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Innovative Technology Verification Report

XRF Technologies for Measuring Trace Elements in Soil and Sediment

Rigaku ZSX Mini II XRF Analyzer

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Prepared by

Tetra Tech EM Inc.
Cincinnati, Ohio 45202-1072

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Dr. Stephen Billets
Characterization and Monitoring Branch
Environmental Sciences Division
Las Vegas, Nevada 89193-3478

National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency

Notice

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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, EPA's Office of Research and Development (ORD) 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.

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 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 an 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 ORD's Environmental Sciences Division in Las Vegas, Nevada.

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

Abstract

The Rigaku ZSX Mini II (ZSX Mini II) XRF Services x-ray fluorescence (XRF) analyzer was demonstrated under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program. The field portion of the demonstration was conducted in January 2005 at the Kennedy Athletic, Recreational and Social Park (KARS) at Kennedy Space Center on Merritt Island, Florida. The demonstration was designed to collect reliable performance and cost data for the ZSX Mini II analyzer and seven other commercially available XRF instruments for measuring trace elements in soil and sediment. The performance and cost data were evaluated to document the relative performance of each XRF instrument.

This innovative technology verification report describes the objectives and the results of that evaluation and serves to verify the performance and cost of the ZSX Mini II analyzer. Separate reports have been prepared for the other XRF instruments that were evaluated as part of the demonstration.

The objectives of the evaluation included determining each XRF instrument's accuracy, precision, sample throughput, and tendency for matrix effects. To fulfill these objectives, the field demonstration incorporated the analysis of 326 prepared samples of soil and sediment that contained 13 target elements. The prepared samples included blends of environmental samples from nine different sample collection sites as well as spiked samples with certified element concentrations. Accuracy was assessed by comparing the XRF instrument's results with data generated by a fixed laboratory (the reference laboratory). The reference laboratory performed element analysis using acid digestion and inductively coupled plasma – atomic emission spectrometry (ICP-AES), in accordance with EPA Method 3050B/6010B, and using cold vapor atomic absorption (CVAA) spectroscopy for mercury only, in accordance with EPA Method 7471A.

The ZSX Mini II is a "wavelength-dispersive" XRF analyzer that can analyze for elements ranging in mass from fluorine to uranium. The ZSX Mini II differentiates the x-ray energies emitted from a sample by dispersing the x-rays into different wavelength ranges using crystals. By contrast, more common "energy-dispersive" XRF analyzers differentiate between x-ray energies based on voltages measured by the detector. For some applications, wavelength-dispersive XRF analyzers can achieve high resolutions and very good sensitivity through the reduction of interelement interferences.

Wavelength-dispersive XRFs have historically been large, laboratory-bound instruments with significant requirements for power and cooling. The ZSX Mini II is a smaller, transportable unit that can operate without additional cooling fluids on standard 110-volt circuits. The unit can employ an economical gas proportional counter as a detector rather than a diode detector with a multi-channel analyzer (common in energy-dispersive instruments) because wavelength resolution is achieved with the crystals.

This report describes the results of the evaluation of the ZSX Mini II analyzer based on the data obtained during the demonstration. The method detection limits, accuracy, and precision of the instrument for each of the 13 target analytes are presented and discussed. The cost of element analysis using the ZSX Mini II analyzer is compiled and compared to both fixed laboratory costs and average XRF instrument costs.

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Acronyms, Abbreviations, and Symbols

µg	Micrograms
µA	Micro-amps
AC	Alternating current
ADC	Analog to digital converter
Ag	Silver
Am	Americium
ARDL	Applied Research and Development Laboratory, Inc.
As	Arsenic
ASARCO	American Smelting and Refining Company
BN	Burlington Northern
C	Celsius
Cd	Cadmium
CFR	Code of Federal Regulations
cps	Counts per second
CPU	Central processing unit
Cr	Chromium
CSV	Comma-separated value
Cu	Copper
CVAA	Cold vapor atomic absorption
EDXRF	Energy dispersive XRF
EDD	Electronic data deliverable
EPA	U.S. Environmental Protection Agency
ERA	Environmental Research Associates
ESA	Environmental site assessment
ESD	Environmental Sciences Division
ETV	Environmental Technology Verification (Program)
eV	Electron volts
Fe	Iron
FPT	Fundamental Parameters Technique
FWHM	Full width of peak at half maximum height
GB	Gigabyte
Hg	Mercury
Hz	Hertz

Acronyms, Abbreviations, and Symbols (Continued)

ICP-AES	Inductively coupled plasma-atomic emission spectrometry
ICP-MS	Inductively coupled plasma-mass spectrometry
IR	Infrared
ITVR	Innovative Technology Verification Report
KARS	Kennedy Athletic, Recreational and Social (Park)
keV	Kiloelectron volts
kg	Kilograms
KSC	Kennedy Space Center
kV	Kilovolts
LEAP	Light Element Analysis Program
LiF	Lithium fluoride
LIMS	Laboratory information management system
LOD	Limit of detection
mA	Milli-amps
MB	Megabyte
MBq	Mega Becquerels
MCA	Multi-channel analyzer
mCi	Millicuries
MDL	Method detection limit
mg/kg	Milligrams per kilogram
MHz	Megahertz
mm	Millimeters
MMT	Monitoring and Measurement Technology (Program)
Mo	Molybdenum
MS	Matrix spike
MSD	Matrix spike duplicate
NASA	National Aeronautics and Space Administration
NELAC	National Environmental Laboratory Accreditation Conference
NERL	National Exposure Research Laboratory
Ni	Nickel
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute for Standards and Technology
NRC	Nuclear Regulatory Commission
NSWC	Naval Surface Warfare Center
ORD	Office of Research and Development
OSWER	Office of Solid Waste and Emergency Response

Acronyms, Abbreviations, and Symbols (Continued)

P	Phosphorus
Pb	Lead
PC	Personal computer
PDA	Personal digital assistant
PCB	Polychlorinated biphenyls
Pd	Palladium
PE	Performance evaluation
PeT	Pentaerythritol
ppb	Parts per billion
ppm	Parts per million
Pu	Plutonium
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
r^2	Correlation coefficient
RCRA	Resource Conservation and Recovery Act
Rh	Rhodium
RPD	Relative percent difference
RSD	Relative standard deviation
%RSD	Percent relative standard deviation
SAP	Sampling and analysis plan
SBMM	Sulphur Bank Mercury Mine
Sb	Antimony
Se	Selenium
Si	Silicon
SITE	Superfund Innovative Technology Evaluation
SOP	Standard operating procedure
SRM	Standard reference material
SVOC	Semivolatile organic compound
TAP	Thallium acid phthalate
Tetra Tech	Tetra Tech EM Inc.
Ti	Titanium
TSA	Technical systems audit
TSP	Total suspended particulates
TXRF	Total reflection x-ray fluorescence spectroscopy
U	Uranium
USFWS	U.S. Fish and Wildlife Service

Acronyms, Abbreviations, and Symbols (Continued)

V	Vanadium
V	Volts
VOC	Volatile organic compound
W	Watts
WDXRF	Wavelength-dispersive XRF
WRS	Wilcoxon Rank Sum
XRF	X-ray fluorescence
Zn	Zinc

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Chapter 1
Introduction

The U.S. Environmental Protection Agency (EPA), Office of Research and Development (ORD) conducted a demonstration to evaluate the performance of innovative x-ray fluorescence (XRF) technologies for measuring trace elements in soil and sediment. The demonstration was conducted as part of the EPA Superfund Innovative Technology Evaluation (SITE) Program.

Eight field-portable XRF instruments, which were provided and operated by six XRF technology developers, were evaluated as part of the demonstration. Each of these technology developers and their instruments are listed in Table 1-1. The technology developers brought each of these instruments to the demonstration site during the field portion of the demonstration. The instruments were used to analyze a total of 326 prepared soil and sediment samples that contained 13 target elements. The same sample set was analyzed by a fixed laboratory (the reference laboratory) using established EPA reference methods. The results obtained using each XRF instrument in the field were compared with the results obtained by the reference laboratory to assess instrument accuracy. The results of replicate sample analysis were utilized to assess the precision and the detection limits that each XRF instrument could achieve. The results of these evaluations, as well as technical observations and cost information, were then documented in an Innovative Technology Verification Report (ITVR) for each instrument.

This ITVR documents EPA's evaluation of the Rigaku ZSX Mini II XRF analyzer based on the results of the demonstration.

1.1 Organization of this Report

This report is organized to first present general information pertinent to the demonstration. This information is common to all eight ITVRs that were developed from the XRF demonstration. Specifically, this information includes an introduction (Chapter 1), the locations where the field samples were collected (Chapter 2), the field demonstration (Chapter 3), the evaluation design (Chapter 4), and the reference laboratory results (Chapter 5).

The second part of this report provides information relevant to the specific instrument that is the subject of this ITVR. This information includes a description of the instrument (Chapter 6), a performance evaluation (Chapter 7), a cost analysis (Chapter 8), and a summary of the demonstration results (Chapter 9).

Table 1-1. Participating Technology Developers and Instruments

Developer Full Name	Distributor in the United States	Developer Short Name	Instrument Full Name	Instrument Short Name
Elvatech, Ltd.	Xcalibur XRF Services	Xcalibur	ElvaX	ElvaX
Innov-X Systems	Innov-X Systems	Innov-X	XT400 Series	XT400
NITON Analyzers, A Division of Thermo Electron Corporation	NITON Analyzers, A Division of Thermo Electron Corporation	Niton	XLt 700 Series XLi 700 Series	XLt XLi
Oxford Instruments Analytical, Ltd.	Oxford Instruments Analytical, Ltd.	Oxford	X-Met 3000 TX ED2000	X-Met ED2000
Rigaku, Inc.	Rigaku, Inc.	Rigaku	ZSX Mini II	ZSX Mini II
RÖNTEC AG (acquired by Bruker AXS, 11/2005	RÖNTEC USA	Rontec	PicoTAX	PicoTAX

References are provided in Chapter 10. A verification statement for the instrument is provided as Appendix A. Comments from the instrument developer on the demonstration and any exceptions to EPA's evaluation are presented in Appendix B. Appendices C, D, and E contain the data validation summary report for the reference laboratory data and detailed evaluations of instrument versus reference laboratory results.

1.2 Description of the SITE Program

Performance verification of innovative environmental technologies is an integral part of EPA's regulatory and research mission. The SITE Program was established by the EPA Office of Solid Waste and Emergency Response 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 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 primary objectives: (1) identify and remove obstacles to development and commercial use of innovative technologies; (2) demonstrate promising innovative technologies and gather reliable information on performance and cost to support site characterization and cleanup; and (3) maintain an outreach program to operate existing technologies and identify new opportunities for their use. Additional information on the SITE Program is available on the EPA ORD web site (www.epa.gov/ord/SITE).

The intent of a SITE demonstration is to obtain representative, high-quality data on the performance and cost of one or more innovative technologies so that potential users can assess a technology's suitability for a specific application. The SITE Program includes the following program elements:

- Monitoring and Measurement Technology (MMT) Program – Evaluates technologies that sample, detect, monitor, or measure hazardous and toxic substances. These technologies are expected to provide better, faster, or more cost-effective methods for producing real-time data during site characterization and remediation studies than can conventional technologies.
- Remediation Technology Program – Demonstrates innovative treatment technologies to provide reliable data on performance, cost, and applicability for site cleanups.
- Technology Transfer Program – Provides and disseminates technical information in the form of updates, brochures, and other publications that promote the SITE Program and the participating technologies.

The demonstration of XRF instruments was conducted as part of the MMT Program, which is administered by the Environmental Sciences Division (ESD) of the National Exposure Research Laboratory (NERL) in Las Vegas, Nevada. Additional information on the NERL ESD is available on the EPA web site (www.epa.gov/nerlesd1/). Tetra Tech EM Inc. (Tetra Tech), an EPA contractor, provided comprehensive technical support to the demonstration.

1.3 Scope of the Demonstration

Conventional analytical methods for measuring the concentrations of inorganic elements in soil and sediment are time-consuming and costly. For this reason, field-portable XRF instruments have been proposed as an alternative approach, particularly where rapid and cost-effective assessment of a site is a goal. The use of a field XRF instrument for elemental analysis allows field personnel to quickly assess the extent of contamination by target elements at a site. Furthermore, the near instantaneous data provided by field-portable XRF instruments can be used to quickly identify areas where there may be increased risks and allow development of a more focused and cost-effective sampling strategy for conventional laboratory analysis.

EPA-sponsored demonstrations of XRF technologies have been under way for more than a decade. The first SITE MMT demonstration of XRF occurred in 1995, when six instruments were evaluated for their ability to analyze 10 target elements. The results of this demonstration were published in individual reports for each instrument (EPA 1996a, 1996b, 1998a, 1998b, 1998c, and 1998d). In 2003, two XRF instruments were included in a demonstration of field methods for analysis of mercury in soil and sediment.

Individual ITVRs were also prepared for each of these two instruments (EPA 2004a, 2004b).

Although XRF spectrometry is now considered a mature technology for elemental analysis, field-portable XRF instruments have evolved considerably over the past 10 years, and many of the instruments that were evaluated in the original demonstration are no longer manufactured. Advances in electronics and data processing, coupled with new x-ray tube source technology, have produced substantial improvements in the precision and speed of XRF analysis. The current demonstration of XRF instruments was intended to evaluate these new technologies, with an expanded set of target elements, to provide information to potential users on current state-of-the-art instrumentation and its associated capabilities.

During the demonstration, performance data regarding each field-portable XRF instrument were collected through analysis of a sample set that included a broad range of soil/sediment types and target element concentrations. To develop this sample set, soil and sediment samples that contain the target elements of concern were collected in bulk quantities at nine sites from across the U.S. These bulk samples of soil and sediment were homogenized, characterized, and packaged into demonstration samples for the evaluation. Some of the batches of soil and sediment were spiked with selected target elements to ensure that representative concentration ranges were included for all target elements and that the sample design was robust. Replicate samples of the material in each batch were included in the final set of demonstration samples to assess instrument precision and detection limits. The final demonstration sample set therefore included 326 samples.

Each developer analyzed all 326 samples during the field demonstration using its XRF instrument and in accordance with its standard operating procedure. The field demonstration was conducted during the week of January 24, 2005, at the Kennedy Athletic, Recreational and Social (KARS) Park, which is part of the Kennedy Space Center on Merritt Island, Florida. Observers were assigned to each XRF instrument during the field demonstration to collect detailed information on the instrument and operating procedures, including sample processing times, for subsequent evaluation. The reference laboratory also analyzed a complete set of the demonstration samples for the target elements using acid digestion and inductively coupled plasma-atomic emission spectrometry (ICP-AES), in accordance with EPA Method 3050B/6010B, and using cold vapor atomic absorption (CVAA) spectroscopy (for mercury only) in accordance with EPA Method 7471A. By assuming that the results from the reference laboratory were essentially “true” values, instrument accuracy was assessed by comparing the results obtained using the XRF instrument with the results from the reference laboratory. The data obtained using the XRF instrument were also assessed in other ways, in accordance with the objectives of the demonstration, to provide information on instrument precision, detection limits, and interferences.

1.4 General Description of XRF Technology

XRF spectroscopy is an analytical technique that exposes a solid sample to an x-ray source. The x-rays from the source have the appropriate excitation energy that causes elements in the sample to emit characteristic x-rays. A qualitative elemental analysis is possible from the characteristic energy, or wavelength, of the fluorescent x-rays emitted. A quantitative elemental analysis is possible by counting the number (intensity) of x-rays at a given wavelength.

Three electron shells are generally involved in emissions of x-rays during XRF analysis of samples: the K, L, and M shells. Multiple-intensity peaks are generated from the K, L, or M shell electrons in a typical emission pattern, also called an emission spectrum, for a given element. Most XRF analysis focuses on the x-ray emissions from the K and L shells because they are the most energetic lines. K lines are typically used for elements with atomic numbers from 11 to 46 (sodium to palladium), and L lines are used for elements above atomic number 47 (silver). M-shell emissions are measurable only for metals with an atomic number greater than 57 (lanthanum).

As illustrated in Figure 1-1, characteristic radiation arises when the energy from the x-ray source exceeds the absorption edge energy of inner-shell electrons, ejecting one or more electrons. The vacancies are filled by electrons that cascade in from the outer shells. The energy states of the electrons in the outer shells are higher than those of the inner-shell electrons, and the outer-shell electrons emit energy in the form of x-rays as they cascade down. The energy of this x-ray radiation is unique for each element.

An XRF analyzer consists of three major components: (1) a source that generates x-rays (a radioisotope or x-ray tube); (2) a detector that converts x-rays emitted from the sample into measurable electronic signals; and (3) a data processing unit that records the emission or fluorescence energy signals and calculates the elemental concentrations in the sample.

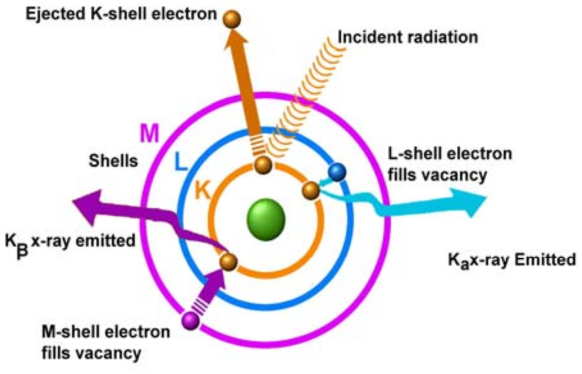

Figure 1-1. The XRF process.

Measurement times vary (typically ranging from 30 to 600 seconds), based primarily on data quality objectives. Shorter analytical measurement times (30 seconds) are generally used for initial screening, element identification, and hot-spot delineation, while longer measurement times (300 seconds or more) are typically used to meet higher goals for precision and accuracy. The length of the measuring time will also affect the detection limit; generally, the longer the measuring time, the lower the detection limit. However, detection limits for individual elements may be increased because of sample heterogeneity or the presence of other elements in the sample that fluoresce with similar x-ray energies.

The main variables that affect precision and accuracy for XRF analysis are:

1. Physical matrix effects (variations in the physical character of the sample).
2. Chemical matrix effects (absorption and enhancement phenomena) and Spectral interferences (peak overlaps).
3. Moisture content above 10 percent, which affects x-ray transmission.

Because of these variables, it is important that each field XRF characterization effort be guided by a well-considered sampling and analysis plan. Sample preparation and homogenization, instrument calibration, and laboratory confirmation analysis are all important aspects of an XRF sampling and analysis plan. EPA SW-846 Method 6200 provides additional guidance on sampling and analytical methodology for XRF analysis.

1.5 Properties of the Target Elements

This section describes the target elements selected for the technology demonstration and the typical characteristics of each. Key criteria used in selecting the target elements included:

- The frequency that the element is determined in environmental applications of XRF instruments.
- The extent that the element poses an environmental consequence, such as a potential risk to human or environmental receptors.
- The ability of XRF technology to achieve detection limits below typical remediation goals and risk assessment criteria.
- The extent that the element may interfere with the analysis of other target elements.

In considering these criteria, the critical target elements selected for this study were antimony, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, vanadium, and zinc. These 13 target elements are of significant concern for site cleanups and human health risk assessments because most are highly toxic or interfere with the analysis of other elements. The demonstration therefore focused on the analysis of these 13 elements in evaluating the various XRF instruments.

1.5.1 Antimony

Naturally occurring antimony in surface soils is typically found at less than 1 to 4 milligrams per kilogram (mg/kg). Antimony is mobile in the environment and is bioavailable for uptake by plants; concentrations greater than 5 mg/kg are potentially phytotoxic, and concentrations above 31 mg/kg in soil may be hazardous to humans. Antimony may be found along with arsenic in mine wastes, at shooting ranges, and at industrial facilities. Typical detection limits for field-portable XRF instruments range from 10 to 40 mg/kg. Antimony is typically analyzed with success by ICP-AES; however, recovery of antimony in soil matrix spikes is often below quality control (QC) limits (50 percent or less) as a result of loss through volatilization during acid digestion. Therefore, results using ICP-AES may be lower than are obtained by XRF.

1.5.2 Arsenic

Naturally occurring arsenic in surface soils typically ranges from 1 to 50 mg/kg; concentrations above 10 mg/kg are potentially phytotoxic. Concentrations of arsenic greater than 0.39 mg/kg may cause carcinogenic effects in humans, and concentrations above 22 mg/kg may result in adverse noncarcinogenic effects. Typical detection limits for field-portable XRF instruments range from 10 to 20 mg/kg arsenic. Elevated concentrations of arsenic are associated with mine wastes and industrial facilities. Arsenic is successfully analyzed by ICP-AES; however, spectral interferences between peaks for arsenic and lead can affect detection limits and accuracy in XRF analysis when the ratio of lead to arsenic is 10 to 1 or more. Risk-based screening levels and soil screening levels for arsenic may be lower than the detection limits of field-portable XRF instruments.

1.5.3 Cadmium

Naturally occurring cadmium in surface soils typically ranges from 0.6 to 1.1 mg/kg; concentrations greater than 4 mg/kg are potentially phytotoxic. Concentrations of cadmium that exceed 37 mg/kg may result in adverse effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 50 mg/kg. Elevated concentrations of cadmium are associated with mine wastes and industrial facilities. Cadmium is successfully analyzed by both ICP-AES and field-portable XRF; however, action levels for cadmium may be lower than the detection limits of field-portable XRF instruments.

1.5.4 Chromium

Naturally occurring chromium in surface soils typically ranges from 1 to 1,000 mg/kg; concentrations greater than 1 mg/kg are potentially phytotoxic, although specific phytotoxicity levels for naturally occurring chromium have not been documented. The variable oxidation states of chromium affect its behavior and toxicity. Concentrations of hexavalent chromium above 30 mg/kg and of trivalent chromium above 10,000 mg/kg may cause adverse health effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 50 mg/kg. Hexavalent chromium is typically associated with metal plating or other industrial facilities. Trivalent chromium may be found in mine waste and at industrial facilities. Neither ICP-AES nor field-portable XRF can distinguish between oxidation states for chromium (or any other element).

1.5.5 Copper

Naturally occurring copper in surface soils typically ranges from 2 to 100 mg/kg; concentrations greater than 100 mg/kg are potentially phytotoxic. Concentrations greater than 3,100 mg/kg may result in adverse health effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 50 mg/kg. Copper is mobile and is a common contaminant in soil and sediments. Elevated concentrations of copper are associated with mine wastes and industrial facilities. Copper is successfully analyzed by ICP-AES and XRF; however, spectral interferences between peaks for copper and zinc may affect the detection limits and accuracy of the XRF analysis.

1.5.6 Iron

Although iron is not considered an element that poses a significant environmental consequence, it interferes with measurement of other elements and was therefore included in the study. Furthermore, iron is often used as a target reference element in XRF analysis.

Naturally occurring iron in surface soils typically ranges from 7,000 to 550,000 mg/kg, with the iron content originating primarily from parent rock. Typical detection limits for field-portable XRF instruments are in the range of 10 to 60 mg/kg. Iron is easily analyzed by both ICP-AES and XRF; however, neither technique can distinguish among iron species in soil. Although iron in soil may pose few environmental consequences, high levels of iron may interfere with analyses of other elements in both techniques (ICP-AES and XRF). Spectral interference from iron is mitigated in ICP-AES analysis by applying inter-element correction factors, as required by the analytical method. Differences in analytical results between ICP-AES and XRF for other target elements are expected when concentrations of iron are high in the soil matrix.

1.5.7 Lead

Naturally occurring lead in surface soils typically ranges from 2 to 200 mg/kg; concentrations greater than 50 mg/kg are potentially phytotoxic. Concentrations greater than 400 mg/kg may result in adverse effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 20 mg/kg. Lead is a common contaminant at many sites, and human and environmental exposure can occur through many routes. Lead is frequently found in mine waste, at lead-acid battery recycling facilities, at oil refineries, and in lead-based paint. Lead is successfully analyzed by ICP-AES and XRF; however, spectral interferences between peaks for lead and arsenic in XRF analysis can affect detection limits and accuracy when the ratio of arsenic to lead is 10 to 1 or more. Differences between ICP-AES and XRF results are expected in the presence of high concentrations of arsenic, especially when the ratio of lead to arsenic is low.

1.5.8 Mercury

Naturally occurring mercury in surface soils typically ranges from 0.01 to 0.3 mg/kg; concentrations greater than 0.3 mg/kg are potentially phytotoxic. Concentrations of mercury greater than 23 mg/kg and concentrations of methyl mercury above 6.1 mg/kg may result in adverse health effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 20 mg/kg. Elevated concentrations of mercury are associated with amalgamation of gold and with mine waste and industrial facilities. Native surface soils are commonly enriched by anthropogenic sources of mercury. Anthropogenic sources include coal-fired power plants and metal smelters. Mercury is too volatile to withstand both the vigorous digestion and extreme temperature involved with ICP-AES analysis; therefore, the EPA-approved technique for laboratory analysis of mercury is CVAA spectroscopy. Mercury is successfully measured by XRF, but differences between results obtained by CVAA and XRF are expected when mercury levels are high.

