 3) analyzer leasing depending on current interest rates (NITON, 2003a). Because site and user requirements vary

significantly, all three of these options are discussed to provide each user with the information to make a case-by-case decision.

A more detailed cost analysis was performed on the equipment rental option for three months or less because this case represents the most frequently encountered field scenario. The results of that cost analysis are provided in Section 7.2.

##### 7.1.1 Capital Equipment Cost

The XLi 702 analyzer evaluated during the demonstration was equipped with Cd-109, Am-241 and Fe-55 sources. During the demonstration, only the Cd-109 source was used. The capital equipment costs are based on the analyzer with one source, Cd-109. The XLt 792 uses a low-powered, miniature X-ray tube with a silver target as the excitation source. Both analyzers come equipped with a test stand, soil grinder, sieve set and sample cups. A keyboard and laptop computer are optional, and may be supplied by the customer if the user wants to operate the instrument in the bench-top mode.

The cost quoted by NITON includes freight costs to ship the instrument to the user location when purchasing the instrument, but does not include the license (radioactive source) that may be needed to operate the instrument. The license that is needed to operate the XLi 702 analyzer in the state of Tennessee cost \$900. A \$5,000 dollar fully refundable security deposit is required for all XLi/XLt 700 Series rentals and leases. An eight-hour training session is mandatory for anyone renting, leasing or purchasing an analyzer (NITON, 2003a). NITON offers over 100 user/radiation training classes free-of-charge throughout the year.

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### **7.1.2 Cost of Supplies**

The cost of supplies is minimal, based on the supplies required to analyze demonstration samples. Requirements vary depending upon whether in-situ or intrusive analysis is being performed. For purposes of this cost estimate, only supplies required to analyze soil samples intrusively are factored into the cost estimate. Disposable supplies are not required for in-situ analysis. The supplies used during the demonstration consisted of four consumable items which were:

- XRF sample cups (one per sample)
- Mylar film
- Polyester filling
- Filter-paper discs

The purchase prices and supply sources were obtained from NITON. The analyzers are supplied with supplies for 100 samples. Because the user cannot return unused or remaining portions of supplies, no salvage value was included in the cost of supplies. (NITON, 2003a) PPE supplies were assumed to be part of the overall site investigation or remediation costs; therefore, no PPE costs were included as supplies.

### **7.1.3 Support Equipment Cost**

During the demonstration, the XL-Series 700 Analyzers were operated using both AC power and a lithium ion battery pack. The XLi instrument operated for almost 5 hours using one battery pack. (The XLi instrument observed during the demonstration started at 95% battery life). The XLt unit operated for 8 hours using one battery pack. Only the battery charger requires AC.

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 setup, sample preparation, sample analysis, summary data presentation and instrument packaging at the end of the day. Setup time covered the time required to take the analyzers out of their packaging, setup all components, and ready the devices for operation. Sample preparation

involved transferring samples into the XRF sample cups. Sample preparation was completed easily, requiring about one minute per sample. 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 vendor transcribed results from computer screens to the field chain-of-custody forms. (A printer was not available in the field.) The time required to perform all tasks was rounded to the nearest minute; 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 the two field technicians to analyze and report results for mercury samples. Based on these field observations, a high school graduate with the eight-hour training specific to the 700-Series Analyzers would be qualified to operate the analyzers. For the economic analysis, an hourly rate of \$15 was used for a 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**

NITON was instructed to segregate its waste into three categories during the demonstration: 1) general trash; 2) lightly contaminated PPE and wipes; and 3) contaminated soil (both analyzed and unanalyzed). General trash was not included as IDW, and is not discussed in this document.

Lightly contaminated wastes consisted primarily of used nitrile gloves and Kim-wipes. The gloves were discarded because they posed a potential health and safety risk (holes or tears). The rate of waste generation was in excess of what would be expected in a typical application of these instruments. In addition, the EPA evaluators

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occasionally contributed used gloves to this waste accumulation point. Wipes were used primarily to clean any spilled soil off the table and to clean off any moist or organic material adhering to the spatula which was used to transfer soil into the sample cups. In cases where cross contamination is not a major concern (e.g., field screening or in-situ analysis), lesser amounts of waste would likely be generated.

Contaminated soil consisted primarily of soil placed in the XRF sample cups containing a filter paper disc, polyester filling and then covered with Mylar film. The sample is not destroyed during preparation and analysis; therefore it is possible to send the samples off-site for confirmatory analysis, but for purposes of this economic analysis, it was assumed that they were discarded.

### **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. A free, eight-hour training course is mandatory in order to operate the analyzers. The users' time and travel expenses to attend the course are not included. Any licensing fees required for the radionuclide source were also not included as they vary from state to state.

**Oversight of Sample Analysis Activities.** A typical user of the 700-Series Analyzers 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 reference 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, 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 also 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, were 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 XLi/XLt 700 Series Analyzers Costs**

This subsection presents information on the individual costs of capital equipment, supplies, support equipment, labor, and IDW disposal for the 700 Series Analyzers.