1.5.9 Nickel

Naturally occurring nickel in surface soils typically ranges from 5 to 500 mg/kg; a concentration of 30 mg/kg is potentially phytotoxic. Concentrations greater than 1,600 mg/kg may result in adverse health effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 60 mg/kg. Elevated concentrations of nickel are associated with mine wastes and industrial facilities. Nickel is a common environmental contaminant at metal processing sites. It is successfully analyzed by both ICP-AES and XRF with little interference; therefore, a strong correlation between the methods is expected.

1.5.10 Selenium

Naturally occurring selenium in surface soils typically ranges from 0.1 to 2 mg/kg; concentrations greater than 1 mg/kg are potentially phytotoxic. Its toxicities are well documented for plants and livestock; however, it is also considered a trace nutrient. Concentrations above 390 mg/kg may result in adverse health effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 20 mg/kg. Most selenium is associated with sulfur or sulfide minerals, where concentrations can exceed 200 mg/kg. Selenium can be measured by both ICP-AES and XRF; however, detection limits using XRF usually exceed the ecological risk-based screening levels for soil. Analytical results for selenium using ICP-AES and XRF are expected to be comparable.

1.5.11 Silver

Naturally occurring silver in surface soils typically ranges from 0.01 to 5 mg/kg; concentrations greater than 2 mg/kg are potentially phytotoxic. In addition, concentrations that exceed 390 mg/kg may result in adverse effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 45 mg/kg. Silver is a common contaminant in mine waste, in photographic film processing wastes, and at metal processing sites. It is successfully analyzed by ICP-AES and XRF; however, recovery may be reduced in ICP-AES analysis because insoluble silver chloride may form during acid digestion. Detection limits using XRF may exceed the risk-based screening levels for silver in soil.

1.5.12 Vanadium

Naturally occurring vanadium in surface soils typically ranges from 20 to 500 mg/kg; concentrations greater than 2 mg/kg are potentially phytotoxic, although specific phytotoxicity levels for naturally occurring vanadium have not been documented. Concentrations above 550 mg/kg may result in adverse health effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 50 mg/kg. Vanadium can be associated with manganese, potassium, and organic matter and is typically concentrated in organic shales, coal, and crude oil. It is successfully analyzed by both ICP-AES and XRF with little interference.

1.5.13 Zinc

Naturally occurring zinc in surface soils typically ranges from 10 to 300 mg/kg; concentrations greater than 50 mg/kg are potentially phytotoxic. Zinc at concentrations above 23,000 mg/kg may result in adverse health effects in humans. Typical detection limits for field-portable XRF instruments range from 10 to 30 mg/kg. Zinc is a common contaminant in mine waste and at metal processing sites. In addition, it is highly soluble, which is a common concern for aquatic receptors. Zinc is successfully analyzed by ICP-AES; however, spectral interferences between peaks for copper and zinc may influence detection limits and the accuracy of the XRF analysis.

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Chapter 2
Field Sample Collection Locations

Although the field demonstration took place at KARS Park on Merritt Island, Florida, environmental samples were collected at other sites around the country to develop a demonstration sample that incorporated a variety of soil/sediment types and target element concentrations. This chapter describes these sample collection sites, as well as the rationale for the selection of each.

Several criteria were used to assess potential sample collection sites, including:

- The ability to provide a variety of target elements and soil/sediment matrices.
- The convenience and accessibility of the location to the sampling team.
- Program support and the cooperation of the site owner.

Nine sample collection sites were ultimately selected for the demonstration; one was the KARS Park site itself. These nine sites were selected to represent variable soil textures (sand, silt, and clay) and iron content, two factors that significantly affect instrument performance.

Historical operations at these sites included mining, smelting, steel manufacturing, and open burn pits; one, KARS Park, was a gun range. Thus, these sites incorporated a wide variety of metal contaminants in soils and sediments. Both contaminated and uncontaminated (background) samples were collected at each site.

A summary of the sample collection sites is presented in Table 2-1, which describes the types of metal-contaminated soils or sediments that were found at each site. This information is based on the historical data that were provided by the site owners or by the EPA remedial project managers.

2.1 Alton Steel Mill Site

The Alton Steel Mill site (formerly the Laclede Steel site) is located at 5 Cut Street in Alton, Illinois. This 400-acre site is located in Alton's industrial corridor. The Alton site was operated by Laclede Steel Company from 1911 until it went bankrupt in July 2001. The site was purchased by Alton Steel, Inc., from the bankruptcy estate of Laclede Steel in May 2003. The Alton site is heir to numerous environmental concerns from more than 90 years of steel production; site contaminants include polychlorinated biphenyls (PCBs) and heavy metals. Laclede Steel was cited during its operating years for improper management and disposal of PCB wastes and electric arc furnace dust that contained heavy metals such as lead and cadmium. A Phase I environmental site assessment (ESA) was conducted at the Alton site in May 2002, which identified volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), total priority pollutant metals, and PCBs as potential contaminants of concern at the site.

Based on the data gathered during the Phase I ESA and on discussions with Alton personnel, several soil samples were collected for the demonstration from two areas at the Alton site, including the Rod Patenting Building and the Tube Mill Building. The soil in the areas around these two buildings had not been remediated and was known to contain elevated concentrations of arsenic, cadmium, chromium, lead, nickel, zinc, and iron. The matrix of the contaminated soil samples was a fine to medium sand; the background soil sample was a sand loam.

Table 2-2 presents historical analytical data (the maximum concentrations) for some of the target elements detected at the Alton site.

Table 2-1. Nature of Contamination in Soil and Sediment at Sample Collection Sites

Sample Collection Site	Source of Contamination	Matrix	Site-Specific Metals of Concern for XRF Demonstration											
			Sb	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Se	Ag	Zn
Alton Steel, Alton, IL	Steel manufacturing facility with metal arc furnace dust. The site also includes a metal scrap yard and a slag recovery facility.	Soil		X	X	X		X	X		X			X
Burlington Northern–ASARCO Smelter Site, East Helena, MT	Railroad yard staging area for smelter ores. Contaminated soils resulted from dumping and spilling concentrated ores.	Soil		X	X				X					
KARS Park – Kennedy Space Center, Merritt Island, FL	Impacts to soil from historical facility operations and a former gun range.	Soil	X	X		X	X		X					X
Leviathan Mine Site/Aspen Creek, Alpine County, CA	Abandoned open-pit sulfur and copper mine that has contaminated a 9-mile stretch of mountain creeks, including Aspen Creek, with heavy metals.	Soil and Sediment		X	X	X	X	X			X			
Naval Surface Warfare Center, Crane Division, Crane, IN	Open disposal and burning of general refuse and waste associated with aircraft maintenance.	Soil	X	X	X	X	X	X	X	X	X		X	X
Ramsay Flats–Silver Bow Creek, Butte, MT	Silver Bow Creek was used as a conduit for mining, smelting, industrial, and municipal wastes.	Soil and Sediment		X	X		X	X	X					X
Sulphur Bank Mercury Mine	Inactive mercury mine. Waste rock, tailings, and ore are distributed in piles throughout the property.	Soil	X	X					X	X				
Torch Lake Site (Great Lakes Area of Concern), Houghton County, MI	Copper mining produced mill tailings that were dumped directly into Torch Lake, contaminating the lake sediments and shoreline.	Sediment		X		X	X		X	X		X	X	X
Wickes Smelter Site, Jefferson City, MT	Abandoned smelter complex with contaminated soils and mineral-processing wastes, including remnant ore piles, decomposed roaster brick, slag piles and fines, and amalgamation sediments.	Soil	X	X	X	X	X	X	X		X			X

Notes (in order of appearance in table):

Sb: Antimony
As: Arsenic
Cd: Cadmium
Cr: Chromium
Cu: Copper
Fe: Iron
Pb: Lead
Hg: Mercury
Ni: Nickel
Se: Selenium
Ag: Silver
Zn: Zinc

Note: Vanadium was not a chemical of concern at any of the sites and so does not appear on the table.

Table 2-2. Historical Analytical Data, Alton Steel Mill Site

Metal	Maximum Concentration (mg/kg)
Arsenic	80.3
Cadmium	97
Chromium	1,551
Lead	3,556

2.2 Burlington Northern-ASARCO Smelter Site

The Burlington Northern (BN)-ASARCO Smelter site is located in the southwestern part of East Helena, Montana. The site was an active smelter for more than 100 years and closed in 2002. Most of the ore processed at the smelter was delivered on railroad cars. An area west of the plant site (the BN property) was used for temporary staging of ore cars and consists of numerous side tracks to the primary railroad line into the smelter. This site was selected to be included in the demonstration because it had not been remediated and contained several target elements in soil.

At the request of EPA, the site owner collected samples of surface soil in this area in November 1997 and April 1998 and analyzed them for arsenic, cadmium, and lead; elevated concentrations were reported for all three metals. The site owner collected 24 samples of surface soil (16 in November 1997 and 8 in April 1998). The soils were found to contain up to 2,018 parts per million (ppm) arsenic, 876 ppm cadmium, and 43,907 ppm lead. One sample of contaminated soil and one sample of background soil were collected. The contaminated soil was a light brown sandy loam with low organic carbon content. The background soil was a medium brown sandy loam with slightly more organic material than the contaminated soil sample. Table 2-3 presents the site owner's data for arsenic, cadmium, and lead (the maximum concentrations) from the 1997 and 1998 sampling events.

Table 2-3. Historical Analytical Data, BN-ASARCO Smelter Site

Metal	Maximum Concentration (ppm)
Arsenic	2,018
Cadmium	876
Lead	43,907

2.3 Kennedy Athletic, Recreational and Social Park Site

Soil and sediment at the KARS Park site were contaminated from former gun range operations and contain several target elements for the demonstration. The specific elements of concern for the KARS Park site include antimony, arsenic, chromium, copper, lead, and zinc.

The KARS Park site is located at the Kennedy Space Center on Merritt Island, Florida. KARS Park was purchased in 1962 and has been used by employees of the National Aeronautics and Space Administration (NASA), other civil servants, and guests as a recreational park since 1963. KARS Park occupies an area of Kennedy Space Center just outside the Cape Canaveral base. Contaminants in the park resulted from historical facility operations and impacts from the former gun range. The land north of KARS is owned by NASA and is managed by the U.S. Fish and Wildlife Service (USFWS) as part of the Merritt Island National Wildlife Refuge.

Two soil and two sediment samples were collected from various locations at the KARS Park site for the XRF demonstration. The contaminated soil sample was collected from an impact berm at the small arms range. The background soil sample was collected from a forested area near the gun range. The matrix of the contaminated and background soil samples consisted of fine to medium quartz sand. The sediment samples were collected from intermittently saturated areas within the skeet range. These samples were organic rich sandy loams. Table 2-4 presents historical analytical data (the maximum concentrations) for soil and sediment at KARS Park.

Table 2-4. Historical Analytical Data, KARS Park Site

Metal	Maximum Concentration (mg/kg)
Antimony	8,500
Arsenic	1,600
Chromium	40.2
Copper	290,000
Lead	99,000
Zinc	16,200

2.4 Leviathan Mine Site

The Leviathan Mine site is an abandoned copper and sulfur mine located high on the eastern slopes of the Sierra Nevada Mountain range near the California-Nevada border. Development of the Leviathan Mine began in 1863, when copper sulfate was mined for use in the silver refineries of the Comstock Lode. Later, the underground mine was operated as a copper mine until a mass of sulfur was encountered. Mining stopped until about 1935, when sulfur was extracted for use in refining copper ore. In the 1950s, the mine was converted to an open-pit sulfur mine. Placement of excavated overburden and waste rock in nearby streams created acid mine drainage and environmental impacts in the 1950s. Environmental impacts noted at that time included large fish kills.

Historical mining distributed waste rock around the mine site and created an open pit, adits, and solution cavities through mineralized rock. Oxygen in contact with the waste rock and mineralized rock in the adits oxidizes sulfur and sulfide minerals, generating acid. Water contacting the waste rock and flowing through the mineralized rock mobilizes the acid into the environment. The acid dissolves metals, including arsenic, copper, iron, and nickel, which creates conditions toxic to insects and fish in Leviathan, Aspen, and Bryant Creeks, downstream of the Leviathan Mine. Table 2-5 presents historical analytical data (the maximum concentrations) for the target elements detected at elevated concentrations in sediment samples collected along the three creeks. Four sediment and one soil sample were collected. One of the sediment samples was collected from the iron precipitate terraces formed from the acid mine drainage. The matrix of this sample appeared to be an orange silty clay loam. A second sediment sample was collected from the settling pond at the wastewater treatment system. The matrix of this sample was orange clay. A third sample was collected from the salt crust at the settling pond. This sample incorporated white crystalline material. One background sediment and one background soil sample were collected upstream of the mine. These samples consisted of light brown sandy loam.

Table 2-5. Historical Analytical Data, Leviathan Mine Site

Metal	Maximum Concentration (mg/kg)
Arsenic	2,510
Cadmium	25.7
Chromium	279
Copper	837
Nickel	2,670

2.5 Navy Surface Warfare Center, Crane Division Site

The Old Burn Pit at the Naval Surface Warfare Center (NSWC), Crane Division, was selected to be included in the demonstration because 6 of the 13 target elements were detected at significant concentration in samples of surface soil previously collected at the site.

The NSWC, Crane Division, site is located near the City of Crane in south-central Indiana. The Old Burn Pit is located in the northwestern portion of NSWC and was used daily from 1942 to 1971 to burn refuse. Residue from the pit was buried along with noncombustible metallic items in a gully north of the pit. The burn pit was covered with gravel and currently serves as a parking lot for delivery trailers. The gully north of the former burn pit has been revegetated. Several soil samples were collected from the revegetated area for the demonstration because the highest concentrations of the target elements were detected in soil samples collected previously from this area. The matrix of the contaminated and background soil samples was a sandy loam. The maximum concentrations of the target elements detected in surface soil during previous investigations are summarized in Table 2-6.

Table 2-6. Historical Analytical Data, NSWC Crane Division-Old Burn Pit

Metal	Maximum Concentration (mg/kg)
Antimony	301
Arsenic	26.8
Cadmium	31.1
Chromium	112
Copper	1,520
Iron	105,000
Lead	16,900
Mercury	0.43
Nickel	62.6
Silver	7.5
Zinc	5,110

2.6 Ramsay Flats-Silver Bow Creek Site

The Ramsay Flats-Silver Bow Creek site was selected to be included in the demonstration because 6 of the 13 target elements were detected in samples of surface sediment collected previously at the site. Silver Bow Creek originates north of Butte, Montana, and is a tributary to the upper Clark Fork River.

More than 100 years of nearly continuous mining have altered the natural environment surrounding the upper Clark Fork River. Early wastes from mining, milling, and smelting were dumped directly into Silver Bow Creek and were subsequently transported downstream. EPA listed Silver Bow Creek and a contiguous portion of the upper Clark Fork River as a Superfund site in 1983.

A large volume of tailings was deposited in a low-gradient reach of Silver Bow Creek in the Ramsay Flats area. Tailings at Ramsay Flats extend several hundred feet north of the Silver Bow Creek channel. About 18 inches of silty tailings overlie texturally stratified natural sediments that consist of low-permeability silt, silty clay, organic layers, and stringers of fine sand.

Two sediment samples were collected from the Ramsay Flats tailings area and were analyzed for a suite of metals using a field-portable XRF. The contaminated sediment sample was collected in Silver Bow Creek adjacent to the mine tailings. The matrix of this sediment sample was orange-brown silty fine sand with interlayered black organic material. The background sediment sample was collected upstream of Butte, Montana. The matrix of this sample was organic rich clayey silt with approximately 25 percent fine sand. The maximum concentrations of the target elements in the samples are summarized in Table 2-7.

Table 2-7. Historical Analytical Data, Ramsay Flats-Silver Bow Creek Site

Metal	Maximum Concentration (mg/kg)
Arsenic	176
Cadmium	141
Copper	1,110
Iron	20,891
Lead	394
Zinc	1,459

2.7 Sulphur Bank Mercury Mine Site

The Sulphur Bank Mercury Mine (SBMM) is a 160-acre inactive mercury mine located on the eastern shore of the Oaks Arm of Clear Lake in Lake County, California, 100 miles north of San Francisco. Between 1864 and 1957, SBMM was the site of underground and open-pit mining at the hydrothermal vents and hot springs. Mining disturbed about 160 acres of land at SBMM and generated large quantities of waste rock (rock that did not contain economic concentrations of mercury and was removed to gain access to ore), tailings (the waste material from processes that removed the mercury from ore), and ore (rock that contained economic concentrations of mercury that was mined and stockpiled for mercury extraction). The waste rock, tailings, and ore are distributed in piles throughout the property.

Table 2-8 presents historical analytical data (the maximum concentrations) for the target elements detected at elevated concentrations in surface samples collected at SBMM. Two contaminated soil samples and one background soil sample were collected at various locations for the demonstration project. The mercury sample was collected from the ore stockpile and consisted of medium to coarse sand. The second contaminated soil sample was collected from the waste rock pile and consisted of coarse sand and gravel with trace silt. The matrix of the background soil sample was brown sandy loam.

Table 2-8. Historical Analytical Data, Sulphur Bank Mercury Mine Site

Metal	Maximum Concentration (mg/kg)
Antimony	3,724
Arsenic	532
Lead	900
Mercury	4,296

2.8 Torch Lake Superfund Site

The Torch Lake Superfund site was selected because native and contaminated sediment from copper mining, milling, and smelting contained the elements targeted for the demonstration. The specific metals of concern for the Torch Lake Superfund site included arsenic, chromium, copper, lead, mercury, selenium, silver, and zinc.

The Torch Lake Superfund site is located on the Keweenaw Peninsula in Houghton County, Michigan. Wastes were generated at the site from the 1890s until 1969. The site was included on the National Priorities List in June 1986. Approximately 200 million tons of mining wastes were dumped into Torch Lake and reportedly filled about 20 percent of the lake's original volume. Contaminated sediments are believed to be up to 70 feet thick in some locations. Wastes occur both on the uplands and in the lake and are found in four forms, including poor rock piles, slag and slag-enriched sediments, stamp sands, and abandoned settling ponds for mine slurry.

EPA initiated long-term monitoring of Torch Lake in 1999; the first monitoring event (the baseline study) was completed in August 2001. Table 2-9 presents analytical data (the maximum concentrations) for eight target elements in sediment samples collected from Torch Lake during the baseline study. Sediment samples were collected from the Torch Lake site at various locations for the demonstration. The matrix of the sediment samples was orange silt and clay.

Table 2-9. Historical Analytical Data, Torch Lake Superfund Site

Metal	Maximum Concentration (mg/kg)
Arsenic	40
Chromium	90
Copper	5,850
Lead	325
Mercury	1.2
Selenium	0.7
Silver	6.2
Zinc	630

2.9 Wickes Smelter Site

The roaster slag pile at the Wickes Smelter site was selected to be included in the demonstration because 12 of the 13 target elements were detected in soil samples collected previously at the site.

The Wickes Smelter site is located in the unincorporated town of Wickes in Jefferson County, Montana. Wastes at the Wickes Smelter site include waste rock, slag, flue bricks, and amalgamation waste. The wastes are found in discrete piles and are mixed with soil. The contaminated soil sample was collected from a pile of roaster slag at the site. The slag was black, medium to coarse sand and gravel. The matrix of the background soil sample was a light brown sandy loam. Table 2-10 presents historical analytical data (maximum concentrations) for the roaster slag pile.

Table 2-10. Historical Analytical Data, Wickes Smelter Site-Roaster Slag Pile

Metal	Maximum Concentration (mg/kg)
Antimony	79
Arsenic	3,182
Cadmium	70
Chromium	13
Copper	948
Iron	24,780
Lead	33,500
Nickel	7.3
Silver	83
Zinc	5,299

Chapter 3
Field Demonstration

The field demonstration required a sample set and a single location (the demonstration site) where all the technology developers could assemble to analyze the sample set under the oversight of the EPA/Tetra Tech field team. This chapter describes how the sample set was created, how the demonstration site was selected, and how the field demonstration was conducted. Additional detail regarding these topics is available in the *Demonstration and Quality Assurance Project Plan* (Tetra Tech 2005).

3.1 Bulk Sample Processing

A set of samples that incorporated a variety of soil and sediment types and target element concentrations was needed to conduct a robust evaluation. The demonstration sample set was generated from the bulk soil and sediment samples that were collected from the nine sample collection sites described in Chapter 2. Both contaminated (environmental) and uncontaminated (background) bulk samples of soil and sediment were collected at each sample collection site. The background sample was used as source material for a spiked sample when the contaminated sample did not contain the required levels of target elements. By incorporating a spiked background sample into the sample set, the general characteristics of the soil and sediment sample matrix could be maintained. At the same time, this spiked sample assured that all target elements were present at the highest concentration levels needed for a robust evaluation.

3.1.1 Bulk Sample Collection and Shipping

Large quantities of soil and sediment were needed for processing into well-characterized samples for this demonstration. As a result, 14 soil samples and 11 sediment samples were collected in bulk quantity from the nine sample collection sites across the U.S. A total of approximately 1,500 kilograms of unprocessed soil and sediment was collected, which yielded more than 1,000 kilograms of soil and sediment after the bulk samples had been dried.

Each bulk soil sample was excavated using clean shovels and trowels and then placed into clean, plastic 5-gallon (19-liter) buckets at the sample collection site. The mass of soil and sediment in each bucket varied, but averaged about 25 kilograms per bucket. As a result, multiple buckets were needed to contain the entire quantity of each bulk sample.

Once it had been filled, a plastic lid was placed on each bucket, the lid was secured with tape, and the bucket was labeled with a unique bulk sample number. Sediment samples were collected in a similar method at all sites except at Torch Lake, where sediments were collected using a Vibracore or Ponar sediment sampler operated from a boat. Each 5-gallon bucket was overpacked in a plastic cooler and was shipped under chain of custody via overnight delivery to the characterization laboratory, Applied Research and Development Laboratory (ARDL).

3.1.2 Bulk Sample Preparation and Homogenization

Each bulk soil or sediment sample was removed from the multiple shipping buckets and then mixed and homogenized to create a uniform batch. Each bulk sample was then spread on a large tray at ARDL's laboratory to promote uniform air drying. Some bulk samples of sediment required more than 2 weeks to dry because of the high moisture content.

The air-dried bulk samples of soil and sediment were sieved through a custom-made screen to remove coarse material larger than about 1 inch. Next, each bulk sample was mechanically crushed using a hardened stainless-steel hammer mill until the particle size was sub-60-mesh sieve (less than 0.2 millimeters). The particle size of the processed bulk soil and sediment was measured after each round of crushing using standard sieve technology, and the particles that were still larger than 60-mesh were returned to the crushing process. The duration of the crushing process for each bulk sample varied based on soil type and volume of coarse fragments.

After each bulk sample had been sieved and crushed, the sample was mixed and homogenized using a Model T 50A Turbula shaker-mixer. This shaker was capable of handling up to 50 gallons (190 liters) of sample material; thus, this shaker could handle the complete volume of each bulk sample. Bulk samples of smaller volume were mixed and homogenized using a Model T 10B Turbula shaker-mixer that was capable of handling up to 10 gallons (38 liters).

Aliquots from each homogenized bulk sample were then sampled and analyzed in triplicate for the 13 target elements using ICP-AES and CVAA. If the relative percent difference between the highest and lowest result exceeded 10 percent for any element, the entire batch was returned to the shaker-mixer for additional homogenization. The entire processing scheme for the bulk samples is shown in Figure 3-1.

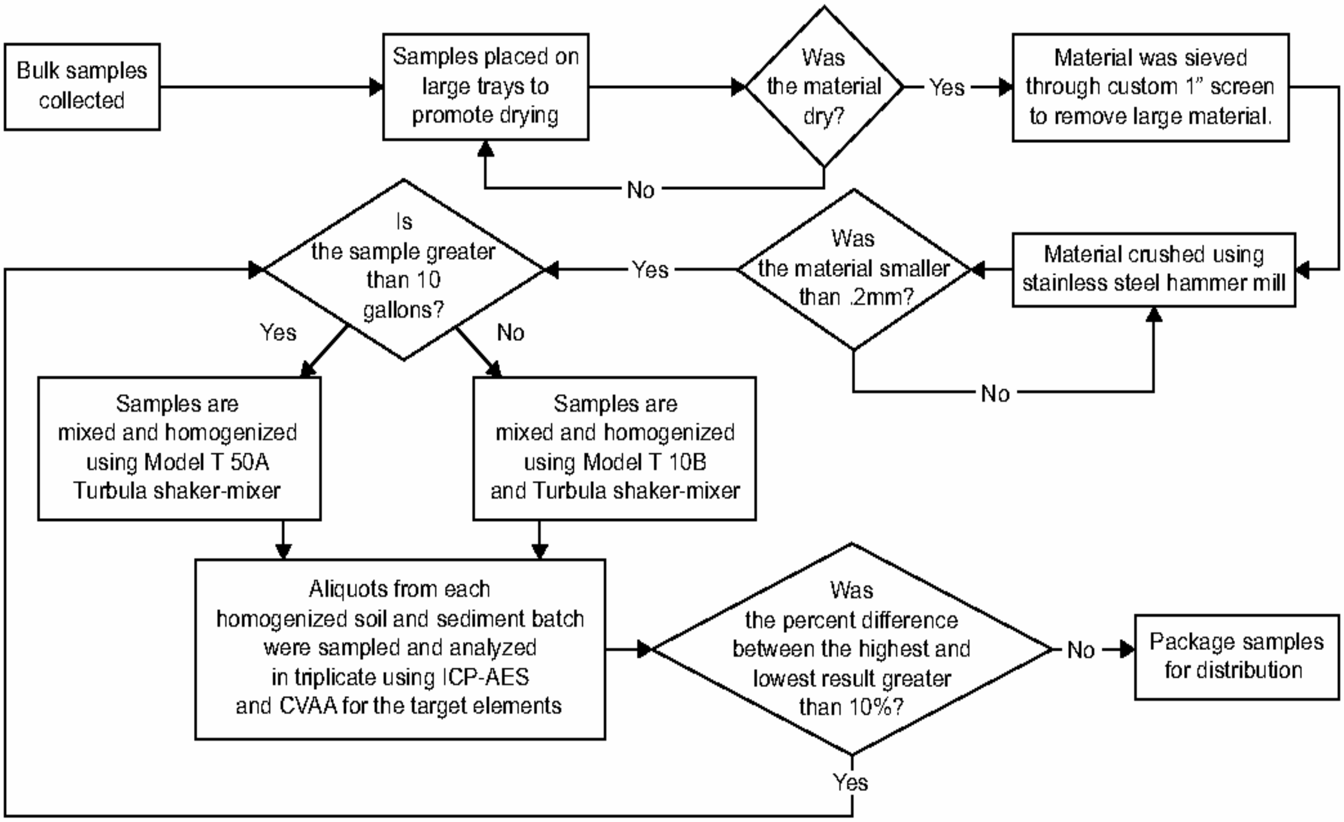


Figure 3-1. Bulk sample processing diagram.