### **7.2.1 Capital Equipment Cost**

During the demonstration, each 700 Series Analyzer operated for three days, and was used to analyze 197 samples. Figures 7-1 and 7-2 show the relative costs for the basic capital equipment. These costs reflect the XLi equipped with Cd-109, while the XLt used a miniature X-ray tube as the excitation source. Table 7-1 summarizes the

700 Series Analyzers capital costs for the three procurement options: rental, lease, and purchase. As would be expected, Table 7-1 clearly shows that leasing is the most cost-effective option (in terms of capital costs), followed by rental, for short-term projects. As project duration (or use on multiple projects) approaches two years, the purchase option becomes the most cost-effective. These scenarios cover only capital cost, not the cost of optional or user-supplied equipment, supplies, support equipment, labor, and IDW disposal.

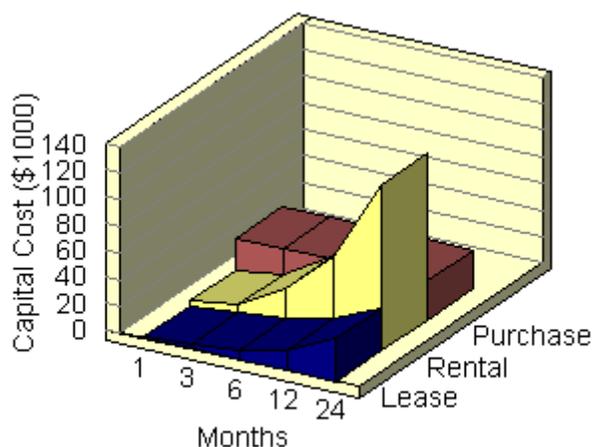


Figure 7-1. Capital costs for the XLi (isotope).

The XLi (with Cd-109) sells for \$29,095. The cadmium source (10 mCi) used during the demonstration needs to be replaced about every 15 months. The cost of replacing the source is \$2,700 and includes source disposal and software upgrade.

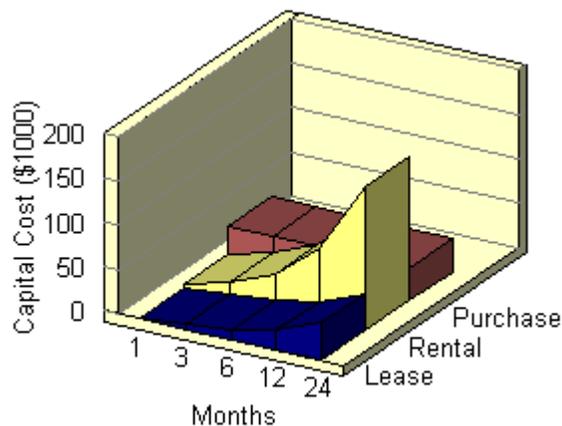


Figure 7-2. Capital costs for the XLt (X-ray tube).

The XLt (with miniature X-ray tube) sells for \$38,095. As miniature X-ray tubes are quite new, not enough data has been collected to estimate tube lifetime. The cost of replacing the X-ray tube is \$5000 and includes a new power supply and software upgrade.

Table 7-1. Capital Cost Summary for the XLi/XLt 700 Series Analyzers

Item	Quantity	Unit Cost (\$)	Total Cost for Selected Project Duration				
			1-Month	3-Month	6-Month	12-Month	24-Month
Purchase XLi 702 (Isotope)	1	\$29,095	\$29,095	\$29,095	\$29,095	\$29,095	\$29,095
Monthly Rental of XLi 702	1	\$5,190	\$5,190	\$15,570	\$31,140	\$62,280	\$124,560
Monthly Lease of XLi 702 <sup>a</sup>	1	\$1,333	\$1,333	\$3,999	\$7,998	\$15,996	\$31,992
Purchase XLt 792 (X-ray tube)	1	\$38,095	\$38,095	\$38,095	\$38,095	\$38,095	\$38,095
Monthly Rental of XLt 792	1	\$6,800	\$6,800	\$20,400	\$40,800	\$81,600	\$163,200
Monthly Lease of XLt 792 <sup>b</sup>	1	\$1,745	\$1,745	\$5,235	\$10,470	\$20,940	\$41,880

a \$1,333 per month (24-month lease with \$1 buyout).

b \$1,745 per month (24-month lease with \$1 buyout).

## 7.2.2 Cost of Supplies

Supplies used during the demonstration included XRF sample cups, Mylar film, 2.4 cm filters and polyester filling. NIST soil SRMs were also used during the demonstration and are included with an instrument purchase.

## 7.2.3 Support Equipment Cost

NITON 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

Two technicians were utilized for three days (17.5 hours, or 35 man hours total) during the demonstration to complete sample preparation and analysis for both instruments. Based on a labor rate of \$600 per day, total labor cost for application of both 700 Series Analyzers was \$1,800 for the three-day period. Labor costs assume qualified technicians are available locally, and that no per diem costs or travel costs are applicable. Table 7-2 summarizes labor costs for various operational periods, assuming 21 work days per month (on average), 252 work days per year and one technician per job site. The costs presented do not include supervision and quality assurance because these would be associated with use of any analytical instrument and are a portion of the overhead multiplier built into the labor rates.

## 7.2.5 Investigation-Derived Waste Disposal Cost

NITON generated PPE waste and soil waste, including sample cups, Mylar film, filter discs and polyester filling. The PPE waste was charged to the overall project due to

site constraints. The minimum waste volume is a 5-gallon container. Mobilization and container drop off fees were \$1,040; disposal of a 5-gallon waste soil drum cost \$400. (These costs were based on a listed waste stream with hazardous waste number U151.) The total IDW disposal cost was \$1,440. These costs may vary significantly from site-to-site, depending on whether the waste is classified as hazardous or nonhazardous and whether sample material is generated that requires disposal. Table 7-3 presents IDW costs for various operational periods, assuming that waste generation rates were similar to those encountered during the demonstration.

**Table 7-2. 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

**Table 7-3. IDW Costs**

Item	Months				
	1	3	6	12	24
Drop Fee	\$1,040	\$3,120	\$6,240	\$12,480	\$24,960
Disposal	\$400	\$1,200	\$2,400	\$4,800	\$9,600
Total	\$1,440	\$4,320	\$8,640	\$17,280	\$34,560

## 7.2.6 Summary of XLi/XLt 700 Series Costs

The total cost for performing mercury analysis is summarized in Tables 7-4 and 7-5. These tables reflect costs for projects ranging from 1-24 months. The rental option was used for estimating the equipment cost.

Capital cost for equipment rental exceed those for purchase at approximately six months, so rental is not as cost-effective for projects exceeding this duration. Finally, a lease agreement may be a cost-effective alternative to either rental or purchase for projects lasting less than 21 months. At that point, equipment purchase may be more cost-effective; however, the decision on which purchase option to utilize should be made on a case-by-case basis.

**Table 7-4. Summary of Rental Costs for the XLi 702 (Isotope)**

Item	Quantity	Unit	Unit Cost (\$)	Total Cost for Selected Project Duration				
				1-Month	3-Month	6-Month	12-Month	24-Month
Capital Equipment								
Monthly Rental	1	NA	\$5,190	\$5,190	\$15,570	\$31,140	\$62,280	\$124,560
Support Equipment								
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 weather only) - weekly	1	each	\$270	\$800	\$800	\$800	\$800	\$800
Total Support Equipment Cost	--	-----	-----	\$830	\$885	\$960	\$1,000	\$1,000
Labor								
Field Technician (person day)	1	hour	\$38	\$6,300	\$18,900	\$37,800	\$75,600	\$151,200
IDW								
Container and Drop Fee			\$1,040	\$1,040	\$3,120	\$6,240	\$12,480	\$24,960
Disposal	NA	week	\$400	\$400	\$1,200	\$2,400	\$4,800	\$9,600
Total IDW Costs	--	-----	-----	\$1,440	\$4,320	\$8,640	\$17,280	\$34,560
Total Cost				\$13,760	\$39,675	\$78,540	\$156,160	\$311,320

**Table 7-5. Summary of Rental Costs for the XLt 792 (X-ray Tube)**

Item	Quantity	Unit	Unit Cost (\$)	Total Cost for Selected Project Duration				
				1-Month	3-Month	6-Month	12-Month	24-Month
Capital Equipment								
Monthly Rental	1	NA	\$6,800	\$6,800	\$20,400	\$40,800	\$81,600	\$163,200
Support Equipment								
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 weather only) - weekly	1	each	\$270	\$800	\$800	\$800	\$800	\$800
Total Support Equipment Cost	--	-----	-----	\$830	\$885	\$960	\$1,000	\$1,000
Labor								
Field Technician (person day)	1	hour	\$38	\$6,300	\$18,900	\$37,800	\$75,600	\$151,200
IDW								
Container and Drop Fee			\$1,040	\$1,040	\$3,120	\$6,240	\$12,480	\$24,960
Disposal	NA	week	\$400	\$400	\$1,200	\$2,400	\$4,800	\$9,600
Total IDW Costs	--	-----	-----	\$1,440	\$4,320	\$8,640	\$17,280	\$34,560
Total Cost				\$15,370	\$44,505	\$88,200	\$175,480	\$349,960

Tables 7-6 and 7-7 summarize costs for the actual demonstration. Note that the one-month rental costs of the XLi/XLt 700 Series units was used for capital costs. 35 hours were required by both technicians to prepare and analyze the samples for both instruments over a three-day period. The labor rate presented in this Chapter assumes one person performs sample preparation and analysis on 197 samples for one instrument over a two-day period.