3.2 Demonstration Samples

After the bulk soil and sediment sample material had been processed into homogenized bulk samples for the demonstration, the next consideration was the concentrations of target elements. The goal was to create a demonstration sample set that would cover the concentration range of each target element that may be reasonably found in the environment. Three concentration levels were identified as a basis for assessing both the coverage of the environmental samples and the need to generate spiked samples. These three levels were: (1) near the detection limit, (2) at intermediate concentrations, and (3) at high concentrations. A fourth concentration level (very high) was added for lead, iron, and zinc in soil and for iron in sediment. Table 3-1 lists the numerical ranges of the target elements for each of these levels (1 through 4).

3.2.1 Environmental Samples

A total of 25 separate environmental samples were collected from the nine sample collection sites described in Chapter 2. This bulk environmental sample set included 14 soil and 11 sediment samples. The concentrations of the target elements in some of these samples, however, were too high or too low to be used for the demonstration. Therefore, the initial analytical results for each bulk sample were used to establish different sample blends for each sampling location that would better cover the desired concentration ranges.

The 14 bulk soil samples were used to create 26 separate sample blends and the 11 bulk sediment samples were used to create 19 separate sample blends. Thus, there were 45 environmental sample blends in the final demonstration sample set. Either five or seven replicate samples of each sample blend were included in the sample set for analysis during the demonstration. Table 3-2 lists the number of sample blends and the number of demonstration samples (including replicates) that were derived from the bulk environmental samples for each sampling location.

3.2.2 Spiked Samples

Spiked samples that incorporated a soil and sediment matrix native to the sampling locations were created by adding known concentrations of target elements to the background samples. The spiked concentrations were selected to ensure that a minimum of three samples was available for all concentration levels for each target element.

After initial characterization at ARDL's laboratory, all bulk background soil and sediment samples were shipped to Environmental Research Associates (ERA) to create the spiked samples. The spiked elements were applied to the bulk sample in an aqueous solution, and then each bulk spiked sample was blended for uniformity and dried before it was repackaged in sample bottles.

Six bulk background soil samples were used at ERA's laboratory to create 12 separate spiked sample blends, and four bulk sediment samples were used to create 13 separate spiked sample blends. Thus, a total of 10 bulk background samples were used to create 25 spiked sample blends. Three or seven replicate samples of each spiked sample blend were included in the demonstration sample set. Table 3-3 lists the number of sample blends and the number of demonstration samples (including replicates) that were derived from the bulk background samples for each sampling location.

3.2.3 Demonstration Sample Set

In total, 70 separate blends of environmental and spiked samples were created and a set of 326 samples was developed for the demonstration by including three, five, or seven replicates of each blend in the final demonstration sample set. Thirteen sets of the demonstration samples, consisting of 326 individual samples in 250-milliliter clean plastic sample bottles, were prepared for shipment to the demonstration site and reference laboratory.

Table 3-1. Concentration Levels for Target Elements in Soil and Sediment

Analyte	Level 1 Target Range (mg/kg)	Level 2 Target Range (mg/kg)	Level 3 Target Range (mg/kg)	Level 4 Target Range (mg/kg)
SOIL				
Antimony	40 – 400	400 – 2,000	>2,000	
Arsenic	20 – 400	400 – 2,000	>2,000	
Cadmium	50 – 500	500 – 2,500	>2,500	
Chromium	50 – 500	500 – 2,500	>2,500	
Copper	50 – 500	500 – 2,500	>2,500	
Iron	60 – 5,000	5,000 – 25,000	25,000 – 40,000	>40,000
Lead	20 – 1,000	1,000 – 2,000	2,000 – 10,000	>10,000
Mercury	20 – 200	200 – 1,000	>1,000	
Nickel	50 – 250	250 – 1,000	>1,000	
Selenium	20 – 100	100 – 200	>200	
Silver	45 – 90	90 – 180	>180	
Vanadium	50 – 100	100 – 200	>200	
Zinc	30 – 1,000	1,000 – 3,500	3,500 – 8,000	>8,000
SEDIMENT				
Antimony	40 – 250	250 – 750	>750	
Arsenic	20 – 250	250 – 750	>750	
Cadmium	50 – 250	250 – 750	>750	
Chromium	50 – 250	250 – 750	>750	
Copper	50 – 500	500 – 1,500	>1,500	
Iron	60 – 5,000	5,000 – 25,000	25,000 – 40,000	>40,000
Lead	20 – 500	500 – 1,500	>1,500	
Mercury	20 – 200	200 – 500	>500	
Nickel	50 – 200	200 – 500	>500	
Selenium	20 – 100	100 – 200	>200	
Silver	45 – 90	90 – 180	>180	
Vanadium	50 – 100	100 – 200	>200	
Zinc	30 – 500	500 – 1,500	>1,500	

Table 3-2. Number of Environmental Sample Blends and Demonstration Samples

Sampling Location	Number of Sample Blends	Number of Demonstration Samples
Alton Steel Mill Site	2	10
Burlington Northern-ASARCO East Helena Site	5	29
Kennedy Athletic, Recreational and Social Park Site	6	32
Leviathan Mine Site	7	37
Naval Surface Warfare Center, Crane Division Site	1	5
Ramsay Flats—Silver Bow Creek Superfund Site	7	37
Sulphur Bank Mercury Mine Site	9	47
Torch Lake Superfund Site	3	19
Wickes Smelter Site	5	31
TOTAL *	45	247

* Note: The totals in this table add to those for the spiked blends and replicates as summarized in Table 3-3 to bring the total number of blends to 70 and the total number of samples to 326 for the demonstration.

Table 3-3. Number of Spiked Sample Blends and Demonstration Samples

Sampling Location	Number of Spiked Sample Blends	Number of Demonstration Samples
Alton Steel Mill Site	1	3
Burlington Northern-ASARCO East Helena Site	2	6
Leviathan Mine Site	5	15
Naval Surface Warfare Center, Crane Division Site	2	6
Ramsey Flats—Silver Bow Creek Superfund Site	6	22
Sulphur Bank Mercury Mine Site	3	9
Torch Lake Superfund Site	4	12
Wickes Smelter Site	2	6
TOTAL *	25	79

* Note: The totals in this table add to those for the unspiked blends and replicates as summarized in Table 3-2 to bring the total number of blends to 70 and the total number of samples to 326 for the demonstration.

3.3 Demonstration Site and Logistics

The field demonstration occurred during the week of January 24, 2005. This section describes the selection of the demonstration site and the logistics of the field demonstration, including sample management.

3.3.1 Demonstration Site Selection

The demonstration site was selected from among the list of sample collection sites to simulate a likely field deployment. The following criteria were used to assess which of the nine sample collection sites might best serve as the demonstration site:

- Convenience and accessibility to participants in the demonstration.
- Ease of access to the site, with a reasonably sized airport that can accommodate the travel schedules for the participants.
- Program support and cooperation of the site owner.
- Sufficient space and power to support developer testing.
- Adequate conference room space to support a visitors day.
- A temperate climate so that the demonstration could occur on schedule in January.

After an extensive search for candidates, the site selected for the field demonstration was KARS Park, which is part of the Kennedy Space Center on Merritt Island, Florida. KARS Park was selected as the demonstration site for the following reasons:

- Access and Site Owner Support — Representatives from NASA were willing to support the field demonstration by providing access to the site, assisting in logistical support during the demonstration, and hosting a visitors day.

- Facilities Requirements and Feasibility — The recreation building was available and was of sufficient size to accommodate all the demonstration participants. Furthermore, the recreation building had adequate power to operate all the XRF instruments simultaneously and all the amenities to fully support the demonstration participants, as well as visitors, in reasonable comfort.

- Ease of Access to the Site — The park, located about 45 minutes away from Orlando International Airport, was selected because of its easy accessibility by direct flight from many airports in the country. In addition, many hotels are located within 10 minutes of the site along the coast at Cocoa Beach, in a popular tourist area. Weather in this area of central Florida in January is dry and sunny, with pleasant daytime temperatures into the 70s (F) and cool nights.

3.3.2 Demonstration Site Logistics

The field demonstration was held in the recreation building, which is just south of the gunnery range at KARS Park. Photographs of the KARS Park recreation building, where all the XRF instruments were set up and operated, are shown in Figures 3-2 and 3-3.

A visitors day was held on January 26, 2005 when about 25 guests came to the site to hear about the demonstration and to observe the XRF instruments in operation. Visitors day presentations were conducted in a conference building adjacent to the recreation building at KARS Park (see Figure 3-4). Presentations by NASA and EPA representatives were followed by a tour of the XRF instruments in the recreation building while demonstration samples were being analyzed.

Figure 3-2. KARS Park recreation building.

Figure 3-3. Work areas for the XRF instruments in the recreation building.

Figure 3-4. Visitors day presentation.

3.3.3 EPA Demonstration Team and Developer Field Team Responsibilities

Each technology developer sent its instrument and a field team to the demonstration site for the week of January 24, 2005. The developer's field team was responsible for unpacking, setting up, calibrating, and operating the instrument. The developer's field team was also responsible for any sample preparation for analysis using the XRF instrument.

The EPA/Tetra Tech demonstration team assigned an observer to each instrument. The observer sat beside the developer's field team, or was nearby, throughout the field demonstration and observed all activities involved in setup and operation of the instrument. The observer's specific responsibilities included:

- Guiding the developer's field team to the work area in the recreation building at KARS Park and assisting with any logistical issues involved in instrument shipping, unpacking, and setup.
- Providing the demonstration sample set to the developer's field team in accordance with the sample management plan.
- Ensuring that the developer was operating the instrument in accordance with standard procedures and questioning any unusual practices or procedures.
- Communications with the developer's field team regarding schedules and fulfilling the requirements of the demonstration.
- Recording information relating to the secondary objectives of the evaluation (see Chapter 4) and for obtaining any cost information that could be provided by the developer's field team.
- Receiving the data reported by the developer's field team for the demonstration samples, and loading these data into a temporary database on a laptop computer.

Overall, the observer was responsible for assisting the developer's field team throughout the field demonstration and for recording all pertinent information and data for the evaluation. However, the observer was not allowed to advise the developer's field team on sample processing or to provide any feedback based on preliminary inspection of the XRF instrument data set.

3.3.4 Sample Management during the Field Demonstration

The developer's field team analyzed the demonstration sample set with its XRF instrument during the field demonstration. Each demonstration sample set was shipped to the demonstration site with only a reference number on each bottle as an identifier. The reference number was tied to the source information in the EPA/Tetra Tech database, but no information was provided on the sample label that might provide the developer's field team any insight as to the nature or content of the sample. Spiked samples were integrated with the environmental samples in a random manner so that the spiked samples could not be distinguished.

The demonstration sample set was divided into 13 subsets, or batches, for tracking during the field demonstration. The samples provided to each developer's field team were randomly distributed in two fashions. First, the order of the jars within each batch was random, so that the sample order for a batch was different for each developer's field team. Second, the distribution of sample batches was random, so that each developer's field team received the sample batches in a different order.

The observer provided the developer's field team with one batch of samples at a time. When the developer's field team reported that analysis of a batch was complete, the observer would reclaim all the unused sample material from that batch and then provide the next batch of samples for analysis. Chain-of-custody forms were used to document all sample transfers. When the analysis of all batches was complete, the observer assisted the developer's field team in cleanup of the work area and repackaging the instrument and any associated equipment. The members of the developer's field team were not allowed to take any part of the demonstration samples with them when they left the demonstration site.

Samples that were not in the possession of the developer's field team during the demonstration were held in a secure storage room adjacent to the demonstration work area (see Figure 3-5). The storage room was closed and locked except when the observer retrieved samples from the room. Samples were stored at room temperature during the demonstration, in accordance with the quality assurance/quality control (QA/QC) requirements established for the project.

Figure 3-5. Sample storage room.

3.3.5 Data Management

Each of the developer's field teams was able to complete analysis of all 326 samples during the field demonstration (or during the subsequent week, in one case when the developer's field team arrived late at the demonstration site because of delays in international travel). The data produced by each developer's field team were submitted during or at the end of the field demonstration in a standard Microsoft Excel® spreadsheet. (The EPA/Tetra Tech field team had provided a template.) Since each instrument provided data in a different format, the developer's field team was responsible for reducing the data before they were submitted and for transferring the data into the Excel spreadsheet.

The observer reviewed each data submittal for completeness, and the data were then uploaded into a master Excel spreadsheet on a laptop computer for temporary storage. Only the EPA/Tetra Tech field team had access to the master Excel spreadsheet during the field demonstration.

Once the EPA/Tetra Tech field team returned to their offices, the demonstration data were transferred to an Microsoft Access® database for permanent storage. Each developer's data, as they existed in the Access database, were then provided to the developer for review. Any errors the developers identified were corrected, and the database was then finalized. All statistical analysis and data evaluation took place on this final database.

Chapter 4
Evaluation Design

This chapter presents the approach for evaluating the performance of the XRF instruments. Specifically, the sections below describe the objectives of the evaluation and the experimental design.

The *Demonstration and Quality Assurance Project Plan* (Tetra Tech 2005) provides additional details on the overall demonstration approach. However, some deviations from the plan, involving data evaluation and laboratory audits, occurred after the demonstration plan was written. For completeness, the primary changes to the written plan are documented in the final section of this chapter.

4.1 Evaluation Objectives

The overall purpose of the XRF technology demonstration was to evaluate the performance of various field XRF instruments in detecting and quantifying trace elements in soils and sediments from a variety of sites around the U.S. The performance of each XRF instrument was evaluated in accordance with primary and secondary objectives. Primary objectives are critical to the evaluation and require the use of quantitative results to draw conclusions about an instrument's performance. Secondary objectives pertain to information that is useful but that will not necessarily require use of quantitative results to draw conclusions about an instrument's performance.

The primary and secondary objectives for the evaluation are listed in Table 4-1. These objectives were based on:

- Input from MMT Program stakeholders, including developers and EPA staff.
- General expectations of users of field measurement instruments.
- The time available to complete the demonstration.
- The capabilities of the instruments that the developers participating in the demonstration intended to highlight.

4.2 Experimental Design

To address the first four primary objectives, each XRF instrument analyzed the demonstration sample set for the 13 target elements. The demonstration samples originated from multiple sampling locations across the country, as described in Chapter 2, to provide a diverse set of soil and sediment matrices. The demonstration sample set included both blended environmental samples and spiked background samples, as described in Chapter 3, to provide a wide range of concentrations and combinations of elements.

When the field demonstration was completed, the results obtained using the XRF instruments were compared with data from a reference laboratory to evaluate the performance of each instrument in terms of accuracy and comparability (Primary Objective 2). The results for replicate samples were used to evaluate precision in various concentration ranges (Primary Objective 3) and the method detection limits (MDL) (Primary Objective 1). Each of these quantitative evaluations of instrument performance was carried out for each target element. The effect of chemical and spectral interferences and of soil characteristics (Primary Objectives 4 and 5) were evaluated to help explain extreme deviations or outliers observed in the XRF results when compared with the reference laboratory results.

A second important comparison involved the average performance of all eight XRF instruments that participated in the demonstration. For the first three primary objectives (MDL, accuracy, precision), the performance of each individual instrument was compared to the overall average performance of all eight instruments. Where the result of the instrument under consideration was less than 10 percent different than the average result for all eight instruments, the result was considered "equivalent." A similar comparison was conducted with respect to cost (Primary Objective 7). These comparisons were intended to illustrate the performance of each XRF instrument in relation to its peers.

The evaluation design for meeting each objective, including data analysis procedures, is discussed in more detail in the sections below. Where specific deviations from these procedures were necessary for the data set associated with specific instruments, these deviations are described as part of the performance evaluation in Chapter 7.

4.2.1 Primary Objective 1 — Method Detection Limits

The MDL for each target element was evaluated based on the analysis of sets of seven replicate samples that contained the target element at concentrations near the detection limit. The MDL was calculated using the procedures found in Title 40 Code of Federal Regulations (CFR) Part 136, Appendix B, Revision 1.11. The following equation was used:

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

where

MDL = method detection limit
t = Student's t value for a 99 percent confidence level and a standard deviation estimate with *n-1* degrees of freedom
n = number of samples
s = standard deviation.

Table 4-1. Evaluation Objectives

Objective	Description
Primary Objective 1	Determine the MDL for each target element.
Primary Objective 2	Evaluate the accuracy and comparability of the XRF measurement to the results of laboratory reference methods for a variety of contaminated soil and sediment samples.
Primary Objective 3	Evaluate the precision of XRF measurements for a variety of contaminated soil and sediment samples.
Primary Objective 4	Evaluate the effect of chemical and spectral interference on measurement of target elements.
Primary Objective 5	Evaluate the effect of soil characteristics on measurement of target elements.
Primary Objective 6	Measure sample throughput for the measurement of target elements under field conditions.
Primary Objective 7	Estimate the costs associated with XRF field measurements.
Secondary Objective 1	Document the skills and training required to properly operate the instrument.
Secondary Objective 2	Document health and safety concerns associated with operating the instrument.
Secondary Objective 3	Document the portability of the instrument.
Secondary Objective 4	Evaluate the instrument's durability based on its materials of construction and engineering design.
Secondary Objective 5	Document the availability of the instrument and of associated customer technical support.

Based on the data provided by the characterization laboratory before the demonstration, a total of 12 sample blends (seven for soil and five for sediment) were identified for use in the MDL determination.

The demonstration approach specified the analysis of seven replicates for each of these sample blends by both the developer and the reference laboratory. It was predicted that these blends would allow the determination of a minimum of one MDL for soil and one MDL for sediment for each element, with the exception of iron. This prediction was based on the number of sample blends that contained concentrations less than 50 percent lower or higher than the lower limit of the Level 1 concentration range (from 20 to 50 ppm, depending on the element), as presented in Table 3-1.

After the field demonstration, the data sets obtained by the developers and the reference laboratory for the MDL sample blends were reviewed to confirm that they were appropriate to use in calculating MDLs. The requirements of 40 CFR 136, Appendix B, were used as the basis for this evaluation. Specifically, the CFR states that samples to be used for MDL determinations should contain concentrations in the range of 1 to 5 times the predicted MDL. On this basis, and using a nominal predicted reporting limit of 50 ppm for the target elements based on past XRF performance and developer information, a concentration of 250 ppm (5 times the "predicted" nominal MDL) was used as a threshold in selecting samples to calculate the MDL. Thus, each of the 12 MDL blends that contained mean reference laboratory concentrations less than 250 ppm were used in calculating MDLs for a given target element. Blends with mean reference laboratory concentrations greater than 250 ppm were discarded for evaluating this objective.

For each target element, an MDL was calculated for each sample blend with a mean concentration within the prescribed range. If multiple MDLs could be calculated for an element from different sample blends, these results were averaged to arrive at an overall mean MDL for the demonstration. The mean MDL for each target element was then categorized as either low (MDL less than 20 ppm), medium (MDL between 20 and 100 ppm), or high (MDL exceeds 100 ppm). No blends were available to calculate a detection limit for iron because all the blends contained substantial native concentrations of iron.

4.2.2 Primary Objective 2 — Accuracy

Accuracy was assessed based on a comparison of the results obtained by the XRF instrument with the results from the reference laboratory for each of the 70 blends in the demonstration sample set. The results from the reference laboratory were essentially used as a benchmark in this comparison, and the accuracy of the XRF instrument results was judged against them. The limitations of this approach should be recognized, however, because the reference laboratory results were not actually "true values." Still, there was a high degree of confidence in the reference laboratory results for most elements, as described in Chapter 5.

The following data analysis procedure was followed for each of the 13 target elements to assess the accuracy of an XRF instrument:

1. The results for replicate samples within a blend were averaged for both the data from the XRF instrument and the reference laboratory. Since there were 70 sample blends, this step created a maximum of 70 paired results for the assessment.
2. A blend that exhibited one or more non-detect values in either the XRF instrument or the reference laboratory analysis was excluded from the evaluation.
3. A blend was excluded from the evaluation when the average result from the reference laboratory was below a minimum concentration. The minimum concentration for exclusion from the accuracy assessment was identified as the lower limit of the lowest concentration range (Level 1 in Table 3-1), which is about 50 ppm for most elements.
4. The mean result for a blend obtained with the XRF instrument was compared with the corresponding mean result from the reference laboratory by calculating a relative percent difference (RPD). This comparison was carried out for each of the paired XRF and reference laboratory results included in the evaluation (up to 70 pairs) as follows:

$$\text{RPD} = \frac{(M_R - M_D)}{\text{average}\,(M_R, M_D)}$$

where

M_R = the mean reference laboratory measurement
M_D = the mean XRF instrument measurement.

5. Steps 1 through 4 provided a set of up to 70 RPDs for each element (70 sample blends minus the number excluded in steps 1 and 2). The absolute value of each of the RPDs was taken and summary statistics (minimum, maximum, mean and median) were then calculated.

6. The accuracy of the XRF instrument for each target element was then categorized, based on the median of the absolute values of the RPDs, as either excellent (RPD less than 10 percent), good (RPD between 10 percent and 25 percent), fair (RPD between 25 percent and 50 percent), or poor (RPD above 50 percent).

7. The set of absolute values of the RPDs for each instrument and element was further evaluated to assess any trends in accuracy versus concentration. These evaluations involved grouping the RPDs by concentration range (Levels 1 through 3 and 4, as presented in Table 3-1), preparing summary statistics for each range, and assessing differences among the grouped RPDs.

The absolute value of the RPDs was taken in step 5 to provide a more sensitive indicator of the extent of differences between the results from the XRF instrument and the reference laboratory. However, the absolute value of the RPDs does not indicate the direction of the difference and; therefore, does not reflect bias.

The populations of mean XRF and mean reference laboratory results were assessed through linear correlation plots to evaluate bias. These plots depict the linear relationships between the results for the XRF instrument and reference laboratory for each target element using a linear regression calculation with an associated correlation coefficient (r^2). These plots were used to evaluate the existence of general bias between the data sets for the XRF instrument and the reference laboratory.

4.2.3 Primary Objective 3 — Precision

The precision of the XRF instrument analysis for each target element was evaluated by comparing the results for the replicate samples in each blend. All 70 blends in the demonstration sample set (including environmental and spiked samples) were included in at least triplicate so that precision could be evaluated across all concentration ranges and across different matrices.

The precision of the data for a target element was evaluated for each blend by calculating the mean relative standard deviation (RSD) with the following equation:

$$RSD = \left|\frac{SD}{\overline{C}}\right| x\ 100$$

where

RSD = Relative standard deviation
SD = Standard deviation
$\overline{C}$ = Mean concentration.

The standard deviation was calculated using the equation:

$$SD = \left[\frac{1}{n-1}\sum_{k=1}^{n}\left(C_k - \overline{C}\right)^2\right]^{\frac{1}{2}}$$

where

SD = Standard deviation
n = Number of replicate samples
C_k = Concentration of sample K
$\overline{C}$ = Mean concentration.

The following specific procedure for data analysis was followed for each of the 13 target elements to assess XRF instrument precision:

1. The RSD for the replicate samples in a blend was calculated for both data from the XRF instrument and the reference laboratory. Since there were 70 sample blends, this step created a maximum of 70 paired RSDs for the assessment.

2. A blend that exhibited one or more non-detect values in either the XRF or the reference laboratory analysis was excluded from the evaluation.

3. A blend was excluded from the evaluation when the average result from the reference laboratory was below a minimum concentration. The minimum concentration for exclusion from the precision assessment was identified as the lower limit of the lowest concentration range (Level 1 in Table 3-1), which was about 50 ppm for most elements.

4. The RSDs for the various blends for both the XRF instrument and the reference laboratory were treated as a statistical population. Summary statistics (minimum, maximum, mean and median) were then calculated and compared for the data set as a whole and for the different concentration ranges (Levels 1 through 3 or 4).