**Table 7-6. XLi 702 (Isotope) Costs by Category**

Category	Category Cost (\$)	Percentage of Total costs
Instrument	\$5,190	66.7%
Supplies	\$280	3.6%
Support Equipment	\$276	3.5%
Labor	\$600	7.7%
IDW Disposal	\$1,440	18.5%
Total	\$7,786	100.0%

Note: The percentages in Table 7-6 are rounded to one decimal place; the total percentage is 100%.

The cost per analysis when renting the XLi 702, based upon 197 samples, is \$39.52 per sample. The cost per analysis for the 197 samples, excluding instrument rental cost is \$13.18 per sample.

The cost per analysis when renting the XLt 792, based upon 197 samples, is \$47.69 per sample. The cost per analysis for the 197 samples, instrument rental cost is \$13.18 per sample.

**Table 7-7. XLt 792 (X-Ray Tube) Costs by Category**

Category	Category Cost (\$)	Percentage of Total costs
Instrument	\$6,800	72.4%
Supplies	\$280	3.0%
Support Equipment	\$276	2.9%
Labor	\$600	6.4%
IDW Disposal	\$1,440	15.3%
Total	\$9,396	100.0%

Note: The percentages in Table 7-7 are rounded to one decimal place; the total percentage is 100%.

### 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 analyses 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, preparation of a data package. The total cost for 197 samples at \$35 would be \$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 a 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.

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## Chapter 8

### Summary of Demonstration Results

As discussed previously in this ITVR, the NITON XLi/XLt 700 Series Analyzers were evaluated by having the vendor analyze 197 soil and sediment samples. These 197 samples consisted of 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 the different matrices, concentrations, and types of mercury needed to perform a comprehensive evaluation of the XLi/XLt 700 Series Analyzers.

#### 8.1 Primary Objectives

The primary objectives of the demonstration were centered on evaluation of the field instruments 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 NITON XLi/XLt 700 Series Analyzers. Quantitative results were reviewed. NITON results were determined to be more precise than laboratory analyses and were comparable in accuracy to SRMs. Differences between laboratory data and NITON field data were likely the result of matrix interferences.

The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Following procedures established in 40 CFR Part 136, the MDL for the NITON XLT (X-ray) instrument is between 13.9 and 69.8 mg/kg. It is likely that the MDL is closer to the lower end of this range based upon the results for sample lot 62 (referee laboratory value = 14.6 mg/kg) and sample lot 47 (SRM value = 32.4 mg/kg) which both had one of the seven results

reported as below the NITON detection level indicating that these values are on the edge of the instruments detection capability. The lowest calculated MDL for the NITON XLi instrument is 39.3 mg/kg. Based upon results presented in the report for samples analyzed close to this detection limit, it appears that the MDL for the NITON XLi field instrument is somewhere close to 32 mg/kg. The equivalent calculated MDL for the referee laboratory is 0.0026 mg/kg. The calculated MDL is only intended as a statical estimation and not a true test of instrument sensitivity.

The NITON XLT PQL is somewhere between 62.9 mg/kg and 99.8 mg/kg. The %D for the 99.8 mg/kg SRM is 8.2%. The NITON XLi PQL is also somewhere between 62.9 mg/kg and 99.8 mg/kg. The %D for the average NITON XLT result for the 99.8 mg/kg SRM is 9.2%. The referee laboratory PQL confirmed during the demonstration and based upon a lower calibration standard is 0.005mg/kg. The %D is <10%.

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. The results from the XLi/XLt 700 Series Analyzers were compared to the 95% prediction interval for the SRM materials and to the referee laboratory results (Method 7471B). NITON XLT data were within SRM 95% prediction intervals 93% of the time, which suggests significant equivalence to certified standards. NITON XLi data were within SRM 95% prediction intervals 91% of the time, which also suggest significant equivalence to certified standards.

The statistical comparison between the NITON XLT field data and the referee laboratory results suggest that the two data sets are not the same. The statistical comparison

between the NITON XLi field data and the referee laboratory results also suggest that these two data sets are not the same. Because the NITON data compare favorably to the SRM values, the differences between NITON and the referee laboratory are likely the result of matrix interferences for field sample analysis. The number of NITON XLt average values less than 30% different from the referee laboratory results or SRM reference values; however, was 14 of 26 different sample lots. Only one of 26 NITON XLt average results have relative percent differences greater than 100% for this same group of samples. The number of NITON XLi average values less than 30% different from the referee laboratory results or SRM reference values was 14 of 24 different sample lots. Zero of 24 NITON XLi average results have relative percent differences greater than 100% for this same group of samples. Both NITON XLt and XLi results therefore, can often provide a reasonable estimate of accuracy for field determination.