5. The precision of the XRF instrument for each target element was then categorized, based on the median RSDs, as either excellent (RSD less than 5 percent), good (RSD between 5 percent and 10 percent), fair (RSD between 10 percent and 20 percent), or poor (RSD above 20 percent).

One primary evaluation was a comparison of the mean RSD for each target element between the XRF instrument and the reference laboratory. Using this comparison, the precision of the XRF instrument could be evaluated against the precision of accepted fixed-laboratory methods. Another primary evaluation was a comparison of the mean RSD for each target element between the XRF instrument and the overall average of all XRF instruments. Using this comparison, the precision of the XRF instrument could be evaluated against its peers.

4.2.4 Primary Objective 4 — Impact of Chemical and Spectral Interferences

The potential in the XRF analysis for spectral interference between adjacent elements on the periodic table was evaluated for the following element pairs: lead/arsenic, nickel/copper, and copper/zinc. The demonstration sample set included multiple blends where the concentration of one of these elements was greater than 10 times the concentration of the other element in the pair to facilitate this evaluation. Interference effects were identified through evaluation of the RPDs for these sample blends, which were calculated according to the equation in Section 4.2.2, since spectral interferences would occur only in the XRF data and not in the reference laboratory data.

Summary statistics for RPDs (mean, median, minimum, and maximum) were calculated for each potentially affected element for the sample blends with high relative concentrations (greater than 10 times) of the potentially interfering element. These summary statistics were compared with the RPD statistics for sample blends with lower concentrations of the interfering element. It was reasoned that spectral interference should be directly reflected in increased RPDs for the interference samples when compared with the rest of the demonstration sample set.

In addition to spectral interferences (caused by overlap of neighboring spectral peaks), the data sets were assessed for indications of chemical interferences. Chemical interferences occur when the x-rays characteristic of an element are absorbed or emitted by another element within the sample, causing low or high bias. These interferences are common in samples that contain high levels of iron, where low biases for copper and high biases for chromium can result. The evaluations for Primary Objective 4 included RPD comparisons between sample blends with high concentrations of iron (more than 50,000 ppm) and other sample blends. These RPD comparisons were performed for the specific target elements of interest (copper, chromium, and others) to assess chemical interferences from iron. Outliers and subpopulations in the RPD data sets for specific target elements, as identified through graphical means (probability plots and box plots), were also examined for potential interference effects.

The software that is included with many XRF instruments can correct for chemical interferences. The results of this evaluation were therefore intended to differentiate the instruments that incorporated effective software for addressing chemical interferences.

4.2.5 Primary Objective 5 — Effects of Soil Characteristics

The demonstration sample set included soil and sediment samples from nine locations across the U.S. and a corresponding variety of soil types and lithologies. The accuracy and precision statistics (RPD and RSD) were grouped by soil type (sample location) and the groups were compared to assess the effects of soil characteristics. Outliers and subpopulations in the RPD data sets, as identified through graphical means (correlation plots and box plots), were also examined for matrix effects.

4.2.6 Primary Objective 6 — Sample Throughput

Sample throughput is a calculation of the total number of samples that can be analyzed in a specified time. The primary factors that affect sample throughput are the time required to prepare a sample for analysis, to conduct the analytical procedure for each sample, and to process and tabulate the resulting data. The time required to prepare and to analyze demonstration samples was recorded each day that demonstration samples were analyzed.

Sample throughput can also be affected by the time required to set up and calibrate the instrument as well as the time required for quality control. The time required to perform these activities was also recorded during the field demonstration.

An overall mean processing time per sample and an overall sample throughput rate was calculated based on the total time required to complete the analysis of the demonstration sample set from initial instrument setup through data reporting. The overall mean processing time per sample was then used as the primary basis for comparative evaluations.

4.2.7 Primary Objective 7 — Technology Costs

The costs for analysis are an important factor in the evaluation and include the cost for the instrument, analytical supplies, and labor. The observer collected information on each of these costs during the field demonstration.

Based on input from each technology developer and from distributors, the instrument cost was established for purchase of the equipment and for daily, weekly, and monthly rental. Some of the technologies are not yet widely available, and the developer has not established rental options. In these cases, an estimated weekly rental cost was derived for the summary cost evaluations based on the purchase price for the instrument and typical rental to purchase price ratios for similar instruments. The costs associated with leasing agreements were also specified in the report, if available.

Analytical supplies include sample cups, spoons, x-ray film, Mylar®, reagents, and personal protective equipment. The rate that the supplies are consumed was monitored and recorded during the field demonstration. The cost of analytical supplies was estimated per sample from these consumption data and information on unit costs.

Labor includes the time required to prepare and analyze the samples and to set up and dismantle the equipment. The labor hours associated with preparing and analyzing samples and with setting up and dismantling the equipment were recorded during the demonstration. The labor costs were calculated based on this information and typical labor rates for a skilled technician or chemist.

In addition to the assessment of the above-described individual cost components, an overall cost for a field effort similar to the demonstration was compiled and compared to the cost of fixed laboratory analysis. The results of the cost evaluation are presented in Chapter 8.

4.2.8 Secondary Objective 1 — Training Requirements

Each XRF instrument requires that the operator be trained to safely set up and operate the instrument. The relative level of education and experience that is appropriate to operate the XRF instrument was assessed during the field demonstration.

The amount of specific training required depends on the complexity of the instrument and the associated software. Most developers have established training programs. The time required to complete the developer's training program was estimated and the content of the training was identified.

4.2.9 Secondary Objective 2 — Health and Safety

The health and safety requirements for operation of the instrument were identified, including any that are associated with potential exposure from radiation and to reagents. Not included in the evaluation were potential risks from exposure to site-specific hazardous materials or physical safety hazards associated with the demonstration site.

4.2.10 Secondary Objective 3 — Portability

The portability of the instrument depends on size, weight, number of components, power requirements, and reagents required. The size of the instrument, including physical dimensions and weight, was recorded (see Chapter 6). The number of components, power requirements, support structures, and reagent requirements were also recorded. A qualitative assessment of portability was conducted based on this information.

4.2.11 Secondary Objective 4 — Durability

The durability of the instrument was evaluated by gathering information on the warranty and expected lifespan of the radioactive source or x-ray tube. The ability to upgrade software or hardware also was evaluated. Weather resistance was evaluated if the instrument is intended for use outdoors by examining the instrument for exposed electrical connections and openings that may allow water to penetrate.

4.2.12 Secondary Objective 5 — Availability

The availability of the instrument from the developer, distributors, and rental agencies was documented. The availability of replacement parts and instrument-specific supplies was also noted.

4.3 Deviations from the Demonstration Plan

Although the field demonstration and subsequent data evaluations generally followed the *Demonstration and Quality Assurance Project Plan* (Tetra Tech 2005), there were some deviations as new information was uncovered or as the procedures were reassessed while the plan was executed. These deviations are documented below for completeness and as a supplement to the demonstration plan:

1. An in-process audit of the reference laboratory was originally planned while the laboratory was analyzing the demonstration samples. However, the reference laboratory completed all analysis earlier than expected, during the week of the field demonstration, and thereby created a schedule conflict. Furthermore, it was decided that the original pre-award audit was adequate for assessing the laboratory's procedures and competence.

2. The plan suggested that each result for spiked samples from the reference laboratory would be replaced by the "certified analysis" result, which was quantitative based on the amount of each element spiked, whenever the RPD between these two results was greater than 10 percent. The project team agreed that 10 percent was too stringent for this evaluation, however, and decided to use 25 percent RPD as the criterion for assessing reference laboratory accuracy against the spiked samples. Furthermore, it was found during the data evaluations that replacing individual reference laboratory results using this criterion would result in a mixed data set. Therefore, the 25 percent criterion was applied to the overall mean RPD for each element, and the "certified analysis" data set for a specific target element was used as a supplement to the reference laboratory result when this criterion was exceeded.

3. Instrument accuracy and comparability in relation to the reference laboratory (Primary Objective 2) was originally planned to be assessed based on a combination of percent recovery (instrument result divided by reference laboratory result) and RPD. It was decided during the data analysis, however, that the RPD was a much better parameter for this assessment. Specifically, it was found that the mean or median of the absolute values of the RPD for each blend was a good discriminator of instrument performance for this objective.

4. Although this step was not described in the plan, some quantitative results for each instrument were compared with the overall average of all XRF instruments. Since there were eight instruments, it was believed that a comparison of

this type did not violate EPA's agreement with the technology developers that one instrument would not be compared with another. Furthermore, this comparison provides an easy-to-understand basis for assessing instrument performance.

5. The plan proposed statistical testing in support of Primary Objectives 4 and 5. Specifically, the Wilcoxon Rank Sum (WRS) test was proposed to assist in evaluating interference effects, and the Rosner outlier test was proposed in evaluating other matrix effects on XRF data quality (EPA 2000; Gilbert 1987). However, these statistical tests were not able to offer any substantive performance information over and above the evaluations based on RPDs and regression plots because of the limited sample numbers and scatter in the data. On this basis, the use of these two statistical tests was not further explored or presented.

Chapter 5
Reference Laboratory

As described in Chapter 4, a critical part of the evaluation was the comparison of the results obtained for the demonstration sample set by the XRF instrument with the results obtained by a fixed laboratory (the reference laboratory) using conventional analytical methods. Therefore, a significant effort was undertaken to ensure that data of the highest quality were obtained as the reference data for this demonstration. This effort included three main activities:

- Selection of the most appropriate methods for obtaining reference data,
- Selection of a high-quality reference laboratory, and
- Validation of reference laboratory data and evaluation of QA/QC results.

This chapter describes the information that confirms the validity, reliability, and usability of the reference laboratory data based on each of the three activities listed above (Sections 5.1, 5.2, and 5.3). Finally, this chapter presents conclusions (Section 5.4) on the level of data quality and the usability of the data obtained by the reference laboratory.

5.1 Selection of Reference Methods

Methods for analysis of elements in environmental samples, including soils and sediments, are well established in the environmental laboratory industry. Furthermore, analytical methods appropriate for soil and sediment samples have been promulgated by EPA in the compendium of methods, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846) (EPA 1996c). Therefore, the methods selected as reference methods for the demonstration were the SW-846 methods most typically applied by environmental laboratories to soil and sediment samples, as follows:

- Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), in accordance with EPA SW-846 Method 3050B/6010B, for all target elements except mercury
- Cold vapor atomic absorption (CVAA) spectroscopy, in accordance with EPA SW-846 Method 7471A, for mercury only

Selection of these analytical methods for the demonstration was supported by the following additional considerations: (1) the methods are widely available and widely used in current site characterizations, remedial investigations, risk assessments, and remedial actions; (2) substantial historical data are available for these methods to document that their accuracy and precision are adequate to meet the objectives of the demonstration; (3) these methods have been used extensively in other EPA investigations where confirmatory data were compared with XRF data; and (4) highly sensitive alternative methods were less suitable given the broad range of concentrations that were inherent in the demonstration sample set. Specific details on the selection of each method are presented below.

Element Analysis by ICP-AES. Method 6010B (ICP-AES) was selected for 12 of the target elements because its demonstrated accuracy and precision meet the requirements of the XRF demonstration in the most cost-effective manner. The ICP-AES method is available at most environmental laboratories and substantial data exist to support the claim that the method is both accurate and precise enough to meet the objectives of the demonstration.

Inductively coupled plasma-mass spectrometry (ICP-MS) was considered as a possible analytical technique; however, fewer data were available to support the claims of accuracy and precision. Furthermore, it was available in less than one-third of the laboratories solicited for this project. Finally, ICP-MS is a technique for analysis of trace elements and often requires serial dilutions to mitigate the effect of high concentrations of interfering ions or other matrix interferences. These dilutions can introduce the possibility of error and contaminants that might bias the results. Since the matrices (soil and sediment) for this demonstration are designed to contain high concentrations of elements and interfering ions, ICP-AES was selected over ICP-MS as the instrumental method best suited to meet the project objectives. The cost per analysis is also higher for ICP-MS in most cases than for ICP-AES.

Soil/Sediment Sample Preparation by Acid Digestion. The elements in soil and sediment samples must be dissolved from the matrix into an aqueous solution by acid digestion before analysis by ICP-AES. Method 3050B was selected as the preparation method and involves digestion of the matrix using a combination of nitric and hydrochloric acids, with the addition of hydrogen peroxide to assist in degrading organic matter in the samples. Method 3050B was selected as the reference preparation method because extensive data are available that suggest it efficiently dissolves most elements, as required for good overall recoveries and method accuracy. Furthermore, this method was selected over other digestion procedures because it is the most widely used dissolution method. In addition, it has been used extensively as the digestion procedure in EPA investigations where confirmatory data were compared with XRF data.

The ideal preparation reference method would completely digest silicaceous minerals. However, total digestion is difficult and expensive and is therefore seldom used in environmental analysis. More common strong acid-based extractions, like that used by EPA Method 3050B, recover most of the heavy element content. In addition, stronger and more vigorous digestions may produce two possible drawbacks: (1) loss of elements through volatilization, and (2) increased dissolution of interfering species, which may result in inaccurate concentration values.

Method 3052 (microwave-assisted digestion) was considered as an alternative to Method 3050B, but was not selected because it is not as readily available in environmental laboratories.

Soil/Sediment Sample Preparation for Analysis of Mercury by CVAA. Method 7471A (CVAA) is the only method approved by EPA and promulgated for analysis of mercury. Method 7471A includes its own digestion procedure because more vigorous digestion of samples, like that incorporated in Method 3050B, would volatilize mercury and produce inaccurate results. This technique is widely available, and extensive data are available that support the ability of this method to meet the objectives of the demonstration.

5.2 Selection of Reference Laboratory

The second critical step in ensuring high-quality reference data was selection of a reference laboratory with proven credentials and quality systems. The reference laboratory was procured via a competitive bid process. The procurement process involved three stages of selection: (1) a technical proposal, (2) an analysis of performance audit samples, and (3) an on-site laboratory technical systems audit (TSA). Each stage was evaluated by the project chemist and a procurement specialist.

In Stage 1, 12 analytical laboratories from across the U.S. were invited to bid by submitting extensive technical proposals. The technical proposals included:

- A current statement of qualifications.
- The laboratory quality assurance manual.
- Standard operating procedures (SOP) (including sample receipt, laboratory information management, sample preparation, and analysis of elements).
- Current instrument lists.
- Results of recent analysis of performance evaluation samples and audits.
- Method detection limit studies for the target elements.
- Professional references, laboratory personnel experience, and unit prices.

Nine of the 12 laboratories submitted formal written proposals. The proposals were scored based on technical merit and price, and a short list of five laboratories was identified. The scoring was weighed heavier for technical merit than for price. The five laboratories that received the highest score were advanced to stage 2.

In stage 2, each of the laboratories was provided with a set of six samples to analyze. The samples consisted of three certified reference materials (one soil and two sediment samples) at custom spiking concentrations, as well as three pre-demonstration soil samples. The results received from each laboratory were reviewed and assessed. Scoring at this stage was based on precision (reproducibility of results for the three pre-demonstration samples), accuracy (comparison of results to certified values for the certified reference materials), and completeness of the data package (including the hard copy and electronic data deliverables). The two laboratories that received the highest score were advanced to stage 3.

In stage 3, the two candidate laboratories were subjected to a thorough on-site TSA by the project chemist. The audit consisted of a direct comparison of the technical proposal to the actual laboratory procedures and conditions. The audit also tracked the pre-demonstration samples through the laboratory processes from sample receipt to results reporting. When the audit was conducted, the project chemist verified sample preparation and analysis for the three pre-demonstration samples. Each laboratory was scored on identical checklists.

The reference laboratory was selected based on the highest overall score. The weights of the final scoring selection were as follows:

Scoring Element	Relative Importance
Audits (on site)	40%
Performance evaluation samples, including data package and electronic data deliverable	50%
Price	10%

Based on the results of the evaluation process, Shealy Environmental Services, Inc. (Shealy), of Cayce, South Carolina, received the highest score and was therefore selected as the reference laboratory. Shealy is accredited by the National Environmental Laboratory Accreditation Conference (NELAC). Once selected, Shealy analyzed all demonstration samples (both environmental and spiked samples) concurrently with the developers' analysis during the field demonstration. Shealy analyzed the samples by ICP-AES using EPA SW-846 Method 3050B/6010B and by CVAA using EPA SW-846 Method 7471A.

5.3 QA/QC Results for Reference Laboratory

All data and QC results from the reference laboratory were reviewed in detail to determine that the reference laboratory data were of sufficiently high quality for the evaluation. Data validation of all reference laboratory results was the primary review tool that established the level of quality for the data set (Section 5.3.1). Additional reviews included the on-site TSA (Section 5.3.2) and other evaluations (Section 5.3.3).

5.3.1 Reference Laboratory Data Validation

After all demonstration samples had been analyzed, reference data from Shealy were fully validated according to the EPA validation document, *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (EPA 2004c) as required by the *Demonstration and Quality Assurance Project Plan* (Tetra Tech 2005). The reference laboratory measured 13 target elements, including antimony, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, vanadium, and zinc. The reference laboratory reported results for 22 elements at the request of EPA; however, only the data for the 13 target elements were validated and included in data comparisons for meeting project objectives. A complete summary of the validation findings for the reference laboratory data is presented in Appendix C.

In the data validation process, results for QC samples were reviewed for conformance with the acceptance criteria established in the demonstration plan. Based on the validation criteria specified in the demonstration plan, all reference laboratory data were declared valid (were not rejected). Thus, the completeness of the data set was 100 percent. Accuracy and precision goals were met for most of the QC samples, as were the criteria for comparability, representativeness, and sensitivity. Thus, all reference laboratory data were deemed usable for comparison to the data obtained by the XRF instruments.

Only a small percentage of the reference laboratory data set was qualified as undetected as a result of blank contamination (3.3 percent) and estimated because of matrix spike and matrix spike duplicate (MS/MSD) recoveries (8.7 percent) and serial dilutions results (2.5 percent). Table 5.1 summarizes the number of validation qualifiers applied to the reference laboratory data according to QC type. Of the three QC types, only the MS/MSD recoveries warranted additional evaluation. The MS/MSD recoveries for antimony were marginally low (average recovery of 70.8 percent) when compared with the QC criterion of 75 to 125 percent recovery. It was concluded that low recoveries for antimony are common in analysis of soil and sediment by the prescribed methods and likely result from volatilization during the vigorous acid digestion process or spectral interferences found in soil and sediments matrices (or both). In comparison to antimony, high or low recoveries were observed only on an isolated basis for the other target metals (for example, lead and mercury) such that the mean and median percent recoveries were well within the required range. Therefore, the project team decided to evaluate the XRF data against the reference laboratory data for all 13 target elements and to evaluate the XRF data a second time against the ERA certified spike values for antimony only. These comparisons are discussed in Section 7.1. However, based on the validation of the complete reference data set and the low occurrence of qualified data, the reference laboratory data set as a whole was declared of high quality and of sufficient quality to make valid comparisons to XRF data.

5.3.2 Reference Laboratory Technical Systems Audit

The TSA of the Shealy laboratory was conducted by the project chemist on October 19, 2004, as part of the selection process for the reference laboratory. The audit included the review of element analysis practices (including sample preparation) for 12 elements by EPA Methods 3050B and 6010B and for total mercury by EPA Method 7471A. All decision-making personnel for Shealy were present during the TSA, including the laboratory director, QA officer, director of inorganics analysis, and the inorganics laboratory supervisor.

Project-specific requirements were reviewed with the Shealy project team as were all the QA criteria and reporting requirements in the demonstration plan. It was specifically noted that the demonstration samples would be dried, ground, and sieved before they were submitted to the laboratory, and that the samples would be received with no preservation required (specifically, no chemical preservation and no ice). The results of the performance audit were also reviewed.

No findings or nonconformances that would adversely affect data quality were noted. Only two minor observations were noted; these related to the revision dates of two SOPs. Both observations were discussed at the debriefing meeting held at the laboratory after the TSA. Written responses to each of the observations were not required; however, the laboratory resolved these issues before the project was awarded. The auditor concluded that Shealy complied with the demonstration plan and its own SOPs, and that data generated at the laboratory should be of sufficient and known quality to be used as a reference for the XRF demonstration.

5.3.3 Other Reference Laboratory Data Evaluations

The data validation indicated that all results from the reference laboratory were valid and usable for comparison to XRF data, and the pre-demonstration TSA indicated that the laboratory could fully comply with the requirements of the demonstration plan for producing data of high quality. However, the reference laboratory data were evaluated in other ways to support the claim that reference laboratory data are of high quality. These evaluations included the (1) assessment of accuracy based on ERA-certified spike values, (2) assessment of precision based on replicate measurements within the same sample blend, and (3) comparison of reference laboratory data to the initial characterization data that was obtained when the blends were prepared. Each of these evaluations is briefly discussed in the following paragraphs.

Blends 46 through 70 of the demonstration sample set consisted of certified spiked samples that were used to assess the accuracy of the reference laboratory data. The summary statistics from comparing the "certified values" for the spiked samples with the reference laboratory results are shown in Table 5-2. The target for percent recovery was 75 to 125 percent. The mean percent recoveries for 12 of the 13 target elements were well within this accuracy goal. Only the mean recovery for antimony was outside the goal (26.8 percent). The low mean percent recovery for antimony supported the recommendation made by the project team to conduct a secondary comparison of XRF data to ERA-certified spike values for antimony. This secondary evaluation was intended to better understand the impacts on the evaluation of the low bias for antimony in the reference laboratory data. All other recoveries were acceptable. Thus, this evaluation further supports the conclusion that the reference data set is of high quality.

Table 5-1. Number of Validation Qualifiers

Element	Number and Percentage of Qualified Results per QC type[1]					
	Method Blank		MS/MSD		Serial Dilution	
	Number	Percent[2]	Number	Percent[2]	Number	Percent[2]
Antimony	5	1.5	199	61.0	8	2.4
Arsenic	12	3.7	3	0.9	10	3.1
Cadmium	13	4.0	0	0	6	1.8
Chromium	0	0	0	0	10	3.1
Copper	1	0.3	0	0	8	2.4
Iron	0	0	0	0	10	3.1
Lead	0	0	34	10.5	11	3.4
Mercury	68	20.9	31	9.5	4	1.2
Nickel	0	0	0	0	10	3.1
Selenium	16	4.9	0	0	3	0.9
Silver	22	6.7	102	31.3	7	2.1
Vanadium	0	0	0	0	9	2.8
Zinc	1	0.3	0	0	10	3.1
Totals	138	3.3	369	8.7	106	2.5

Notes:

MS	Matrix spike.
MSD	Matrix spike duplicate.
QC	Quality control.

[1] This table presents the number of "U" (undetected) and "J" (estimated) qualifiers added to the reference laboratory data during data validation. Though so qualified, these results are considered usable for the demonstration. As is apparent in the "Totals" row at the bottom of this table, the amount of data that required qualifiers for any specific QC type was invariably less than 10 percent. No reference laboratory data were rejected (that is, qualified "R") during the data validation.

[2] Percents for individual elements are calculated based on 326 results per element. Total percents at the bottom of the table are calculated based on the total number of results for all elements (4,238).

All blends (1 through 70) were prepared and delivered with multiple replicates. To assess precision, percent RSDs were calculated for the replicate sample results submitted by the reference laboratory for each of the 70 blends. Table 5-3 presents the summary statistics for the reference laboratory data for each of the 13 target elements. These summary statistics indicate good precision in that the median percent RSD was less than 10 percent for 11 out of 13 target elements (and the median RSD for the other two elements was just above 10 percent). Thus, this evaluation further supports the conclusion that the reference data set is of high quality.

ARDL, in Mount Vernon, Illinois, was selected as the characterization laboratory to prepare environmental samples for the demonstration. As part of its work, ARDL analyzed several samples of each blend to evaluate whether the concentrations of the target elements and the homogeneity of the blends were suitable for the demonstration. ARDL analyzed the samples using the same methods as the reference laboratory; however, the data from the characterization laboratory were not validated and were not intended to be equivalent to the reference laboratory data. Rather, the intent was to use the results obtained by the characterization laboratory as an additional quality control check on the results from the reference laboratory.

A review of the ARDL characterization data in comparison to the reference laboratory data indicated that ARDL obtained lower recoveries of several elements. When expressed as a percent of the average reference laboratory result (percent recovery), the median ARDL result was below the lower QC limit of 75 percent recovery for three elements — chromium, nickel, and selenium. This discrepancy between data from the reference laboratory and ARDL was determined to have no significant impact on reference laboratory data quality for three reasons: (1) the ARDL data were obtained on a rapid turnaround basis to evaluate homogeneity — accuracy was not a specific goal, (2) the ARDL data were not validated, and (3) all other quality measurement for the reference laboratory data indicated a high level of quality.

5.4 Summary of Data Quality and Usability

A significant effort was undertaken to ensure that data of high quality were obtained as the reference data for this demonstration. The reference laboratory data set was deemed valid, usable, and of high quality based on the following:

- Comprehensive selection process for the reference laboratory, with multiple levels of evaluation.
- No data were rejected during data validation and few data qualifiers were added.
- The observations noted during the reference laboratory audit were only minor in nature; no major findings or non-conformances were documented.
- Acceptable accuracy (except for antimony, as discussed in Section 5.3.3) of reference laboratory results in comparison to spiked certified values.
- Acceptable precision for the replicate samples in the demonstration sample set.

Based on the quality indications listed above, the reference laboratory data were used in the evaluation of XRF demonstration data. A second comparison was made between XRF data and certified values for antimony (in Blends 46 through 70) to address the low bias exhibited for antimony in the reference laboratory data.

Table 5-2. Percent Recovery for Reference Laboratory Results in Comparison to ERA Certified Spike Values for Blends 46 through 70

Statistic	Sb	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Se	Ag	V	Zn
Number of %R values	16	14	20	12	20	NC	12	15	16	23	20	15	10
Minimum %R	12.0	65.3	78.3	75.3	51.7	NC	1.4	81.1	77.0	2.2	32.4	58.5	0.0
Maximum %R	36.1	113.3	112.8	108.6	134.3	NC	97.2	243.8	116.2	114.2	100.0	103.7	95.2
Mean %R[1]	**26.8**	88.7	90.0	94.3	92.1	NC	81.1	117.3	93.8	89.9	78.1	90.4	90.6
Median %R[1]	**28.3**	90.1	87.3	97.3	91.3	NC	88.0	93.3	91.7	93.3	84.4	95.0	91.3

Notes:

[1] Values shown in bold fall outside the 75 to 125 percent acceptance criterion for percent recovery.

ERA = Environmental Resource Associates, Inc.

NC = Not calculated.

%R = Percent recovery.

Source of certified values: Environmental Resource Associates, Inc.

Sb	Antimony
As	Arsenic
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
Pb	Lead
Hg	Mercury
Ni	Nickel
Se	Selenium
Ag	Silver
V	Vanadium
Zn	Zinc

Table 5-3. Precision of Reference Laboratory Results for Blends 1 through 70

Statistic	Sb	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Se	Ag	V	Zn
Number of %RSDs	43	69	43	69	70	70	69	62	68	35	44	69	70
Minimum %RSD	1.90	0.00	0.91	1.43	0.00	1.55	0.00	0.00	0.00	0.00	1.02	0.00	0.99
Maximum %RSD	78.99	139.85	40.95	136.99	45.73	46.22	150.03	152.59	44.88	37.30	54.21	43.52	48.68
Mean %RSD[1]	17.29	13.79	12.13	11.87	10.62	10.56	14.52	16.93	10.28	13.24	12.87	9.80	10.94
Median %RSD[1]	11.99	10.01	9.36	8.29	8.66	8.55	9.17	7.74	8.12	9.93	8.89	8.34	7.54

Notes:

[1] Values shown in bold fall outside precision criterion of less than or equal to 25 %RSD.

%RSD = Percent relative standard deviation.

Based on the three to seven replicate samples included in Blends 1 through 70.

Sb	Antimony
As	Arsenic
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
Pb	Lead
Hg	Mercury
Ni	Nickel
Se	Selenium
Ag	Silver
V	Vanadium
Zn	Zinc

Chapter 6
Technology Description

The ZSX Mini II XRF analyzer is manufactured by Rigaku, Inc. This chapter provides a technical description of the ZSX Mini II based on information obtained from Rigaku and observation of this analyzer during the field demonstration. This section also identifies a Rigaku company contact, where additional technical information may be obtained.

6.1 General Description

The ZSX Mini II is a wavelength-dispersive XRF analyzer that operates differently from an energy-dispersive XRF analyzer. Wavelength-dispersive XRF analyzers differentiate the x-ray energies emitted from a sample by dispersing the x-rays into different wavelength ranges using crystals. Conversely, energy-dispersive XRF analyzers differentiate between x-ray energies emitted based on the voltages measured by the detector. For some applications, wavelength-dispersive XRF analyzers can achieve high resolutions and good sensitivity. For example, laboratory-grade wavelength-dispersive XRF analyzers have resolved significant concentrations of arsenic and lead in many sample matrixes that pose challenges to energy-dispersive instruments.

Wavelength-dispersive XRFs have historically been large, laboratory-bound instruments with significant requirements for power and cooling. The ZSX Mini II, however, is a smaller, transportable unit that can operate without additional cooling fluids on standard 110-volt circuits. The unit can employ an economical gas proportional counter as a detector rather than a diode detector with a multi-channel analyzer (used by energy-dispersive analyzers) because wavelength resolution is achieved with the crystals. The ZSX Mini II is shown in a benchtop configuration in Figure 6-1. Technical specifications for the ZSX Mini II are presented in Table 6-1.

Figure 6-1. Rigaku ZSX Mini II XRF analyzer set up for bench-top analysis.

6.2 Instrument Operations during the Demonstration

The ZSX Mini II and accessories were shipped by a professional freight service to the demonstration site in two wooden shipping crates with styrofoam padding. The ZSX Mini II is transportable; however, a sturdy table is required for bench-top configuration because it weighs approximately 260 pounds (120 kg). Peripheral equipment included the 12-position sample changer; a vacuum pump used to evacuate the sample chamber to reduce formation of oxides in the sample matrix; and a personal computer (PC) loaded with Microsoft Windows XP® and the ZSX Mini II calibration and operational software.

6.2.1 Setup and Calibration

Rigaku assembled the ZSX Mini II and initialized the application software in about 1.5 hours. An experienced technician can set up the analyzer in 1 to 2 hours; an inexperienced technician may need 2 to 3

Table 6-1. Rigaku ZSX Mini II XRF Technical Specifications

Weight:	260 pounds (120 kg).
Dimensions:	570 millimeters (mm) wide, 500 mm deep, 250 mm high
Excitation Source:	50-Watt, 40-kilovolt (kV), 1.25-milli-amp, air-cooled end-window x-ray tube (with palladium or rhodium as an anode material).
X-ray Optics:	Analyzing crystals for x-ray dispersion include lithium fluoride (LiF), pentaerythritol (PeT), and thallium acid phthalate (TAP) operating on a revolving changer. Optional crystals include RX35 and germanium.
Detector:	Scintillation detector for analysis of titanium through uranium. Can be equipped with a gas proportional counter for light elements, requiring management of argon/methane carrier gas. Optional vacuum or helium environments for enhanced performance in analyzing light elements.
Signal Processing:	Digital signal processing unit.
Software:	Windows XP-based, multi-function software package for instrument control, spectra accumulation, calibration, and quantification (includes fundamental parameters methods).
Element Range:	From fluorine to uranium.
Operating Environment:	Temperature: 15 to 28 °C; less than 75 percent relative humidity (non-condensing).
Sample Container:	25-mm plastic sample cups with polypropylene windows.
Variants:	ZSX Mini II with single sample changer. (Sample spinner is available.) ZSX Mini II with 12-position sample changer. ZSX Mini II can be adapted to accommodate oversize or irregular objects.
Power:	AC single phase 110 Volts, 10 Amps, 50/60 Hertz

hours for setup. A factory-new XRF analyzer may take 4 to 6 hours to uncrate, set up, and initialize all computer software. The Rigaku XRF analyzer software was observed to be self-explanatory in terms of analyzer start up. Menus guided the user through turning on the x-ray tube and initializing the XRF spectrometer optics and detector. The 13 individual elements, their characteristic energy wavelengths for monitoring, and the units of measure were selected using the software.

The ZSX Mini II can be calibrated using the fundamental parameters procedure or empirically using reference standards and site-specific calibration materials. The ZSX Mini II used the factory calibration for this demonstration and verified the results using a calibration reference material provided by the U.S. Geological Survey. After the analyzer was set up at the demonstration site, the stored calibration curve information was used to calibrate the instrument, and known reference materials were analyzed to verify that the calibration curve was loaded. A single empirical calibration curve was used for all analysis during the demonstration. Other quality control samples used during the demonstration included a silicon dioxide blank and other standard reference materials as calibration verification checks.

6.2.2 Demonstration Sample Processing

Rigaku sent a two-man team to the demonstration site to process the demonstration samples using the ZSX Mini II. The field team including an instrument applications specialist, who operated the instrument and reduced the data, and a sales representative, who served as the sample preparation technician.

Sample preparation by Rigaku for this demonstration involved assembling the polypropylene sample cups; attaching a snap ring to support a Mylar® film across one end, filling the cup with the sample, and attaching a Teflon® film across the other end (see Figure 6-2). The Teflon® film was perforated to allow venting and minimize rupture of the sample when a vacuum was applied during analysis. A unique sample identification (ID) number was marked in permanent marker on the Teflon® film for sample identification. The sequence of events for each sample batch involved:

- Loading a batch of 12 sample cups into the 12-position sample changer and placing it into the XRF analyzer (see Figure 6-3).
- Starting the XRF analysis included sequential readings of wavelength and the intensity of the characteristic fluorescence produced by each sample. The intensity of the fluorescence at the characteristic wavelength for each element was converted to milligrams per kilogram based on the calibration.
- Reviewing the data after the sample batch had been analyzed and verifying the sample ID numbers.
- Downloading data for each sample batch onto a Microsoft Excel® spreadsheet.
- Transferring the daily results from the ZSX Mini II data processor to a USB portable storage device for transfer to the demonstration oversight team.

Each day, the results from the previous day were transferred to the Tetra Tech demonstration team via a USB portable storage drive.

Figure 6-2. Rigaku technician filling a sample cup for analysis.

Figure 6.3. Samples placed into the 12-position sample changer awaiting analysis.

6.3 General Demonstration Results

Rigaku analyzed all 326 soil and sediment samples in 4 days using the ZSX Mini II wavelength-dispersive XRF analyzer. Rigaku was able to prepare, analyze, and report 80 to 90 samples in a 12-hour day during the demonstration. (Rigaku had expected to analyze about 120 to 150 samples each day.)

Data processing for the demonstration samples was completed within the ZSX Mini II data processor that is part of the XRF analyzer. The ZSX Mini II data processor stopped acquiring data several times during the demonstration, which required re-analysis of entire sample batches. Data acquisition issues continued to plague the analyzer even after the ZSX Mini II computer had been replaced, new application names for each batch had been created and saved, and smaller batch sizes run. The computer issue was random, except that it always stopped while the instrument was analyzing for vanadium. It was unclear whether the issue was related to hardware or software.

6.4 Contact Information

Additional information on Rigaku's ZSX Mini II XRF analyzer is available from the following source:

Mr. Jose Brum
Rigaku Inc.
14 Ruth Circle
Haverhill, Massachusetts 01832
Telephone: (978) 374-7725
Email: jbrum@RigakuMSC.com

Chapter 7
Performance Evaluation

As discussed in Chapter 6, Rigaku analyzed all 326 demonstration samples of soil and sediment at the field demonstration site between January 24 and 27, 2005. A complete set of electronic data in Microsoft Excel® spreadsheet format was delivered to the EPA and Tetra Tech field team before Rigaku demobilized from the site on January 28, 2005. All data Rigaku provided at the close of the demonstration are tabulated and compared with the reference laboratory data and the ERA-certified spike concentrations, as applicable, in Appendix D.

The data set for the ZSX Mini II was reviewed and evaluated in accordance with the primary and secondary objectives of the demonstration. The findings of the evaluation for each objective are presented below.

7.1 Primary Objective 1 — Method Detection Limits

Samples were selected to calculate MDLs for each target element from the 12 potential MDL sample blends, as described in Section 4.2.1. Rigaku reported the instrument response for each target element in each sample; the instrument response — whether positive or negative — was used to calculate the MDL.

The MDLs calculated for the ZSX Mini II are presented in Table 7-1. As shown, the data for the MDL blends allowed between eight and 12 individual MDLs to be calculated for each target element. (Iron was not included in the MDL evaluation, as was discussed in Section 4.2.1.) The mean MDLs in Table 7-1 are classified as follows:

- Very low (1 to 20 ppm): copper, mercury, nickel, selenium, and zinc.
- Low (20 to 50 ppm): arsenic, lead, silver, and vanadium.
- Medium (50 to 100 ppm): antimony, cadmium, and chromium.
- High (greater than 100 ppm): none.

Instrument response remained fairly consistent, with very few extreme values, for the target elements in the “very low” and “low” categories. No trends could be discerned in terms of sample matrix (soil versus sediment) or blend. For antimony and cadmium, however, the MDLs may be inflated by analytical results that were biased high. For the 12 MDL sample blends, the ZSX Mini II measured concentrations of antimony that ranged from 124 ppm to 565 ppm with a mean of 283 ppm, while the reference laboratory reported seven non-detect concentrations and a maximum concentration of 118 ppm. Similarly, the ZSX Mini II measured concentrations of cadmium that ranged from 328 ppm to 896 ppm with a mean of 609 ppm, while the reference laboratory reported six non-detect concentrations and a maximum concentration of 91 ppm. It is possible that a systematic high bias in the ZSX Mini II was a cause of the high MDLs for antimony and cadmium. (The correlation plots in Section 7.2 below also indicated positive biases at low concentrations for these and other target elements.) The mean MDL for chromium (61 ppm) appears to reasonably represent true instrument sensitivity for this element because the concentrations reported from the ZSX Mini II for the detection limit blends did not illustrate any major discrepancies when compared to the results from the reference laboratory.

Table 7-1. Evaluation of Sensitivity — Method Detection Limits for the ZSX Mini II[1]

		Antimony			Arsenic			Cadmium			Chromium		
Matrix	**Blend No.**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**
Soil	2	**111**	451	17	**34**	102	1.5	**118**	896	ND	**107**	115	167
Soil	5	**43**	159	ND	**45**	58	47	**34**	603	1.9	**62**	98	121
Soil	6	**77**	456	8	NC	213	477	**35**	578	12	**46**	112	133
Soil	8	**306**	450	118	NC	1,537	3,943	**32**	328	91	**78**	138	55
Soil	10	**66**	211	ND	**44**	48	39	**109**	661	0.96	**67**	79	116
Soil	12	**105**	565	62	NC	306	559	**NC**	671	263	**99**	90	101
Soil	18	**65**	200	ND	**20**	17	9	**60**	601	ND	**38**	154	150
Sediment	29	**41**	124	ND	**20**	-21	10	**41**	490	ND	**39**	72	63
Sediment	31	**43**	170	ND	**40**	-11	11	**30**	534	ND	**56**	105	133
Sediment	32	**40**	191	ND	**22**	34	31	**62**	618	ND	**30**	70	75
Sediment	39	**45**	208	ND	**61**	13	14	**41**	645	ND	**44**	81	102
Sediment	65	**92**	205	11	NC	181	250	**62**	681	44	**NC**	200	303
Mean		**86**			**36**			**57**			**61**		

		Copper			Lead			Mercury			Nickel		
Matrix	**Blend No.**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**
Soil	2	**15**	60	47	NC	780	1,200	**18**	62	ND	**10**	92	83
Soil	5	**13**	42	49	**17**	6	78	**8**	26	ND	**7**	41	60
Soil	6	**9**	99	160	NC	1,993	3,986	**11**	27	0.83	**13**	44	70
Soil	8	NC	739	1,243	NC	17,262	33,429	**13**	19	15	**9**	54	57
Soil	10	**10**	25	31	**13**	-14	72	**15**	27	0.14	**9**	44	60
Soil	12	NC	494	747	NC	2,180	4,214	**21**	26	1.8	**10**	58	91
Soil	18	**5**	30	50	**26**	-50	17	**15**	44	56	**13**	101	213
Sediment	29	NC	930	1,986	**27**	-65	33	**17**	6	0.24	**8**	44	72
Sediment	31	NC	708	1,514	**22**	-56	51	**27**	15	ND	**11**	98	196
Sediment	32	**11**	27	36	**20**	-38	26	**7**	32	ND	**6**	75	174
Sediment	39	**13**	68	94	**20**	-29	27	**31**	48	ND	**11**	99	202
Sediment	65	**8**	56	69	**19**	-22	25	**21**	58	32	**25**	134	214
Mean		**11**			**21**			**17**			**11**		

Table 7-1. Evaluation of Sensitivity — Method Detection Limits for the ZSX Mini II[1] (Continued)

		Selenium			**Silver**			**Vanadium**			**Zinc**		
Matrix	**Blend No.**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**	**Calc. MDL[2]**	**ZSX Mini Conc.[3]**	**Ref. Lab Conc.[4]**
Soil	2	**4**	16	ND	**37**	305	ND	**14**	22	1.2	**22**	44	24
Soil	5	**3**	8	ND	**20**	207	0.93	**29**	73	55	**12**	146	229
Soil	6	**4**	8	ND	**15**	196	14	**24**	69	56	NC	401	886
Soil	8	**4**	17	ND	**8**	115	144	**16**	59	34	NC	2,538	5,657
Soil	10	**3**	6	ND	**22**	226	ND	**21**	67	51	**29**	74	92
Soil	12	**4**	11	15	**19**	201	38	**19**	62	45	NC	1,217	2,114
Soil	18	**3**	6	ND	**17**	207	ND	**41**	119	67	**2**	63	90
Sediment	29	**4**	1	ND	**24**	170	ND	**22**	141	96	**10**	92	160
Sediment	31	**3**	2	ND	**9**	188	6.2	**17**	122	76	**9**	71	137
Sediment	32	**4**	7	4.6	**18**	215	ND	**12**	85	57	**33**	58	69
Sediment	39	**8**	10	ND	**27**	217	ND	**15**	55	38	**12**	90	137
Sediment	65	**6**	16	22	**30**	226	41	**15**	51	31	NC	1,125	1,843
Mean		**4**			**21**			**20**			**16**		

Notes:

[1] Detection limits and concentrations are milligrams per kilogram (mg/kg), or parts per million (ppm).

[2] Cells that appear in bold typeface show MDLs calculated for the ZSX Mini II from the 12 MDL sample blends in this technology demonstration.

[3] This column lists the mean concentration reported for this MDL sample blend by the ZSX Mini II.

[4] This column lists the mean concentration reported for this MDL sample blend by the reference laboratory.

Calc.	Calculated.
Conc.	Concentration.
MDL	Method detection limit.
NC	The MDL was not calculated because reference laboratory concentrations exceeded five times the expected MDL range (approximately 50 ppm, depending on the element) or an insufficient number of detected concentrations were reported.
ND	One or more results for this blend were reported as “Not Detected.” Blends with one or more ND result as reported by the XRF were not used for calculating the MDL for this element.
Ref. Lab.	Reference laboratory.

The mean MDLs calculated for the ZSX Mini II are compared in Table 7-2 with the mean MDLs for all eight XRF instruments that participated in the demonstration and with the mean MDLs derived from performance data presented in EPA Method 6200 (EPA 1998e). As shown, the mean MDLs for the ZSX Mini II are generally lower than were calculated from EPA Method 6200 data. The exception is antimony where, as noted above, high bias for the ZSX Mini II data appears to have produced a mean MDL that is higher than the available Method 6200 data. When compared with the all-instrument mean MDLs, the ZSX Mini II exhibited high relative mean MDLs for antimony and arsenic. Mean MDLs for the ZSX Mini II were less than one-half the all-instrument means for copper, nickel, selenium, silver, and zinc.

7.2 Primary Objective 2 — Accuracy and Comparability

The number of demonstration sample blends that met the criteria for evaluation of accuracy, as described in Section 4.2.2, were adequate for all the target elements and ranged from 24 (mercury) to 70 (iron). RPDs between the mean concentrations obtained from the ZSX Mini II and the reference laboratory were calculated for each blend that met the criteria for an element.

Table 7-3 presents the median RPDs, along with the number of RPD results used to calculate the median, for each target element. These statistics are provided for the demonstration as a whole, as well as for subpopulations grouped by medium (soil versus sediment) and concentration level (Levels 1 through 4, as documented in Table 3-1). Additional summary statistics for the RPDs (minimum, maximum, and mean) are provided in Appendix E (Table E-1).

Table 7-2. Comparison of ZSX Mini II MDLs to All–Instrument Mean MDLs and EPA Method 6200 Data[1]

Element	ZSX Mini II Mean MDLs[2]	All XRF Instrument Mean MDLs[3]	EPA Method 6200 Mean Detection Limits[4]
Antimony	86	61	55 [5]
Arsenic	36	26	92
Cadmium	57	70	NR
Chromium	61	83	376
Copper	11	23	171
Lead	21	40	78
Mercury	17	23	NR
Nickel	11	50	100 [5]
Selenium	4	8	NR
Silver	21	42	NR
Vanadium	20	28	NR
Zinc	16	38	89

Notes:

[1] Detection limits are in units of milligrams per kilogram (mg/kg), or parts per million (ppm).

[2] The mean MDLs calculated for this technology demonstration, as presented in Table 7-1.

[3] The mean MDLs calculated for all eight XRF instruments that participated in the technology demonstration.

[4] Mean values calculated from Table 4 of Method 6200 (EPA 1998e, www.epa.gov/sw-846).

[5] Only one value reported.

EPA U.S. Environmental Protection Agency.

MDL Method detection limit.

NR Not reported; no MDLs reported for this element.

Accuracy was classified as follows for the target elements based on the overall median RPDs:

- Very good: (median RPD less than 10 percent): none.
- Good (median RPD between 10 and 25 percent): none.
- Fair (median RPD between 25 percent and 50 percent): arsenic, chromium, copper, silver, vanadium, and zinc.
- Poor (median RPD greater than 50 percent): antimony, cadmium, iron, lead, mercury, nickel, and selenium.

The highest overall median RPD of 101 percent was calculated for selenium.

The median RPD was used for this evaluation because it is less affected by extreme values than is the mean. (The initial evaluation of the RPD populations showed that they were right-skewed or lognormal.) However, the classification of the elements based on accuracy generally stayed the same when the mean rather than the median RPD was used for the evaluation (Table E-1). The ability to evaluate the classification by medium (soil versus sediment) or by concentration range is limited by the variability of the data set.

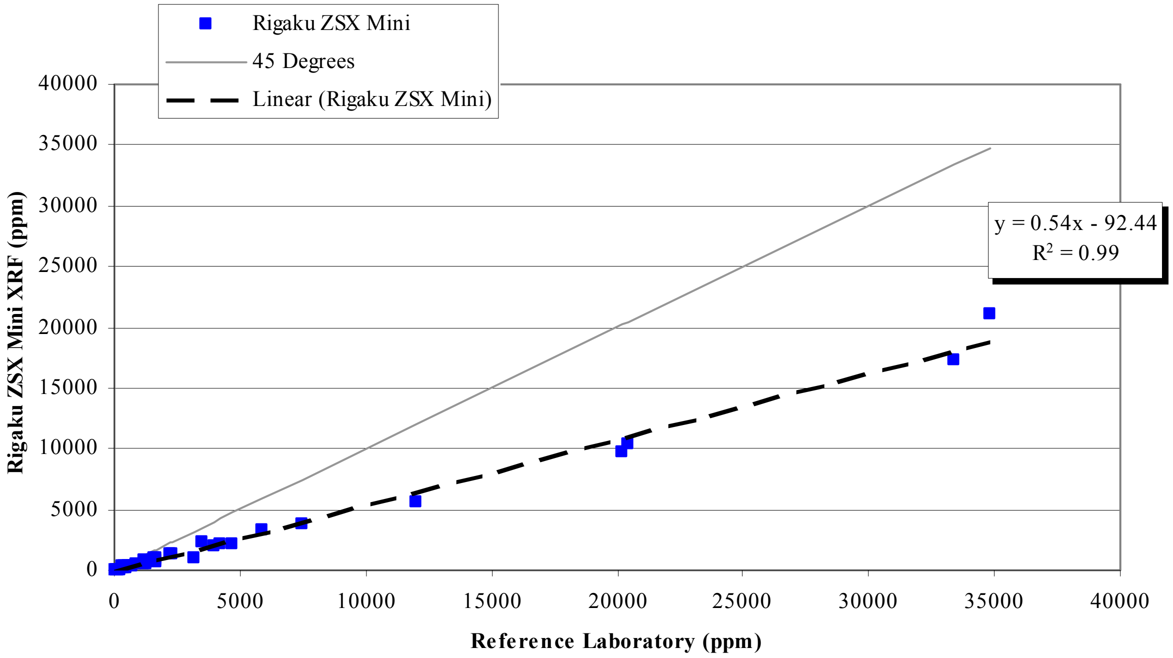
The only significant difference or trend noted in terms of sample matrix or concentration levels were low relative median RPDs in the Level 1 concentration samples when compared with the higher concentration levels. This effect was observed for a majority of the target elements (10 of 13) in soil and a smaller number (four) in sediment. For many target elements (arsenic, chromium, copper, iron, lead, selenium, and zinc), the effect was significant with median RPDs falling into the “good” to “very good” categories as compared with generally “poor” accuracy in the higher concentration levels. This observation implies that the ZSX Mini II may provide greater accuracy for less complex sample matrixes that contain lower concentrations of target elements. The developer may need to further refine instrument calibration and quantitation algorithms to better analyze samples that contain high concentrations of multiple target elements.

Section 5.3.3 indicated that reference laboratory data for antimony were consistently biased low when compared with the ERA-certified spike concentrations. This effect may be caused by volatilization of the antimony compounds used for spiking, resulting in loss of antimony during the sample digestion process at the reference laboratory. Therefore, Table 7-3 includes a second accuracy evaluation for antimony, comparing the results from the ZSX Mini II with the ERA-certified values. However, use of these values did not improve the RPDs for antimony.

As an additional comparison, Table 7-3 overall average of the median RPDs for all eight XRF instruments. Complete summary statistics for the RPDs across all eight XRF instruments are included in Appendix E (Table E-1). Table 7-3 indicates that the median RPDs for the ZSX Mini II were well above the all-instrument medians for 12 of the 13 target elements (vanadium was the only exception). These observations included the RPDs for antimony calculated versus the ERA-certified spike values, which were significantly lower than the RPDs versus the reference laboratory data for many of the other XRF instruments participating in the demonstration.