Precision was determined by analysis of replicate samples. The precision of the NITON XLt and XLi field instruments is better than the referee laboratory precision. The overall average RSD is 20.0% for the referee laboratory, compared to the NITON XLt average RSD of 13.1% and the NITON XLi average RSD of 14.4%. Both the laboratory and NITON precision goals are within the predicted 25% RSD objective for precision; expected from both analytical and sampling variance. Precision was not affected by sample concentration or matrix.

Time measurements were based on the length of time the operator spent performing all phases of the analyses, including setup, calibration, and sample analysis (including all reanalysis). NITON analyzed 197 samples on a single instrument in 1,050 minutes (17.5 hours, times 60 minutes, times 1 analyst per instrument) over three days, which averaged to 5.3 minutes per sample result. Based on this, an operator could be expected to analyze 90 samples (8 hours x 60 minutes ÷ 5.3 minutes/sample) in an 8-hour day.

Cost of the NITON sample analysis 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 the instrument purchase, and as the sample number increases, the cost per sample would decrease. A comparison of the field NITON 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 to the project while waiting for analyses 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 NITON and the Referee Laboratory**

Site	Concentration Range	Soil	Sample Type		SRM
			Sediment	Spiked Soil	
Carson River	Low (1-500 ppb)	0	0	0	0
(Subtotal = 31)	Mid (0.5-50 ppm)	7	0	0	0
	High (50->1,000 ppm)	3	0	7	14
Puget Sound	Low (1 ppb - 10 ppm)	3	0	0	0
(Subtotal = 34)	High (10-500 ppm)	0	10	7	14
Oak Ridge	Low (0.1-10 ppm)	0	3	0	0
(Subtotal = 54)	High (10-800 ppm)	13	10	14	14
Manufacturing	General (5-1,000 ppm)	36	0	14	28
(Subtotal = 78)					
<b>Subtotal</b>		<b>62</b>	<b>23</b>	<b>42</b>	<b>70</b>

**Table 8-2. Summary of NITON XLi/XLt 700 Series Analyzers Results for the Primary Objectives**

Demonstration Objective	Evaluation Basis	Performance Results NITON XLi/XLt 700 Series Analyzers	Reference Method
Instrument Sensitivity	MDL. Method from 40 CFR Part 136.	Between 13.9 and 69.8 mg/kg for the NITON XLt.  Approximately 32 mg/kg for the NITON XLi.	0.0026 mg/kg
	PQL. Low concentration SRMs or samples.	NITON XLt and NITON XLi PQL; between 62.9 mg/kg and 99.8 mg/kg.	0.005 mg/kg
Accuracy	Comparison to SRMs, field, and spiked samples covering the entire range of the instrument calibration.	NITON XLt data were within SRM 95% prediction intervals 93% of the time; NITON XLi data were within SRM 95% prediction intervals 91% of the time. NITON and laboratory data did not statistically compare for all results but NITON results can often provide a reasonable estimate of accuracy for field determination.	
Precision	Determined by analysis of replicate samples at several concentrations.	Overall average RSD is 20.0% for the referee laboratory compared to the NITON XLt average RSD of 13.1% and the NITON XLi average RSD of 14.4%.	
Time per Analysis	Timed daily operations for 3 days and divided the total time by the total number of analyses.	Two technicians performed all setup, calibration checks, sample preparation and analysis, and equipment demobilization. Using one technician individual analyses (excluding sample preparation) took 2 minutes each, but the total time per analysis averaged approximately 5.3 minutes per sample per instrument.	
Cost	Costs were provided by NITON 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.	<p>The cost per analysis based upon 197 samples, when renting the NITON XLi 702, is \$39.52 per sample. The cost per analysis for the 197 samples, excluding capital cost, is \$13.18 per sample. The total cost for equipment rental and necessary supplies during the demonstration is estimated at \$7,786. The cost breakout by category is: capital equipment rental costs, 66.7%; supplies, 3.6%; support equipment, 3.5%; labor, 7.7%; and IDW, 18.5%.</p> <p>The cost per analysis, based upon 197 samples, when renting the NITON XLt 792, is \$47.69 per sample. The cost per analysis for the 197 samples, excluding capital cost, is \$13.18 per sample. The total cost for equipment rental and necessary supplies during the demonstration is estimated at \$9396. The cost breakout by category is: capital equipment rental costs, 72.4%; supplies, 3.0%; support equipment, 2.9%; labor, 6.4%; and IDW, 15.3%.</p>	

**Table 8-3. Summary of NITON XLi/XLt 700 Series Analyzers Results for the Secondary Objectives**

Demonstration Objective	Evaluation Basis	Performance Results
Ease of Use	Field observations during the demonstration.	The NITON XLi/XLt 700 Series Analyzers are very easy to operate, requiring one field technician with a high school education, and 8-hour training on the NITON XLi/XLt 700 Series Analyzers. The analyzers are field screening tools capable of measuring 25 elements in seconds. No data manipulation is required.
Health and Safety Concerns	Observation of equipment, operating procedures, and equipment certifications during the demonstration.	No significant health and safety concerns were noted during the demonstration. The analyzers should never be pointed at any person when the shutters are open.
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 NITON XLi/XLt 700 Series Analyzers are hand-held portable instruments. They are stand-alone units with no cables, and are easy to set up. A sample can be analyzed in less than five minutes.
Instrument Durability	Observation of equipment design and construction, and evaluation of any necessary repairs or instrument downtime during the demonstration.	The NITON XLi/XLt 700 Series Analyzers were well designed and constructed for durability. NITON's XRF analyzers are the product of a decade of continuous research and development in XRF technology.  In addition, the Cd-109 (10 mCi) source should be replaced every 15 months, and only by authorized personnel.
Availability of Vendor Instruments and Supplies	Review of vendor website and telephone calls to the vendor after the demonstration.	The NITON XLi/XLt 700 Series Analyzers are readily available for lease or purchase. A rented analyzer can be received typically within 10-14 days of order placement. Sample cups, Mylar film, filter discs, spatula, and polyester filling are the only supplies needed to analyze samples intrusively and are available from several supply firms or from NITON.

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## Appendix A NITON Comments

NITON LLC was pleased to participate in this EPA SITE program with our new generation of field portable x-ray fluorescence (FPXRF) analyzers. The instruments used in this study were the NITON LLC Model XLi 702 radioisotope excitation spectrometer and the Model XLt 792 with miniature x-ray tube excitation.

Field portable x-ray fluorescence spectrometry has seen application to the determination of metals in soil and sediment for some two decades now (Piorek, 1997). It has become a standard tool in site characterization and remediation (U.S. EPA, 1996). The technology is well known and has been extensively described in the literature (Spittler, et.al., 1985; Piorek, et.al., 1993; Hewitt, 1994; Shefsky, 1997).

### Results

Figure A-1 shows a comparison of laboratory and FPXRF results from the model XLt 792 with miniature X-ray tube. The error bars denote 2-sigma variation of the (generally) seven replicate analyses. We note the consistently worse precision for the laboratory determinations at the higher concentration levels, greater than about 200 ppm. We note that the referee laboratory testing was in accordance with Method 7471A (Cold Vapor Analysis for Mercury Determination) of SW-846, a technique generally applicable to a maximum concentration of about 1 ppm. We suspect the poor precision at the higher levels to be due to the substantial dilutions necessary to apply this

method at these concentrations.

Given these results, samples 32 and 33 should probably be considered outliers. They are labeled and appear in the lower right hand corner of Figure A-1.

We note a slight high bias with respect to laboratory results for both instruments although in most cases the error bars overlap the diagonal indicating a one-to-one correlation. Closer examination of the subset of samples with concentration of about 300 ppm and less (i.e., where the laboratory precision becomes less of an issue) produces the following correlation coefficients: Referee laboratory vs. Tube-excitation,  $R^2 \sim 0.93$ ; Referee laboratory vs. Isotope-excitation,  $R^2 \sim 0.83$ .

Approximate detection limits for a 120 second measurement time are about 25 ppm for model XLi 702 (radioisotope excitation) and 15 ppm for the model XLt 792 (miniature x-ray tube instrument). These LODs are as defined by IUPAC (International Union of Pure and Applied Chemistry) and computed with reference to the precision on a blank sample, i.e., a soil not containing mercury (Thomsen, et.al, 2003, and references therein). They correspond to what is termed IDL in this ITVR. MDLs are generally anywhere from two to five times greater than the IDL, so we can see a correspondence between the LODs reported above and those reported in the ITVR. Of perhaps greater interest are the associated limits of quantitation (LOQ, defined as 3.3 times the LOD), which

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become about 50 ppm for the x-ray tube and 80 ppm for the isotope excitation instrument. Although action levels for mercury in soil vary, some preliminary EPA goals, as noted in this report, are 23 mg/kg (ppm) for residential and 310 mg/kg (ppm) for industrial soil. We can see, therefore, that the FPXRF instrumentation finds primary applicability in the latter field, while still finding use as a screening tool in the former.

### Conclusions

The correlation between laboratory and NITON analyzer results is quite good. Note that the XRF analysis of soil is susceptible to particle size effects, so that sieving to about 250 microns (200 mesh) is recommended. Nevertheless, the close correlation reported here was achieved with minimal sample preparation. Improved results would be expected with additional sample preparation. Precision was also very good, with both analyzers essentially yielding similar or better precision than the referee laboratory.

We note that lead, arsenic, and zinc are potential interferants, but all three are probably not significant at less than about 500 ppm. If lead and arsenic are present at this level, then the site has other serious contamination problems. However, zinc may occur naturally in soil and could well be above this level. For questionable results (e.g., large reported measurement uncertainty) the operator/analyst is counseled to examine the x-ray spectrum itself.

A clear advantage of field portable x-ray fluorescence is its non-destructive nature. This allows the same sample to be sent for confirmatory analysis to eliminate questions or concerns. However, given the similarity in spread between laboratory and FPXRF results, this may be a moot point.