In addition to calculating RPDs, the evaluation of accuracy included preparing linear correlation plots of ZSX Mini II concentration values against the reference laboratory values. These plots are presented for the individual target elements in Figures E-1 through E-13 of Appendix E. The plots include a 45-degree line that shows the “ideal” relationship between the ZSX Mini II data and the reference laboratory data, as well as a “best fit” linear equation ($y = mx + b$, where *m* is the slope of the line and *b* is the y-intercept of the line) and correlation coefficient (r^2) to help illustrate the “actual” relationship between the two methods. To be considered accurate, the correlation coefficient should be greater than 0.9, the slope (m) should be between 0.75 and 1.25, and the y-intercept (b) should be relatively close to zero (that is, plus or minus the mean MDL in Table 7-1). Table 7-4 lists the results for these three correlation parameters and indicates that no target elements met all three accuracy criteria.

Figure 7-1: Linear correlation plot for lead indicating low instrument bias.



The correlation coefficients for arsenic, chromium, copper, iron, lead, mercury, nickel, selenium, and zinc were greater than 0.9, indicating a consistent instrument response to differences in concentration. However, the slopes (m) for each of these target elements were between 0.27 and 0.59, indicating a consistent low bias. Furthermore, only copper had a y-intercept that was less than the detection limit. A correlation plot for lead is presented in Figure 7-1 as an example of representative instrument performance for this group of target elements.

Overall correlation of the ZSX Mini II data with the reference laboratory was low for antimony, cadmium, silver, and vanadium. High intercepts combined with low slopes for cadmium and vanadium actually meant that a significant positive bias changed to a significant negative bias as concentrations increased for these elements. The correlation coefficients for antimony and silver were 0.1 or less, indicating that the instrument response essentially did not correlate with the reference laboratory data. On this basis, it appears that the ZSX Mini II does not provide accurate data for antimony and silver, in that its data cannot be correlated with other reference methods. The correlation plot for silver is presented in Figure 7-2 as an example.

Table 7-3. Evaluation of Accuracy — Relative Percent Differences Versus Reference Laboratory Data for the ZSX Mini II

Matrix	Sample Group	Statistic	Antimony		Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc
			Ref Lab	ERA Spike												
Soil	Level 1	Number	8	1	8	7	23	16	5	4	7	23	4	3	12	19
		Median	161.2%	84.9%	14.0%	116.1%	21.0%	32.2%	93.3%	84.1%	24.3%	50.0%	77.6%	91.9%	57.8%	27.2%
	Level 2	Number	5	1	4	7	4	8	13	4	6	5	5	3	4	6
		Median	32.1%	84.8%	74.4%	21.4%	60.4%	49.3%	48.6%	68.9%	106.6%	60.6%	102.3%	45.1%	21.7%	58.7%
	Level 3	Number	4	3	4	2	2	2	13	8	2	6	4	7	4	9
		Median	28.8%	108.3%	82.4%	49.7%	80.5%	33.0%	60.3%	65.1%	112.1%	74.1%	105.9%	37.0%	36.8%	65.2%
	Level 4	Number	--	--	--	--	--	--	7	5	--	--	--	--	--	--
		Median	--	--	--	--	--	--	70.8%	64.5%	--	--	--	--	--	--
	All Soil	Number	17	5	16	16	29	26	38	21	15	34	13	13	20	34
		Median	116.8%	96.1%	71.3%	49.7%	29.3%	40.0%	58.5%	66.7%	78.3%	57.7%	101.5%	40.4%	31.4%	50.4%
Sediment	Level 1	Number	4	4	8	3	7	8	3	6	2	18	5	5	6	18
		Median	174.4%	101.7%	47.3%	123.3%	9.3%	26.7%	122.4%	82.0%	67.5%	62.0%	89.6%	112.6%	39.2%	39.6%
	Level 2	Number	4	4	3	4	3	4	19	4	4	6	4	4	8	5
		Median	79.9%	83.3%	47.7%	65.0%	52.7%	39.7%	33.4%	70.3%	87.1%	57.1%	108.4%	36.3%	20.9%	59.4%
	Level 3	Number	3	3	2	3	3	10	4	3	3	4	3	3	3	4
		Median	20.6%	116.2%	29.1%	20.9%	52.2%	71.4%	42.7%	54.7%	71.4%	66.0%	109.1%	34.0%	41.4%	68.3%
	Level 4	Number	--	--	--	--	--	--	6	--	--	--	--	--	--	--
		Median	--	--	--	--	--	--	70.5%	--	--	--	--	--	--	--
	All Sediment	Number	11	11	13	10	13	22	32	13	9	28	12	12	17	27
		Median	84.3%	108.9%	45.5%	65.0%	43.7%	40.0%	38.0%	71.4%	71.4%	63.1%	103.2%	65.4%	35.5%	48.6%
All Samples	ZSX Mini	Number	28	16	29	26	42	48	70	34	24	62	25	25	37	61
		Median	92.2%	102.2%	49.2%	60.9%	37.2%	40.0%	52.4%	66.8%	74.2%	60.4%	101.5%	45.1%	35.2%	48.6%
All Samples	All XRF Instruments	Number	206	110	320	209	338	363	558	392	192	403	195	177	218	471
		Median	84.3%	70.6%	26.2%	16.7%	26.0%	16.2%	26.0%	21.5%	58.6%	25.4%	16.7%	28.7%	38.3%	19.4%

Notes:

All median RPDs presented in this table are absolute values.

--	No samples reported by the reference laboratory in this concentration range.
ERA	Environmental Resource Associates, Inc.
NC	Not calculated.
Number	Number of samples appropriate for accuracy evaluation.
Ref	Reference laboratory (Shealy Environmental Services, Inc.).
RPD	Relative percent difference.

Table 7-4. Summary of Correlation Evaluation for the ZSX Mini II

Target Element	m	b	r^2	Correlation	Bias
Antimony (vs. Reference Lab)	0.51	296	0.11	Low	Indeterminate [1]
Antimony (vs. ERA Certified Value)	0.02	258	0	None	Indeterminate [1]
Arsenic	0.45	32	0.90	High	Low
Cadmium	0.42	573	0.82	Moderate	Variable [2]
Chromium	0.43	63	0.95	High	Low
Copper	0.59	5	0.95	High	Low
Iron	0.38	5610 [3]	0.93	High	Low
Lead	0.54	92	0.99	High	Low
Mercury	0.30	29	0.98	High	Low
Nickel	0.42	32	0.93	High	Low
Selenium	0.27	8	0.97	High	Low
Silver	0.04	198	0.01	None	Indeterminate [1]
Vanadium	0.56	53	0.73	Moderate	Variable [2]
Zinc	0.47	47	0.97	High	Low

Notes:

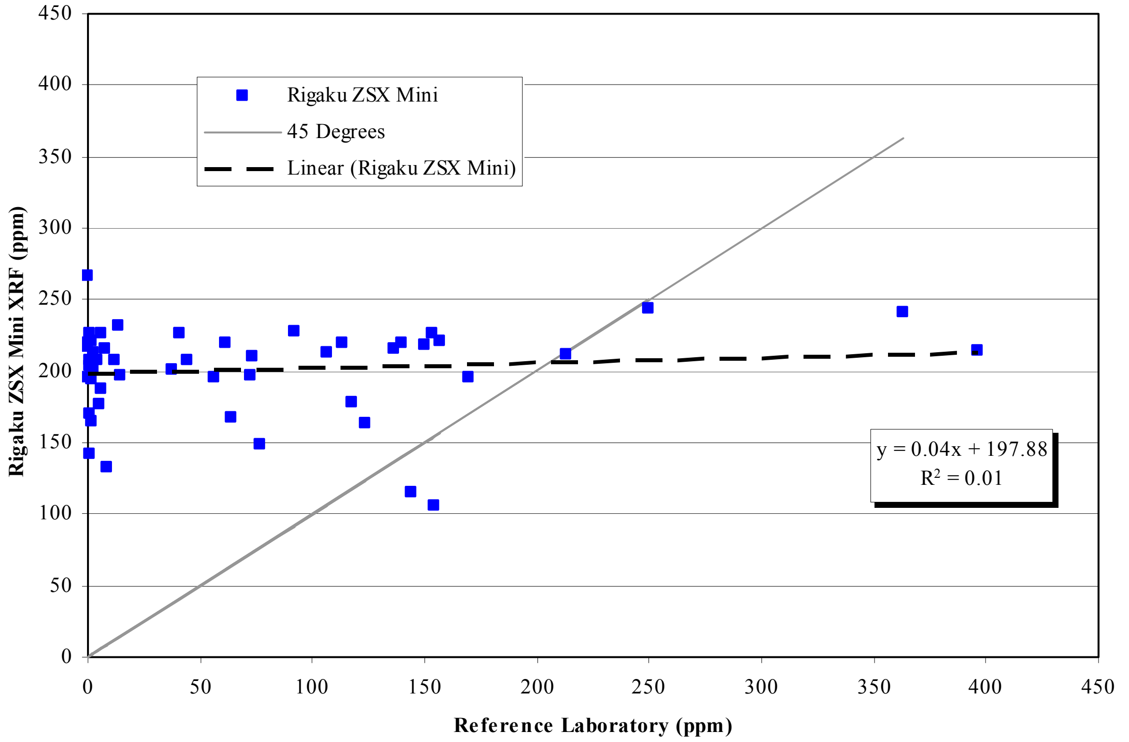
[1] The bias for this element is indeterminate because of the lack of correlation observed with the reference laboratory data.

[2] The bias for this element tended to be high at low concentrations (because of a high intercept) and low at high concentrations (because of a low slope). Overall correlation with the reference laboratory was moderate to low for this element.

[3] For iron, no MDL was calculated and the high intercept value was the result of the extreme range of concentrations in the demonstration samples.

b Y-intercept of correlation line.
m Slope of correlation line.
r^2 Correlation coefficient of correlation line.

Figure 7-2. Linear correlation plot for Rigaku indicating low overall correlation with the reference laboratory for silver.



In conclusion, the demonstration found potential issues with accuracy for the ZSX Mini II. Median RPDs tended to be higher than the other XRF technologies demonstrated, remaining in the “fair” to “poor” range for all target elements. The correlation plots further showed that, although satisfactory correlations with reference laboratory data were obtained for many of the target elements, a significant and consistent low bias was observed (thus producing the high RPDs). The correlation analysis indicated biases that varied from high to low as concentrations increased for some elements, and further showed very poor overall agreement of the ZSX Mini II data with the reference laboratory data for both antimony and silver. The developer indicates that poor performance is expected for antimony, silver, and cadmium because the instrument does not have a primary beam filter to remove interference lines from the x-ray tube (Appendix B). For the remaining target elements, it is possible that a refined, project-specific instrument calibration could have improved the comparability of the data from the ZSX Mini II with that of the reference laboratory.

7.3 Primary Objective 3 — Precision

As described in Section 4.2.3, the precision of the ZSX Mini II data set was evaluated by calculating RSDs for the replicate measurements from each sample blend. Median RSDs for the various concentration levels and media (soil and sediment) are presented in Table 7-5. The table also presents the median RSDs for the demonstration data set as a whole for the ZSX Mini II. Additional summary statistics for the RSDs (including minimum, maximum, and mean) are provided in Appendix E (Table E-2).

The RSD calculation found a high level of precision for the ZSX Mini II across all target elements. Median RSDs for the demonstration data ranged only as high as 14.7 percent (chromium). The ranges into which the median RSDs fell are summarized below:

- Very low (median RSD between 0 and 5 percent): cadmium, copper, iron, lead, mercury, nickel, selenium, silver, and zinc.
- Low (median RSD between 5 and 10 percent): antimony and vanadium.
- Moderate (median RSD between 10 and 20 percent): arsenic and chromium.
- High (median RSD greater than 20 percent): none.

No differences were observed between the RSDs for soil and sediment. Use of the mean as opposed to the median RSDs (Table E-2) indicated a similarly high level of precision in the results from the ZSX Mini II for all elements except mercury. The high overall level of precision may have been facilitated by the level of processing (homogenizing, sieving, crushing, and drying) performed on the sample blends before the demonstration (Chapter 3). This observation is consistent with the previous SITE MMT Program demonstration of XRF technologies that occurred in 1995 (EPA 1996a, 1996b, 1998a, 1998b, 1998c, and 1998d). The high level of sample processing applied during both XRF technology demonstrations was necessary to minimize the effects of sample heterogeneity on the demonstration results and on comparability with the reference laboratories. During project design, site investigation teams that intend to compare XRF and laboratory data should similarly assess the need for sample processing steps to manage sample heterogeneity and improve data comparability.

Further review of the median RSDs in Table 7-5 based on concentration range reveals slightly higher RSDs (in other words, lower precision) for the target elements in Level 1 samples when compared with the rest of the data set. This effect was greatest for arsenic, chromium, and vanadium, where the median RSDs increased to between 10 and 20 percent in Level 1 blends. This observation indicates that, to a minor extent, analytical precision for the ZSX Mini II is concentration-dependent. Furthermore, precision shows the opposite trend from accuracy in that accuracy is higher at low concentrations for many target elements (Section 7.2), while precision is lower. Even for the Level 1 samples, however, the effect of concentration on precision was small; the mean RSDs for the target elements remained relatively good, with the highest RSD at 17.8 percent (for chromium in sediment).

As an additional comparison, Table 7-5 also presents the median RSDs calculated for all XRF instruments that participated in the demonstration. Additional summary statistics for the RSDs calculated across all XRF instruments combined are included in Table E-2. Table 7-5 indicates that the median RSDs for the ZSX Mini II were equivalent to or below the all-instrument medians for all elements except arsenic and chromium, for which slightly higher median RSDs were observed.

Table 7-6 presents median RSD statistics for the reference laboratory and compares these to the summary data for the ZSX Mini II. These reference laboratory median RSD statistics were calculated using the same blends as were used in the RSD statistics for the ZSX Mini II. (Additional summary statistics are provided in Table E-3 of Appendix E.) Table 7-6 indicates that the median RSDs for the ZSX Mini II were equivalent to or lower than the reference laboratory RSDs for 12 of 13 target elements. (Only the RSD for chromium was slightly higher for the ZSX Mini II.) Thus, the ZSX Mini II exhibited slightly better precision overall than the reference laboratory. In comparison to the median RSDs for the ZSX Mini II, Table 7-6 shows that the median RSDs for all XRF instruments participating in the demonstration were lower than the reference laboratory RSDs for 11 out of the 13 target elements (the exceptions were chromium and vanadium).

7.4 Primary Objective 4 — Impact of Chemical and Spectral Interferences

The RPD data from the accuracy evaluation were further processed to assess the effects of interferences. The RPD data for elements considered susceptible to interferences were grouped and compared based on the relative concentrations of potentially interfering elements. Of specific interest for the comparison were the potential effects of:

- High concentrations of lead on the RPDs for arsenic,
- High concentrations of nickel on the RPDs for copper (and vice versa), and
- High concentrations of zinc on RPDs for copper (and vice versa).

Table 7-5. Evaluation of Precision — Relative Standard Deviations for the ZSX Mini II

Matrix	Sample Group	Statistic	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc
Soil	Level 1	Number	8	8	7	23	16	5	4	7	23	4	3	12	19
		Median	6.2%	13.0%	1.8%	14.8%	4.5%	1.0%	7.5%	9.6%	4.7%	7.9%	2.5%	12.3%	4.2%
	Level 2	Number	5	4	7	4	8	13	4	6	5	5	3	4	6
		Median	6.9%	3.2%	2.2%	4.3%	1.9%	0.5%	2.1%	5.2%	2.3%	3.2%	2.0%	5.5%	1.4%
	Level 3	Number	4	4	2	2	2	13	8	2	6	4	7	4	9
		Median	4.9%	1.7%	1.1%	2.7%	0.6%	0.6%	1.8%	2.4%	1.3%	1.9%	2.4%	5.2%	1.0%
	Level 4	Number	--	--	--	--	--	7	5	--	--	--	--	--	--
		Median	--	--	--	--	--	0.7%	0.8%	--	--	--	--	--	--
	All Soil	Number	17	16	16	29	26	38	21	15	34	13	13	20	34
		Median	6.3%	6.1%	1.8%	13.0%	3.4%	0.6%	1.8%	5.3%	3.9%	3.2%	2.4%	11.1%	2.1%
Sediment	Level 1	Number	4	8	3	7	8	3	6	2	18	5	4	6	18
		Median	11.0%	15.8%	1.2%	17.8%	3.4%	0.4%	4.0%	7.6%	4.0%	10.8%	1.4%	4.4%	4.8%
	Level 2	Number	4	3	4	3	4	19	4	4	6	4	4	8	18
		Median	5.5%	11.2%	1.9%	9.1%	2.1%	0.7%	2.3%	7.3%	5.2%	7.2%	1.3%	4.7%	2.8%
	Level 3	Number	3	2	3	3	10	4	3	3	4	3	3	3	4
		Median	7.2%	9.9%	3.0%	18.2%	1.7%	1.1%	2.6%	3.6%	1.6%	3.1%	4.1%	4.7%	2.2%
	Level 4	Number	--	--	--	--	--	6	--	--	--	--	--	--	--
		Median	--	--	--	--	--	0.7%	--	--	--	--	--	--	--
	All Sediment	Number	11	13	10	13	22	32	13	9	28	12	11	17	27
		Median	7.2%	14.4%	1.3%	17.8%	2.1%	0.7%	2.6%	4.5%	3.7%	7.6%	1.5%	4.7%	3.6%
All Samples	ZSX Mini	Number	28	29	26	42	48	70	34	24	62	25	24	37	61
		Median	6.4%	10.1%	1.6%	14.7%	2.3%	0.6%	2.0%	4.9%	3.7%	3.9%	2.4%	5.9%	2.5%
All Samples	All XRF Instruments	Number	206	320	209	338	363	558	392	192	403	195	177	218	471
		Median	6.1%	8.2%	3.6%	12.1%	5.1%	2.2%	4.9%	6.8%	7.0%	4.5%	5.2%	8.5%	5.3%

Notes:

--	No samples reported by the reference laboratory in this concentration ranges.
Number	Number of samples appropriate for precision evaluation.
RSD	Relative standard deviation

Table 7-6. Evaluation of Precision – Relative Standard Deviations for the Reference Laboratory versus the ZSX Mini II and All Demonstration Instruments

Matrix	Sample Group	Statistic	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc
Soil	Ref Lab	Number	17	23	15	34	26	38	33	16	35	13	13	21	35
		Median	9.8%	12.4%	9.0%	10.6%	9.1%	8.7%	13.2%	6.6%	10.0%	7.1%	7.5%	6.6%	9.1%
Sediment	Ref Lab	Number	7	24	10	26	21	31	22	10	27	12	10	17	27
		Median	9.1%	9.2%	8.2%	7.5%	8.9%	8.1%	7.4%	6.9%	7.3%	7.6%	6.6%	8.1%	6.9%
All Samples	Ref Lab	Number	24	47	25	60	47	69	55	26	62	25	23	38	62
		Median	9.5%	9.5%	9.0%	8.4%	8.9%	8.5%	8.6%	6.6%	8.2%	7.4%	7.1%	7.2%	7.4%
All Samples	ZSX Mini	Number	28	29	26	42	48	70	34	24	62	25	24	37	61
		Median	6.4%	10.1%	1.6%	14.7%	2.3%	0.6%	2.0%	4.9%	3.7%	3.9%	2.4%	5.9%	2.5%
All Samples	All XRF Instruments	Number	206	320	209	338	363	558	392	192	403	195	177	218	471
		Median	6.1%	8.2%	3.6%	12.1%	5.1%	2.2%	4.9%	6.8%	7.0%	4.5%	5.2%	8.5%	5.3%

Notes:

Number	Number of demonstration samples evaluated.
Ref. Lab.	Reference laboratory.
XRF	X-ray fluorescence

Interferent-to-element ratios were calculated using the mean concentrations reported for each blend by the reference laboratory, classified as low (less than 5X), moderate (5 to 10X), or high (greater than 10X). Table 7-7 presents median RPD data for arsenic, nickel, copper, and zinc that are grouped based on this classification scheme. Additional summary statistics are presented in Appendix E (Table E-4). The table indicates that the median RPD for arsenic was lower (that is, accuracy was higher) at the higher lead-to-arsenic ratios than at the low or moderate lead-to-arsenic ratios. Typically, the opposite trend is expected: high lead concentrations will tend to cause a high bias and thereby reduce accuracy in XRF measurements of arsenic. However, Section 7.2 listed arsenic among the elements for which the ZSX Mini II results were consistently biased low (Figure E-2). Thus, any high bias caused by the effects of lead may have offset the inherent low bias in the instrument (for example, from calibration or quantitation protocols) to produce results closer to the reference laboratory. Similar effects were indicated in the other interferent/element pairs in that median RPDs remained equivalent or declined slightly as interferent concentrations increased. Overall, therefore, the low accuracy of the ZSX Mini II data set appears to have complicated the evaluation of interelement interferences, and may mask the effects of such interferences.

7.5 Primary Objective 5 — Effects of Soil Characteristics

The population of RPDs between the ZSX Mini II results and the reference laboratory results were further evaluated against sampling site and soil type. Separate sets of summary statistics were developed for the mean RPDs associated with each sampling site for comparison to the other sites and to the demonstration data set as a whole. The site-specific median RPDs are presented in Table 7-8, along with descriptions of soil or sediment type from observations during sampling at each site. Complete RPD summary statistics for each soil type (minimum, maximum, and mean) are presented in Appendix E (Table E-5).

Another perspective on the effects of soil type was developed by graphically assessing outliers and extreme values in the mean RPD data sets for the target elements. This evaluation focused on correlating these values with sample types or locations for multiple elements across the data set. Outliers and extreme values are apparent in the correlation plots (Figures E-1 through E-13) and are further depicted for the various elements on box and whisker plots in Figure E-14.

Review of Table 7-8 indicates that the median RPDs were highly variable and that trends or differences between sample sites were difficult to discern. For many target elements, evaluations relative to sampling site were further complicated by the low numbers of samples (Table 7-8 indicates that only 1 to 3 samples were available from many sampling sites for evaluation of specific target elements.) The degree of variation in RPDs for the target elements was greatest in the samples from KARS Park, where the median RPDs ranged from 11.8 percent (nickel) to 153 percent (antimony). Other sample sites for which the range of RPDs across the different target elements was greater than 100 percent included: Alton Steel, Burlington Northern, Sulphur Bank, and Torch Lake. The smallest RPD range was observed for the Ramsey Flats site, where a minimum RPD of 29.7 percent was noted for vanadium and a maximum RPD of 78.5 percent was calculated for lead.

These observations indicate that the relatively low accuracy and consistently low bias of the Rigaku data may have masked any effects of soil type on the results.

Review of the box and whiskers plot (Figure E-14) and the correlation plots from the accuracy evaluation revealed no other general trends in RPDs relative to sampling site. The high outliers and extreme values apparent in Figure E-14 were distributed among the KARS Park, Alton Steel, Sulphur Bank, and Leviathan Mine sites. However, the plots further demonstrate that sample matrix appeared to have little overall effect on the accuracy of the XRF data. Figure E-14 shows the broad overall distributions of RPDs for many elements such that relatively few high outliers or extreme values could be identified. The identification of high statistical outliers or extreme values was precluded for eight of the target elements, including antimony, cadmium, chromium, lead, mercury, selenium, silver, and vanadium.

Table 7-7. Effects of Interferent Elements on the RPDs (Accuracy) for Other Target Elements[1]

Parameter	Lead Effects on Arsenic			Copper Effects on Nickel			Nickel Effects on Copper			Zinc Effects on Copper			Copper Effects on Zinc		
Interferent/ Element Ratio	<5	5 – 10	>10	<5	5 – 10	>10	<5	5 – 10	>10	<5	5 – 10	>10	<5	5 – 10	>10
Number of Samples	15	7	7	43	5	14	39	1	8	35	2	11	48	3	10
Median RPD of Target Element[2]	45.5%	76.5%	16.3%	62.7%	55.3%	53.3%	46.1%	31.1%	30.1%	40.2%	44.1%	31.0%	53.0%	38.4%	46.2%
Median Interferent Concentration	173	3716	1390	62	700	1017	80	203	963	92	2190	1430	73	676	1301
Median Target Element Concentration	92	487	93	99	88	60	565	57	70	567	532	77	410	88	78

Notes:

1	Concentrations are reported in units of milligrams per kilogram (mg/kg), or parts per million (ppm).
2	All median RPDs presented in this table are based on the population of absolute values of the individual RPDs.
<	Less than.
>	Greater than.
RPD	Relative percent difference.

Table 7-8. Effect of Soil Type on the RPDs (Accuracy) for Target Elements, Rigaku ZSX Mini II

Matrix	Site	Matrix Description	Statistic	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead
Soil	AS	Fine to medium sand (steel processing)	Number	--	--	3	2	3	3	3
			Median	--	--	116.1%	43.4%	74.3%	94.0%	104.1%
Soil	BN	Sandy loam, low organic (ore residuals)	Number	4	6	5	4	6	7	5
			Median	146.1%	64.4%	26.8%	51.4%	40.0%	52.7%	73.5%
Soil	CN	Sandy loam (burn pit residue)	Number	2	1	2	1	3	3	2
			Median	87.4%	3.3%	93.1%	16.5%	31.0%	51.3%	90.0%
Soil & Sediment	KP	Soil: Fine to medium quartz sand. Sed.: Sandy loam, high organic. (Gun and skeet ranges)	Number	2	--	--	3	2	6	6
			Median	153.4%	--	--	37.0%	19.8%	105.0%	42.8%
Sediment	LV	Clay/clay loam, salt crust (iron and other precipitates)	Number	4	3	5	7	4	12	2
			Median	33.7%	82.3%	36.4%	62.9%	40.9%	39.4%	43.6%
Sediment	RF	Silty fine sand (tailings)	Number	5	10	5	6	13	13	8
			Median	75.6%	40.2%	65.4%	42.2%	31.1%	35.2%	78.5%
Soil	SB	Coarse sand and gravel (ore and waste rock)	Number	5	2	1	10	4	12	--
			Median	54.1%	92.1%	42.2%	7.8%	46.9%	59.7%	--
Sediment	TL	Silt and clay (slag-enriched)	Number	3	1	2	2	7	7	2
			Median	90.6%	56.8%	82.7%	14.1%	72.5%	35.4%	78.9%
Soil	WS	Coarse sand and gravel (roaster slag)	Number	3	6	3	7	6	7	6
			Median	116.8%	79.3%	112.8%	29.3%	44.1%	60.3%	57.6%
	All		Number	28	29	26	42	48	70	34
			Median	92.2%	49.2%	60.9%	37.2%	40.0%	52.4%	66.8%

Table 7-8. Effect of Soil Type on RPDs (Accuracy) of Target Elements, Rigaku ZSX Mini II (Continued)

Matrix	Site	Matrix Description	Statistic	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc
Soil	AS	Fine to medium sand (steel processing)	Number	--	3	1	1	1	3
			Median	--	71.3%	97.5%	40.4%	13.7%	81.4%
Soil	BN	Sandy loam, low organic (ore residuals)	Number	1	6	4	4	4	7
			Median	39.9%	62.0%	96.2%	42.8%	26.6%	54.6%
Soil	CN	Sandy loam (burn pit residue)	Number	2	3	2	2	1	3
			Median	42.1%	71.5%	87.9%	91.0%	26.5%	56.1%
Soil & Sediment	KP	Soil: Fine to medium quartz sand. Sed.: Sandy loam, high organic. (Gun and skeet ranges)	Number	--	3	--	--	--	2
			Median	--	11.8%	--	--	--	17.2%
Sediment	LV	Clay/clay loam, salt crust (iron and other precipitates)	Number	4	11	5	4	9	9
			Median	52.8%	65.5%	100.3%	34.7%	19.8%	17.4%
Sediment	RF	Silty fine sand (tailings)	Number	5	13	5	5	3	13
			Median	59.0%	55.9%	97.6%	64.0%	29.7%	48.4%
Soil	SB	Coarse sand and gravel (ore and waste rock)	Number	10	10	3	1	9	10
			Median	112.1%	65.3%	106.6%	38.3%	60.9%	36.2%
Sediment	TL	Silt and clay (slag-enriched)	Number	2	6	4	4	7	7
			Median	128.8%	66.8%	120.3%	58.8%	41.0%	63.9%
Soil	WS	Coarse sand and gravel (roaster slag)	Number	--	7	1	4	3	7
			Median	--	37.6%	101.5%	48.3%	27.6%	60.1%
	All		Number	24	62	25	25	37	61
			Median	74.2%	60.4%	101.5%	45.1%	35.2%	48.6%

Notes:

AS	Alton Steel Mill
BN	Burlington Northern railroad/ASARCO East.
CN	Naval Surface Warfare Center, Crane Division.
KP	KARS Park – Kennedy Space Center.
LV	Leviathan Mine/Aspen Creek.
RF	Ramsey Flats – Silver Bow Creek.
SB	Sulphur Bank Mercury Mine.
TL	Torch Lake Superfund Site.
WS	Wickes Smelter Site.

Other Notes:

--	No samples reported by the reference laboratory in this concentration range.
Number	Number of demonstration samples evaluated.
RPD	Relative percent difference.

7.6 Primary Objective 6 — Sample Throughput

The Rigaku two-person field team was able to analyze all 326 demonstration samples in 4 days at the demonstration site. Once the ZSX Mini II instrument had been set up and operations had been streamlined, the Rigaku field team was able to analyze a maximum of 107 samples during an extended work day. This sample throughput was achieved by using different members of the field team to perform sample preparation and instrumental analysis and by using the autosampler to process samples through the XRF spectrometer. Without an extended work day, and taking into account instrument set-up and demobilization time, it was estimated that the Rigaku field team would have averaged about 69 samples per day.This estimated sample throughput for a normal working day was similar to that observed for the other instruments that participated in the demonstration (average of 66 samples per day).

A detailed discussion of the time required to complete the various steps of sample analysis using the ZSX Mini II is included as part of the labor cost analysis in Section 8.3.

7.7 Primary Objective 7 — Technology Costs

The evaluations pertaining to this primary objective are fully described in Chapter 8, Economic Analysis.

7.8 Secondary Objective 1 — Training Requirements

The instrument operator must be suitably trained to set up and operate the instrument to obtain the level of data quality required for specific projects. The amount of training required depends on the configuration and complexity of the instrument along with the associated software. Most developers have established standard training programs.

Rigaku recommends that the operator have a high school diploma and basic operational training. Field or laboratory technicians are generally qualified to operate this instrument. The Rigaku staff member who operated the instrument during the demonstration held a B.S. degree in chemistry, with several years of experience in operation of the ZSX Mini II.

Rigaku recommends that operators complete at least the training Rigaku offers for instrument users. When an instrument is purchased, a Rigaku service engineer will set it up and provide basic instruction on operation and safety. After about a week, a Rigaku application specialist will come to the site where the instrument will be used to provide a 3-day comprehensive training course adapted for the user's specific application. Additional 3-day training classes are offered for $1,800. Participants are encouraged to bring samples to class to analyze as part of the hands-on exercise for the training. A built-in modem allows a support technician to operate and troubleshoot the instrument from a remote location.

In addition to the general instrument operational instruction and training, the operator and data manager must be familiar with using a personal computer (PC) to acquire and manage analytical data obtained from the instrument. Rigaku provides a copy of its instrument software with each instrument purchase. The software allows direct transfer to analytical results from the instrument to the PC, thereby minimizing the potential for lost data.

7.9 Secondary Objective 2 — Health and Safety

Included in the health and safety evaluation were the potential risks from: (1) potential radiation hazards from the instrument itself, and (2) exposure to any reagents used in preparing and analyzing the samples. However, the evaluation did not include potential risks from exposure to site-specific hazardous materials, such as sample contaminants, or to physical safety hazards. These factors were excluded because of the wide and unpredictable range of sites and conditions that could be encountered in the field during an actual project application of the instrument.

The ZSX Mini II contains an x-ray tube that is positioned to deliver x-rays into a lead-shielded sealing sample chamber. Each instrument is equipped with a sample chamber lock, and large lights indicate when x-rays are being generated. The instrument will not operate if the lock is not latched. The sample chamber lock, lead-shielded sample chamber, and safety lights are designed to minimize possible exposure to the x-ray radiation.

The second potential source of risk to XRF instrument operators is exposure to reagent chemicals used in sample preparation. However, for the ZSX Mini II, there are no risks from this source because no chemical reagents are required for sample preparation. The sample chamber may be placed in a vacuum or purged with inert gas such as helium in some applications (for example, to improve data quality for lighter elements). As an inert gas, helium is relatively harmless, as long as users apply standard safety procedures for management and use of high-pressure gas cylinders. The risks from exposure to radiation or to helium are likewise minimal when the instrument is operated according to the manufacturer's recommendations.

7.10 Secondary Objective 3 — Portability

Portability depends on the size, weight, number of components, and power requirements of the instrument, and the reagent required. The size of the instrument, including physical dimensions and weight, is presented in Table 6-1. The number of components, power requirements, support structures, and reagent requirements are also listed in Table 6-1. Two distinctions were made during the demonstration regarding portability:

(1) The instrument was considered fully portable if the dimensions were such that the instrument could be easily brought directly to the sample location by one person.

(2) The instrument was considered transportable if the dimensions and power requirements were such that the instrument could be moved to a location near the sampling location, but required a larger and more stable environment (for example, a site trailer with AC power and stable conditions).

Based on the dimensions and power requirements, the ZSX Mini II is defined as transportable. It is capable of being transported to a field trailer or other fixed location with the required power supply and a stable weatherproof environment.

7.11 Secondary Objective 4 — Durability

Durability was evaluated by gathering information on the instrument's warranty and the expected lifespan of the radioactive source or x-ray tube. The ability to upgrade software or hardware also was evaluated. Weather resistance was evaluated by examining the instrument for exposed electrical connections and openings that may allow water to penetrate (for portable instruments only).

Rigaku provides a 12-month limited warranty on parts and labor. Additional warranties, optional extended warranties, and service contracts vary by country. Since x-ray tube sources are new to the world of portable instrumentation, no clear data have been obtained on the useful life that can be assumed. Rigaku indicated that the lifespan of an x-ray tube in the ZSX Mini II can be as high as 10,000 hours of operation.

Rigaku is continually upgrading both the instrument and software to enhance environmental analysis. It is expected that Rigaku will continue to provide upgrades to instruments and software as long as there is a market for improved technologies.

The ZSX Mini II instrument is made with hard-tool plastic that is durable and impact-resistant under nearly all field applications. The instrument is not weatherproof and must be located in a stable environment.

7.12 Secondary Objective 5 — Availability

Rigaku LLC was founded in 1931 and has six salespersons in the U.S. and many more worldwide. Rigaku provides product support for all instruments through service contracts tailored to the client's needs. A network of 35 service representatives provides service and customer support for instrument owners.

The ZSX Mini II is available for lease or for long-term rental on a case-specific basis. The ZSX Mini II is not available from third-party vendors for lease or rental.

Chapter 8
Economic Analysis

This chapter provides cost information for the Rigaku ZSX Mini II XRF analyzer. Cost elements that were addressed included instrument purchase or rental, supplies, labor, and ancillary items. Sources of cost information included input from the technology developer and suppliers as well as observations during the field demonstration. Comparisons are provided to average costs for other XRF technologies and for conventional fixed-laboratory analysis to provide some perspective on the relative cost of using the ZSX Mini II instrument.

8.1 Equipment Costs

Capital equipment costs include either purchase or rental of the ZSX Mini II and any ancillary equipment that is generally needed for sample analysis. (See Chapter 6 for a description of available accessories.) Information on purchase price for the analyzer and accessories was obtained from Rigaku.

The ZSX Mini II instrument costs between $80,000 and $85,000, depending on the configuration. The cost includes peripherals such as the x-ray spectrometer, 12-postion sample changer, vacuum pump, and personal computer loaded with the appropriate operational software. At the time of the demonstration, Rigaku indicated that models are not available for rental. However, long-term lease programs are available through Rigaku. For evaluation and comparison purposes later in this chapter, an estimated rental cost was derived based on similar XRF technologies where both purchase and rental prices were available. Purchased models include a 1-year parts and labor warranty. The lifespan of the x-ray tube is about 4 to 5 years for normal usage.

The purchase price and shipping cost for the ZSX Mini II exceed the average costs for all XRF instruments that participated in the demonstration, as shown in Table 8-1.

Table 8-1. Equipment Costs

Cost Element	ZSX Mini II	XRF Demonstration Average *
Shipping	$500	$410
Capital Cost (Purchase)	$82,500	$54,300
Weekly Rental	$4,300	$2,813
Autosampler (for Overnight Analysis)	Included	N/A

Notes:
* Average for all eight demonstration vendors
N/A Not available or not applicable for this comparison

8.2 Supply Costs

The supplies that were included in the cost estimate include sample containers, Mylar® film, spatulas or scoops, wipes, and disposable gloves. The rate of consumption for these supplies was based on observations during the field demonstration. Unit prices for these supplies were based on price quotes from independent vendors of field equipment. Additional costs include purchase of helium or P-10 (argon/methane) gas if an oxygen-free environment is best suited for the analysis.

The ZSX Mini II was operated for 4 days to complete the analysis of the demonstration sample set (326 samples) during the field demonstration. The supplies required to process samples were similar for all XRF instruments that participated in the demonstration and were estimated to cost about $250 for 326 samples or $0.75 per sample.

8.3 Labor Costs

Labor costs were estimated based on the total time required by the field team to complete the analysis of all 326 samples and the number of people in the field team, while making allowances for field team members that had responsibilities other than sample processing during the demonstration. For example, some developers sent sales representatives to the demonstration to communicate with visitors and provide outreach services; this type of staff time was not included in the labor cost analysis.

While overall labor costs were based on the total time required to process samples, the time required to complete each definable activity was also measured during the field demonstration. These activities included:

- Initial setup and calibration
- Sample preparation
- Sample analysis
- Daily shutdown and startup
- End of project packing

The estimated time required to complete each of these activities using the ZSX Mini II is listed in Table 8-2. The "total processing time per sample" was calculated as the sum of all these activities assuming that the activities were conducted sequentially; therefore, it represents how much time it would take a single trained analyst to complete these activities. However, the "total processing time per sample" does not include activities that were less definable in terms of the amount of time taken, such as data management and procurement of supplies, and is therefore not a true total.

The time to complete all sample analysis using the ZSX Mini II is compared with the average of all XRF instruments in Table 8-2 and is compared with the range of all XRF instruments in Figure 8-1. In comparison to other XRF analyzers, the ZSX Mini II exhibited higher-than-average times for initial setup and calibration and for end of project packing. The ZSX Mini II exhibited lower-than-average times for sample preparation, sample analysis, daily shutdown and startup, and total processing time per sample.

Table 8-2. Time Required to Complete Analytical Activities[1]

Activity	ZSX Mini II	Average[2]
Initial Setup and Calibration	90	54
Sample Preparation	2.2	3.1
Sample Analysis	5.7	6.7
Daily Shutdown/Startup	0	10
End of Project Packing	147	43
Total Processing Time per Sample	8.6	10.0

Notes:
[1] All estimates are in minutes
[2] Average for all eight XRF instruments in the demonstration

The Rigaku field team expended about 67 labor hours to complete all sample processing activities during the field demonstration using the ZSX Mini II. This was similar to the overall average of 69 labor hours for all instruments that participated in the demonstration.

8.4 Comparison of XRF Analysis and Reference Laboratory Costs

Two scenarios were evaluated to compare the cost for XRF analysis using the ZSX Mini II with the cost of fixed-laboratory analysis using the reference methods. Both scenarios assumed that 326 samples were to be analyzed, as in the field demonstration. The first scenario assumed that only one element was to be measured in a metal-specific project or application (for example, lead in soil, paint, or other solids) for comparison to laboratory per-metal unit costs. The second scenario assumed that 13 elements were to be analyzed, as in the field demonstration, for comparison to laboratory costs for a full suite of metals.

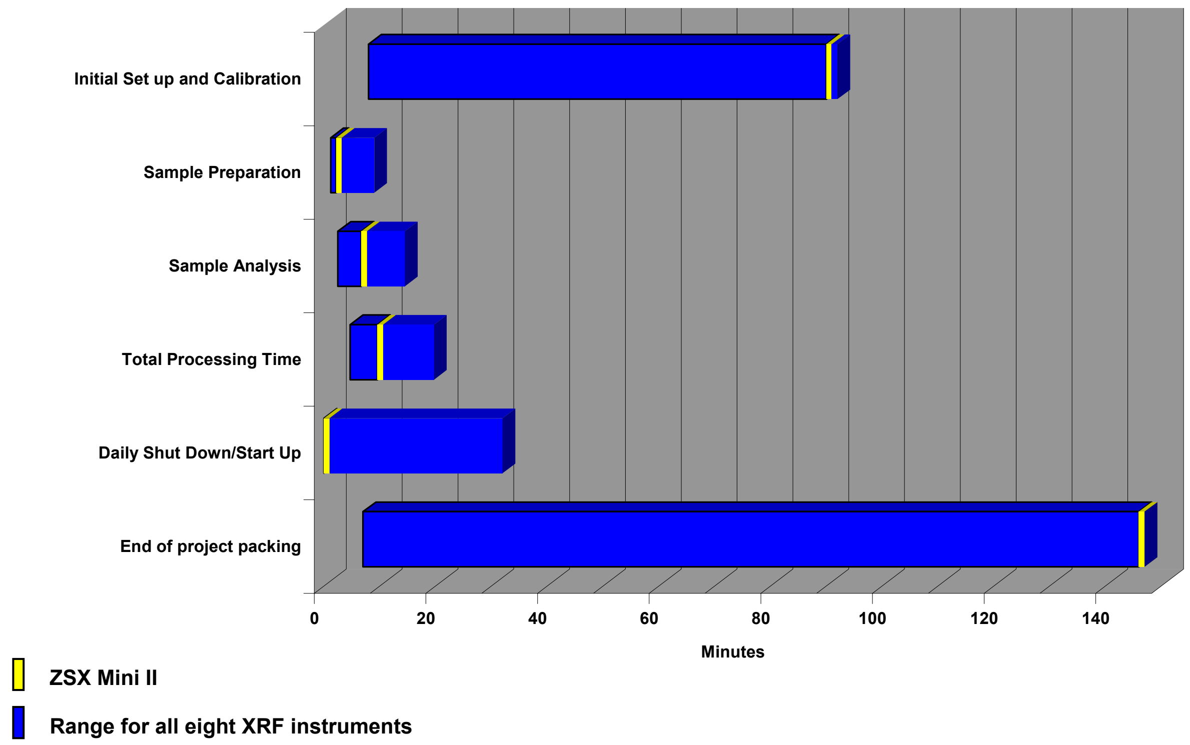


Figure 8-1. Comparison of activity times for the ZSX Mini II versus other XRF instruments.

Typical unit costs for fixed-laboratory analysis using the reference methods were estimated using information on average cost from Tetra Tech's basic ordering agreement with six national laboratories. These unit costs assume a standard turnaround time of 21 days and standard hard copy and electronic data deliverables that summarize results and raw analytical data. No costs were included for field labor that would be specifically associated with off-site fixed laboratory analysis, such as sample packaging and shipment.

The cost for XRF analysis using the ZSX Mini II was based on equipment rental for 1 week, along with labor and supplies estimates established during the field demonstration. As noted previously, the estimate used a hypothetical rental rate for the ZSX Mini II based on a survey of rental versus purchase costs of other XRF instruments. Labor costs were estimated based on the number of people in the field team and the time spent during the field demonstration to complete the analysis of the 326 demonstration samples. Labor costs were added for drying, grinding, and homogenizing the samples (estimated at 10 minutes per sample) since these additional steps in sample preparation are required for XRF analysis but not for analysis in a fixed laboratory. A typical cost for managing investigation-derived waste (IDW), including general trash, personal protective equipment, wipes, and soil, was also added to the cost of XRF analysis because IDW costs are included in the unit cost for fixed-laboratory analysis. The IDW management cost was fixed, based on the average IDW disposal cost per instrument during the demonstration, because IDW generation did not vary significantly between instruments during the demonstration. Since the cost for XRF analysis of one element or multiple elements does not vary significantly (all target elements are determined simultaneously when a sample is analyzed), the ZSX Mini II analysis cost was not adjusted for one element versus 13 elements.

Table 8-3 summarizes the costs for the ZSX Mini II versus the cost for analysis in a fixed laboratory. This comparison shows that the ZSX Mini II compares favorably to a fixed laboratory in terms of overall cost when a large number of elements are to be determined. The ZSX Mini II compares unfavorably to a fixed laboratory when one element is to be determined. Use of the ZSX Mini II will likely produce additional cost savings because analytical results will be available within a few hours after samples are collected, thereby expediting project decisions and reducing or eliminating the need for additional mobilizations.

The total cost for the ZSX Mini II in the example scenario (326 samples) was estimated at $10,421. This estimate compares with the average of $8,932 for all XRF instruments that participated in the demonstration. However, it should be noted that bench-top instruments, such as the ZSX Mini II, typically cost more than the hand-held instruments that were included in the average cost for all XRF instruments. In comparison to other bench-top XRF instruments, the cost of the ZSX Mini II for the example scenario was similar.

Table 8-3. Comparison of XRF Technology and Reference Method Costs

Analytical Approach	**Quantity**	**Item**	**Unit Rate**	**Total**
ZSX Mini II (1 to 13 elements)				
Shipping	1	Roundtrip	$500	$500
Weekly Rental[1]	1	Week	$4,300[1]	$4,300
Supplies	326	Sample	$0.75	$245
Labor	54	Hours	$43.75	$5,286
IDW	N/A	N/A	N/A	$90
Total ZSX Mini II Analysis Cost (1 to 13 elements)				**$10,421**
Fixed Laboratory (1 element)				
(EPA Method 6010, ICP-AES)	326	Sample	$21	$6,846
Total Fixed Laboratory Costs (1 element)				**$6,846**
Fixed Laboratory (13 elements)				
Mercury (EPA Method 7471, CVAA)	326	Sample	$36	$11,736
All other Elements (EPA Method 6010, ICP-AES)	326	Sample	$160	$52,160
Total Fixed Laboratory Costs (13 elements)				**$63,896**

Notes:

[1] Estimated value as Rigaku currently does not have a rental rate for the ZSX Mini II.

Chapter 9
Summary of Technology Performance

The preceding chapters of this report document that the evaluation design succeeded in providing detailed performance data for the Rigaku ZSX Mini II XRF analyzer. The evaluation design incorporated 13 target elements, 70 distinct sample blends, and a total of 326 samples. The blends included both soil and sediment samples from nine sampling locations. A rigorous program of sample preparation and characterization, reference laboratory analysis, QA/QC oversight, and data reduction supported the evaluation of XRF instrument performance.

One important aspect of the demonstration was the sample blending and processing procedures (including drying, sieving, grinding, and homogenization) that significantly reduced uncertainties associated with the demonstration sample set. These procedures minimized the impacts of heterogeneity on method precision and on the comparability between XRF data and reference laboratory data. In like manner, project teams are encouraged to assess the effects of sampling uncertainty on data quality and to adopt appropriate sample preparation protocols before XRF is used for large-scale data collection, particularly if the project will involve comparisons to other methods (such as off-site laboratories). An initial pilot-scale method evaluation, carried out in cooperation with an instrument vendor, can yield site-specific standard operating procedures for sample preparation and analysis to ensure that the XRF method will meet data quality needs, such as accuracy and sensitivity requirements. A pilot study can also help the project team develop an initial understanding of the degree of correlation between field and laboratory data. This type of study is especially appropriate for sampling programs that will involve complex soil or sediment matrices with high concentrations of multiple elements because the demonstration found that XRF performance was more variable under these conditions. Initial pilot studies can also be used to develop site-specific calibrations, in accordance with EPA Method 6200, that adjust instrument algorithms to compensate for matrix effects.

The findings of the evaluation of the ZSX Mini II analyzer for each primary and secondary objective are summarized in Tables 9-1 and 9-2. The ZSX Mini II and the combined performance of all eight instruments that participated in the XRF technology evaluation program are compared in Figure 9-1. The comparison in Figure 9-1 indicates that, when compared with the mean performance of all eight XRF instruments, the ZSX Mini II showed:

- Equivalent or better MDLs for all target elements except antimony and arsenic (iron was not included in the MDL evaluation).
- Equivalent or poorer accuracy (RPDs) for 12 of the 13 target elements (vanadium was the exception). When RPDs for antimony were calculated versus sample spike levels rather than reference laboratory data (which may be biased low), accuracy for antmony remained low relative to the program as whole.
- Equivalent or better precision (RSDs) for 11 of the 13 target elements (arsenic and chromium were the exceptions).

Bench-top instruments, such as the ZSX Mini II, typically provide improved MDLs in comparison to portable instruments, and so the better than average performance in this area was expected. As a bench-top instrument, however, the ZSX Mini II is not fully portable and requires a stable operating environment. The reasons for the poorer than average accuracy for most elements are not known with any certainty but may relate to the algorithms employed to quantify target elements or to inadequate calibration.

Table 9-1. Summary of Rigaku ZSX Mini II Performance – Primary Objectives

Objective	Performance Summary
P1: Method Detection Limits	• Mean MDLs for the target elements ranged as follows: o MDLs of 1 to 20 ppm: copper, mercury, nickel, selenium, and zinc. o MDLs of 20 to 50 ppm: arsenic, lead, silver, and vanadium. o MDLs of 50 to 100 ppm: antimony, cadmium, and chromium. o MDLs greater than 100 ppm: none. (Iron was not included in the MDL evaluation.) • The MDLs for antimony and cadmium may be inflated by high biases in the XRF results in some of the MDL sample blends. • No significant differences were noted between MDLs for soil and sediment, or among different sample blends. • For all the target elements except antimony, the MDLs calculated were lower than reference MDL data from EPA Method 6200.
P2: Accuracy and Comparability	• Median RPDs between the ZSX Mini II and reference laboratory data revealed the following, with lower RPDs indicating greater accuracy: o RPDs less than 25 percent: none. o RPDs of 25 to 50 percent: arsenic, chromium, copper, silver, vanadium, and zinc. o RPDs greater than 50 percent: antimony, cadmium, iron, lead, mercury, nickel, and selenium. • Data review indicated that the reference laboratory results for some spiked demonstration samples may be biased low for antimony due to the volatility of the spiking compounds used. However, unlike a number of other instruments in the XRF technology demonstration, high RPDs for antimony were not improved for the ZSX Mini II when calculated relative to certified spike values rather than reference laboratory results. • Lower RPDs (that is, higher accuracy) were noted in low concentration samples versus higher concentration samples for multiple target elements in both soil and sediment. • Correlation plots relative to reference laboratory data indicated: o Significant negative biases for most of the target elements (or, for cadmium and vanadium, biases that change from high to low as concentrations increase). o Poor to no correlation with the reference laboratory results for antimony and silver.
P3: Precision	• Median RSDs were good for all elements, as follows: o RSDs of 0 to 5 percent: cadmium, copper, iron, mercury, nickel, selenium, silver, and zinc. o RSDs of 5 to 10 percent: antimony and vanadium. o RSDs of 10 to 20 percent: arsenic and chromium. • In contrast to accuracy, the precision of the ZSX Mini II improved slightly as concentration increased. • Median RSDs for the ZSX Mini II for all elements except chromium were equivalent to or lower than the RSDs calculated for the reference laboratory data, indicating slightly better precision for the XRF instrument.