It is also important to point out the multielement nature of this analytical technique as many elements can be analyzed simultaneously. This is certainly an advantage where multiple contaminants may be involved.

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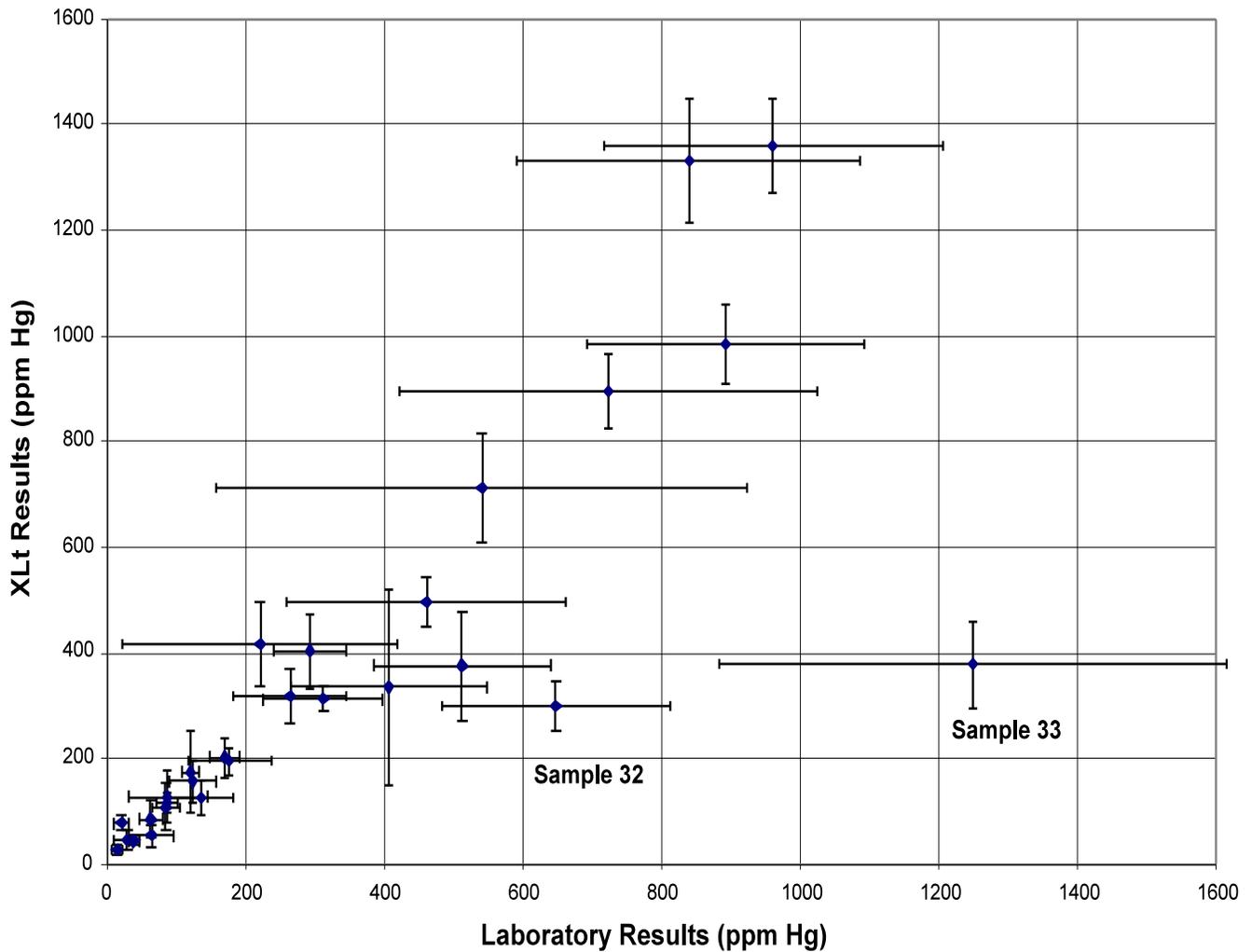


Figure A-1. Comparison of precision, all samples, laboratory and model XLt.

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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 24 separate sample lots for the NITON XLi instrument and all 26 separate sample lots for the NITON XLt instrument) 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 NITON 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  $\mu$ . When the absolute value of the difference is greater than  $\mu$ , then the alternate hypothesis is accepted, and the two sets (laboratory and vendor) are concluded to be different.

To calculate  $\mu$ , 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.

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

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  $\mu$  at the 0.01 level of significance using the following:

$$\mu = t_{1-\{0.005/f\}} \sqrt{V_L + V_V}$$

### Unified Hypothesis Test

For a specified vendor, let  $Y_{ij}$  be the measured Hg concentration for the  $j^{\text{th}}$  replicate of the  $i^{\text{th}}$  sample for  $i=1,2,\dots,I$  and  $j=1,2,\dots,J_i$ . 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  $i^{\text{th}}$  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  $i^{\text{th}}$  sample to be:

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

Now for the reference laboratory, let  $Y'_{ij}$  be the measured Hg concentration for the  $j^{\text{th}}$  replicate of the  $i^{\text{th}}$  sample for  $i=1,2,\dots,I'$  and  $j=1,2,\dots,J'_i$ . 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:

$$H_0: \mu_i = \mu'_i + \delta, \text{ for some } \delta \text{ and } i = 1, \dots, I$$

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

The null hypothesis  $H_0$  is rejected for large values of:

$$\chi^2_{I-1} = \frac{\sum_{i=1}^I (\bar{X}_{i\log} - \bar{X}'_{i\log} - \delta)^2 + (J_i^{-1} + J_i'^{-1})}{s_{\text{pool}}^2}$$

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

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

and

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

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 NITON XLi (Isotope)

SAIC performed a unified hypothesis test analysis to assess the comparability of analytical results provided by NITON XLi and those provided by ALSI. NITON XLi and ALSI both supplied multiple assays on replicates derived from a total of 24 different sample lots, be they field materials or reference materials. The NITON XLi 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 NITON XLi and ALSI population means for a given sample lot. Equality of variances is assumed.

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

$$H_{10}: (\text{NITON XLi lot log mean}) = (\text{ALSI lot log mean})$$

$H_{10}$  was rejected in that the chi-square statistic was 334.59, which exceeds the upper 99<sup>th</sup> percentile of the chi-square distribution with 24 degrees of freedom having a value of 42.97.

The null hypothesis was rejected in part because NITON XLi results tended to exceed those from ALSI for the same

sample lot. To explore this effect, the null hypothesis was revised to include a bias term in the form of

$$H_{20}: (\text{NITON XLi lot log mean}) = (\text{ALSI lot log mean}) + (\text{delta}),$$

where delta is a single value that does not change from one sample lot to another, unlike the lot log means.  $H_{20}$  was rejected strongly in that the chi-square statistic was 312.60, which exceeded the upper 99<sup>th</sup> percentile of the chi-square distribution with 23 degrees of freedom with a value of 41.63. In this analysis, delta was estimated to be 0.0535 in logarithmic (base 10) space, which indicates an average upward bias for NITON XLi of  $10^{0.0535}=1.131$  or about 13%.

For both hypotheses, the large values of the chi-square test statistics summarize the disagreement between the NITON XLi and ALSI analytical results. Furthermore, a

review of the statistical analysis details indicates that the overall discordance between NITON XLi 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 for the NITON XLi Instrument**

Hypothesis	Total Sample Lots	Excluded Lot	DF	$s^2_{\text{pool}}$	Delta	Chi-square	P-value
$H_{10}$	24	None	24	0.00752	0.0000	334.59	0.000000
$H_{20}$	24	None	23	0.00752	0.0535	312.60	0.000000

**Results of Unified Hypothesis Test for NITON XLt (X-ray)**

SAIC performed a unified hypothesis test analysis to assess the comparability of analytical results provided by NITON X-ray and those provided by ALSI. NITON XLt and ALSI both supplied multiple assays on replicates derived from a total of 26 different sample lots, be they field materials or reference materials. The NITON XLt 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 NITON XLt and ALSI population means for given sample lot. Equality of variances is assumed.

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

$$H_{10}: (\text{NITON XLt lot log mean}) = (\text{ALSI lot log mean})$$

$H_{10}$  was rejected in that the chi-square statistic was 266.50, which exceeds the upper 99<sup>th</sup> percentile of the chi-square distribution with 26 degrees of freedom having a value of 45.64.

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

$$H_{20}: (\text{NITON XLt lot log mean}) = (\text{ALSI lot log mean}) + (\text{delta}),$$

where delta is a single value that does not change from one sample lot to another, unlike the lot log means.  $H_{20}$  was rejected strongly in that the chi-square statistic was 249.17, which exceeded the upper 99<sup>th</sup> percentile of the chi-square distribution with 25 degrees of freedom with a value of 44.31. In this analysis, delta was estimated to be 0.0480 in logarithmic (base 10) space, which indicates an average upward bias for NITON XLt of  $10^{0.0480}=1.117$  or about 12%.

For both hypotheses, the large values of the chi-square test statistics summarize the disagreement between the NITON XLt and ALSI analytical results. Furthermore, a review of the statistical analysis details indicates that the overall discordance between NITON XLt 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-2. 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-2 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-2. Unified Hypothesis Test Summary Information for the NITON XLt Instrument**

Hypothesis	Total Sample Lots	Excluded Lot	DF	$s^2_{pool}$	Delta	Chi-square	P-value
$H_{10}$	26	None	26	0.00887	0.0000	266.50	0.000000
$H_{20}$	26	None	25	0.00887	0.0480	249.17	0.000000