Table 9-1. Summary of Rigaku ZSX Mini II Performance – Primary Objectives (continued)

Objective	Performance Summary
P4: Effects of Sample Interferences	• High relative concentrations of lead appeared to slightly improve accuracy for arsenic, reducing the instrument's negative bias. Median RPDs for arsenic decreased from 45.5 percent to 16.3 percent as the concentration of lead increased. • Overall, significant interference effects could not be determined because of the low accuracy of the XRF data.
P5: Effects of Soil Type	• The degree of variation in RPDs for the target elements was greatest in the samples from KARS Park, a former gun range, where the median RPDs ranged from 11.8 percent (nickel) to 153 percent (antimony). Other sample sites for which the range of RPDs across the different target elements was greater than 100 percent included: Alton Steel, Burlington Northern, Sulphur Bank, and Torch Lake. • The high outliers and extreme values were distributed among the KARS Park, Alton Steel, Sulphur Bank, and Leviathan Mine sites. However, the evaluation found that sample matrix had little overall effect on accuracy for the ZSX Mini II, given the broad overall ranges of RPDs observed.
P6: Sample Throughput	• With an average sample preparation time of 2.2 minutes and an instrument analysis time of 5.7 minutes per sample, the total sample processing time was 8.6 minutes per sample. • A maximum sample throughput of 107 samples was achieved during the field demonstration on one extended work day. A typical average sample throughput was estimated to be 69 samples per day for an 8-hour work day.
P7: Costs	• Instrument purchase cost was about $82,500. This cost included an optional autosampler, vacuum pump, and personal computer. According to the developer, short-term and long-term leases are available, but no rates were provided. • The Rigaku field team expended approximately 67 labor hours to complete the processing of the demonstration sample set (326 samples). In comparison, the average for all participating XRF instruments was 69 labor hours. • By approximating a 1-week rental cost (based on similar XRF instruments) and adding labor and shipping/supplies costs, a total project cost of $10,421was estimated for a project the size of the demonstration using the ZSX Mini II. In comparison, the average project cost for all participating XRF instruments was $8,932 and the cost for fixed-laboratory analysis of all 13 elements was $63,896.

Table 9-2. Summary of Rigaku ZSX Mini II Performance – Secondary Objectives

Objective	Performance Summary
S1: Training Requirements	• Field or laboratory technicians with a high school diploma and basic operational training are generally qualified to operate the ZSX Mini II. • Rigaku offers free instrument setup for purchasers, followed by customized training that generally lasts about 3 days. • The ZSX Mini II comes equipped with a modem that allows qualified technicians to remotely troubleshoot the instrument and guide operators.
S2: Health and Safety	• The ZSX Mini II is equipped with safety measures to minimize possible exposure to emissions from the x-ray tube. The instrument cannot be operated if these safety measures are disabled. • Users of the ZSX Mini II should be able to safely manage high pressure gas cylinders (helium) if an inert atmosphere is desired for sample analysis.
S3: Portability	• Based on dimensions, weight, and power requirements, the ZSX Mini II is a transportable (as opposed to fully portable) instrument. It is best used in a field trailer or other fixed location.
S4: Durability	• The ZSX Mini II has a 12-month limited warranty for parts and labor. Additional optional warranties and service contracts are available, depending on the country where the instrument is purchased and used. • The average lifespan of an x-ray tube in the ZSX Mini II is anticipated to be 10,000 hours (7 years) • The ZSX Mini II is encased in durable hard-tool plastic but is not weatherproof. It must be used in a stable, sheltered environment.
S5: Availability	• Rigaku maintains offices in the U.S. and Europe for its XRF division, with 10 sales representatives distributed across North America and Europe. A world-wide network of 35 service representatives provides service and customer support. • The ZSX Mini II is available for short-term rental or long-term lease. Rates vary and are project-specific. The instrument is not available from third-party vendors.

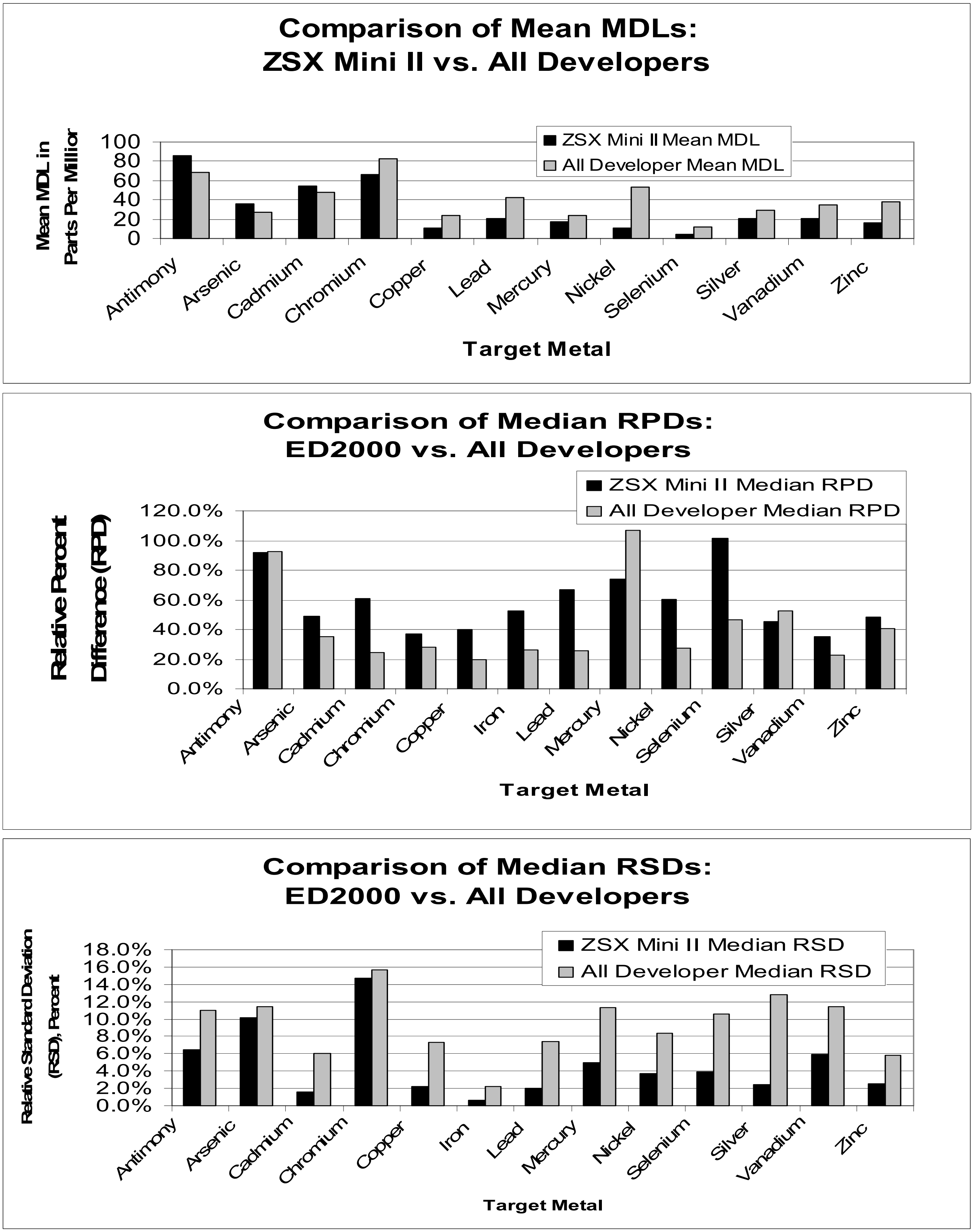


Figure 9-1. Method detection limits (sensitivity), accuracy, and precision of the ZSX Mini II in comparison to the average of all eight XRF instruments.

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Chapter 10
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APPENDIX A

VERIFICATION STATEMENT

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, DC 20460

SITE Monitoring and Measurement Technology Program Verification Statement

TECHNOLOGY TYPE:	X-ray Fluorescence (XRF) Analyzer
APPLICATION:	MEASUREMENT OF TRACE ELEMENTS IN SOIL AND SEDIMENT
TECHNOLOGY NAME:	ZSX Mini II
COMPANY:	Rigaku Incorporated
ADDRESS:	9009 New Trails Drive The Woodlands, TX 77381-5209
PHONE:	281-363-1033
WEB SITE:	www.rigakumsc.com/xrf
E-MAIL:	info@rigakumsc.com

VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) Program to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of this program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The program assists and informs those involved in designing, distributing, permitting, and purchasing environmental technologies. This document summarizes the results of a demonstration of the Rigaku Incorporated ZSX Mini II bench-top x-ray fluorescence (XRF) analyzer for the analysis of 13 target elements in soil and sediment, including antimony, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, vanadium, and zinc.

PROGRAM OPERATION

Under the SITE MMT Program, with the full participation of the technology developers, 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 protocols to produce well-documented data of known quality. EPA's National Exposure Research Laboratory, which demonstrates field sampling, monitoring, and measurement technologies, selected Tetra Tech EM Inc. as the verification organization to assist in field testing technologies for measuring trace elements in soil and sediment using XRF technology.

DEMONSTRATION DESCRIPTION

The field demonstration of eight XRF technologies to measure trace elements in soil and sediment was conducted from January 24 through 28, 2005, at the Kennedy Athletic, Recreational and Social (KARS) Park, which is part of the Kennedy Space Center on Merritt Island, Florida. A total of 326 samples were analyzed by each XRF technology developer, including Rigaku, during the field demonstration. These samples were derived from 70 different blends and spiked blends of soil and sediment collected from nine sites across the U.S. The sample blends were thoroughly dried, sieved, crushed, mixed, and characterized before they were used for the demonstration. Some blends were also spiked to further adjust and refine the concentration ranges of the target elements. Between three and seven replicate samples of each blend were included in the demonstration sample set and analyzed by the technology developers during the field demonstration.

Shealy Environmental Services, Inc. (Shealy), of Cayce, South Carolina, was selected as the reference laboratory to generate comparative data in evaluation of XRF instrument performance. Shealy analyzed all demonstration samples (both environmental and spiked) concurrently with the developers during the field demonstration. The samples were analyzed by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) using EPA SW-846 Method 3050B/6010B and by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using EPA SW-846 Method 7471A (mercury only).

This verification statement provides a summary of the evaluation results for the Rigaku ZSX Mini II XRF instrument. More detailed discussion can be found in the *Innovative Technology Verification Report – XRF Technologies for Measuring Trace Elements in Soil and Sediment: Rigaku ZSX Mini II XRF Analyzer* (EPA/540/R-06/001).

TECHNOLOGY DESCRIPTION

XRF spectroscopy is an analytical technique that exposes a sample (soil, alloy metal, filters, other solids, and thin samples) to an x-ray source. The x-rays from the source have the appropriate excitation energy that causes elements in the sample to emit characteristic x-rays. A qualitative elemental analysis is possible from the characteristic energy, or wavelength, of the fluorescent x-rays emitted. A quantitative elemental analysis is possible from the number (intensity) of x-rays at a given wavelength.

The ZSX Mini II differs from the other XRF technologies evaluated in the SITE MMT demonstration in that it is a "wavelength-dispersive" XRF analyzer. Wavelength-dispersive XRF analyzers differentiate the x-ray energies emitted from a sample by dispersing them into different wavelength ranges using crystals. The other seven technologies participating in the demonstration were "energy-dispersive" XRF analyzers that differentiate x-ray energies based on voltages measured by the detector. Wavelength dispersive XRFs have historically been large, laboratory-bound instruments with significant requirements for power and cooling. The ZSX Mini II is a smaller, transportable unit that can operate at room temperature on standard 110-volt circuits. The ZSX Mini II has a sample chamber that can: accommodate up to 12 samples, be adapted for irregularly-shaped objects, operate under vacuum or helium environments (enhancing performance for light elements), and spin samples during analysis (with an available spinner accessory). Up to five types of analyzing crystals are available for x-ray dispersion, including lithium fluoride, pentaerythritol, thallium acid phthalate, RX35, and germanium. Multiple crystals can be used for a single analysis using a revolving changer. In contrast to energy-dispersive instruments, the unit employs an economical gas proportional counter as a detector rather than a diode array/multi-channel analyzer detector because wavelength resolution is achieved with the crystals.

VERIFICATION OF PERFORMANCE

Method Detection Limit: MDLs were calculated using seven replicate analyses from each of 12 low-concentration sample blends, according to the procedure described in Title 40 Code of Federal Regulations (CFR) Part 136, Appendix B, Revision 1.11. A mean MDL was further calculated for each target element. The ranges into which the mean MDLs fell for the ZSX Mini II are listed below (lower MDL values indicate better sensitivity).

Relative Sensitivity	Mean MDL	Target Elements
High	1 - 20 ppm	Copper, Mercury, Nickel, Selenium, and Zinc.
Moderate	20 – 50 ppm	Arsenic, Lead, Silver, and Vanadium.
Low	50 – 100 ppm	Antimony, Cadmium, and Chromium.
Very Low	>100 ppm	None.

Notes: ppm = Parts per million. Iron was not included in the MDL evaluation.

Accuracy: Accuracy was evaluated based on the agreement of the XRF results with the reference laboratory data. Accuracy was assessed by calculating the absolute relative percent difference (RPD) between the mean XRF and the mean reference laboratory concentration for each blend. Accuracy of the ZSX Mini II was classified from high to very low for the various target elements, as indicated in the table below, based on the overall median RPDs calculated for the demonstration.

Relative Accuracy	Median RPD	Target Elements
High	0% - 10%	None.
Moderate	10% - 25%	None.
Low	25% - 50%	Arsenic, Chromium, Copper, Silver, Vanadium, and Zinc.
Very Low	> 50%	Antimony*, Cadmium, Iron, Lead, Mercury, Nickel, and Selenium.

* Calculation of RPDs versus sample spike concentrations rather than reference laboratory results (due to potential low bias in the reference laboratory results for antimony) failed to improve accuracy.

Accuracy was also assessed through correlation plots between the mean ZSX Mini II and mean reference laboratory concentrations for the various sample blends. Correlation coefficients (r^2) for linear regression analysis of the plots are summarized below, along with any significant biases apparent from the plots in the XRF data versus the reference laboratory data.

	Antimony*	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc
Correlation	0.11	0.90	0.82	0.95	0.95	0.93	0.99	0.98	0.93	0.97	0.01	0.73	0.97
Bias	Indet.	Low	Var.	Low	Low	Low	Low	Low	Low	Low	Indet.	Var.	Low

Notes: Indet. = Indeterminate due to low correlation. Var. = Bias varies from high to low as concentration increases.
* Correlation did not improve when compared to sample spike concentrations as opposed to reference laboratory data.

Precision: Replicates were analyzed for all sample blends. Precision was evaluated by calculating the standard deviation of the replicates, dividing by the average concentration of the replicates, and multiplying by 100 percent to yield the relative standard deviation (RSD) for each blend. Precision of the ZSX Mini II was classified from high to very low for each target element, as indicated in the table below, based on the overall median RSDs. The calculated RSDs indicated a higher level of precision in the ZSX Mini II than in the reference laboratory data for all target elements except arsenic and chromium.

Relative Precision	Median RSD	Target Elements
High	0% - 5%	Cadmium, Copper, Iron, Lead, Mercury, Nickel, Selenium, Silver, and Zinc
Moderate	5% - 10%	Antimony and Vanadium.
Low	10% - 20%	Arsenic and Chromium.
Very Low	> 20%	None.

Effects of Interferences: The RPDs from the evaluation of accuracy were further grouped and compared for a few elements of concern (arsenic, nickel, copper, and zinc) based on the relative concentrations of potentially interfering elements. This evaluation found that high relative lead concentrations (more than 10X), a potential interferent for arsenic, actually improved the apparent accuracy for arsenic results in the ZSX Mini II data set (decreasing the median RPDs for arsenic from 45 percent to 16 percent) by counteracting the inherently low instrument bias. Similar but smaller effects were observed on nickel, copper, and zinc results for other interfering elements.

Effects of Soil Characteristics: The RPDs from the evaluation of accuracy were also further evaluated in terms of sampling site and soil type. This evaluation found high variability in RPD values for multiple target elements in sandy soil from the KARS Park site, a former gun range. Extreme RPD ranges and high RPD outliers were also observed on a more limited basis in blends from other sampling sites; however, sample matrix had little overall effect on accuracy for the ZSX Mini II, given the broad overall ranges of RPDs observed.

Sample Throughput: The total processing time per sample was estimated at 8.6 minutes, which included 2.2 minutes of sample preparation and 5.7 minutes of instrument analysis time. A sample throughput of 69 samples per 8-hour work day was estimated with the use of the instrument's autosampler. As noted above, however, the sample blends had undergone rigorous pre-processing before the demonstration. Sample throughput would have decreased if these sample preparation steps (grinding, drying, sieving) had been performed during the demonstration; these steps can add from 10 minutes to 2 hours to the sample processing time.

Costs: A cost assessment identified a purchase cost of $82,500 plus $500 shipping for the ZSX Mini II. Using a hypothetical rental cost approximated from similar types of instruments, a total cost of $10,421 (with a labor cost of $5,286 at $43.75/hr) associated with sample preparation and analysis was estimated for a project similar to the demonstration (326 samples of soil and sediment). In comparison, the project cost averaged $8,932 for all eight XRF instruments participating in the demonstration and $63,896 for fixed-laboratory analysis of all samples for the 13 target elements.

Skills and training required: Field or laboratory technicians with a high school diploma are generally qualified to operate the ZSX Mini II. Rigaku offers free training for instrument purchasers that generally lasts about 3 days, and the instrument is equipped with a modem for remote troubleshooting.

Health and Safety Aspects: The ZSX Mini II is equipped with safety measures to minimize possible exposure to emissions from the x-ray tube. The instrument cannot be operated if these safety measures are disabled. Users of the ZSX Mini II must be able to safely manage high-pressure gas cylinders (if inert atmosphere analysis is desired).

Portability: Based on dimensions, weight, and power requirements, the ZSX Mini II is a transportable (as opposed to fully portable) instrument. It is best used in a field trailer or other fixed location with the required power supply and a stable, weatherproof environment.

Durability: The ZSX Mini II is encased in durable hard-tool plastic but is not weatherproof. Rigaku offers a 12-month limited warranty for parts and labor. The average lifespan of the x-ray tube source is estimated at 10,000 hours or 7 years.

Availability: New instruments are available from the Rigaku offices in The Woodlands, Texas, and London. Customers are supported by world-wide network of 10 sales and 35 service representatives.

RELATIVE PERFORMANCE

ZSX Mini II overall performance relative to the XRF demonstration as a whole (all 8 instruments) is as follows:

	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Selenium	Silver	Vanadium	Zinc
Sensitivity	0	0	●	●	●	●	●	●	●	●	●	●	●
Accuracy	0	0	0	0	0	0	0	0	0	0	0	●	0
Precision	Same	0	●	0	●	●	●	●	●	●	●	●	●

Key: ● Better 0 Worse

NOTICE: Verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. 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.

APPENDIX B

DEVELOPER DISCUSSION

DEVELOPER DISCUSSION

Although we did not match well with the unknowns certified results, our instrument tracked well with the assayed numbers. In other words, as they went up or down in concentration, so did we.

From our point of view the test went well; the ZSX Mini II demonstrated better sensitivity and repeatability versus all other instruments.

The ZSX Mini II has proven to be excellent for analysis of heavy elements such as Cu, Fe, Ti, or Zr. Elements such as Ag, Cd and Sb were our worst performers for the reason that the ZSX Mini II does not have a Primary Beam Filter. These elements are not possible at low concentrations on the ZSX Mini II due to either sensitivity or interference from tube lines.

The lack of finite standard concentration values was of prime concern for us in this test. The supplied reference materials had a range for the element concentrations, not exact values. We are curious as to how the other vendors obtained more accurate results as the ZSX Mini II always out performs all these instruments in regular competitions. Perhaps we missed some information on this setup?

One of the categories was on portability of the unit. The notation concerning how many people it takes to move the unit indicates that the ZSX Mini II is not field portable. The definition of “field portable” is relative. Its portability is shown in the fact that it was shipped to this site, set up and the tests run in a short period of time. It is not an instrument that is hand carried but definitely portable within the definition of portable for this application and is readily placed in a van, or other smaller vehicles. This is not possible with the larger, full power XRF systems.

For the item where the Mini II was noted as requiring facilities like a stable platform, gas, electricity and temperature controlled environment. Other systems at the site also required many of these facilities while still others needed acids, fume hoods, hot plates, etc.

Rigaku feels that we participated in this test with the intent of simulating a field situation. Although the samples were ground – this would not necessarily be found in the field - they were run as loose powders as would be expected in a remote environment. Our main concern is the method on which we had based our calibrations. The fact that we were poor only in the accuracy aspect relates to improper concentration values of the calibration reference materials. As stated earlier, the Mini II is produced for just such tests and has a proven track record for such analyses.

We thank you for allowing us to participate in this exercise and look forward to any further experiments you may have in the future.

APPENDIX C

DATA VALIDATION SUMMARY REPORT

Contents

Chapter **Page**

APPENDIX

ABBREVIATIONS AND ACRONYMS

CCV	Continuing calibration verification
CVAA	Cold vapor atomic absorption
DVSR	Data validation summary report
EPA	U.S. Environmental Protection Agency
FAR	Federal acquisition regulations
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
ICS	Interference check sample
ICV	Initial calibration verification
LCS	Laboratory control sample
LCSD	Laboratory control sample duplicate
MDL	Method detection limit
mg/kg	Milligram per kilogram
MS	Matrix spike
MSD	Matrix spike duplicate
PARCC	Precision, accuracy, representativeness, completeness, and comparability
PQL	Practical quantitation limit
QA/QC	Quality assurance and quality control
QAPP	Quality assurance project plan
QC	Quality control
RSD	Relative standard deviation
RPD	Relative percent difference
SDG	Sample delivery group
Shealy	Shealy Environmental Services, Inc.
SITE	Superfund Innovative Technology Evaluation
Tetra Tech	Tetra Tech EM Inc.
XRF	X-ray fluorescence

1.0 INTRODUCTION

This data validation summary report (DVSR) summarizes the reference laboratory quality control (QC) data gathered during the x-ray fluorescence (XRF) technologies demonstration conducted under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) program. The reference laboratory was procured following the federal acquisition regulations (FAR) and an extensive selection process. Shealy Environmental Services, Inc. (Shealy), of Cayce, South Carolina, was selected as the reference laboratory for this project. Thirteen target analytes were measured in reference samples and include antimony, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, vanadium, and zinc. The laboratory reported results for 22 metals at the request of EPA; however, for the purposes of meeting project objectives, only the data validation for the 13 target analytes is summarized in this document. The objective of the validation is to determine the validity of the reference data, as well as its usability in meeting the primary objective of comparing reference data to XRF data generated during the demonstration. Shealy provided the data to Tetra Tech EM Inc. (Tetra Tech) in electronic and hardcopy formats; a total of 13 sample delivery groups (SDG) contain all the data for this project.

The DVSR consists of seven sections, including this introduction. Section 2.0 presents the data validation methodology. Section 3.0 presents the results of the reference laboratory data validation. Section 4.0 summarizes the precision, accuracy, representativeness, completeness, and comparability (PARCC) evaluation. Section 5.0 presents conclusions about the overall evaluation of the reference data. Section 6.0 lists the references used to prepare this DVSR. Tables are presented following Section 6.0.

2.0 VALIDATION METHODOLOGY

Data validation is the systematic process for reviewing and qualifying data against a set of criteria to ensure that the reference data are adequate for the intended use. The data validation process assesses acceptability of the data by evaluating the critical indicator parameters of PARCC. The laboratory analytical data were validated according to the procedures outlined in the following documents:

- "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (EPA 2004), hereinafter referred to as the "EPA guidance."
- "Demonstration and Quality Assurance Project Plan, XRF Technologies for Measuring Trace Elements in Soil and Sediment" (Tetra Tech 2005), hereinafter referred to as "the QAPP."

Data validation occurred in the following two stages: (1) a cursory review of analytical reports and quality assurance and quality control (QA/QC) information for 100 percent of the reference data and (2) full validation of analytical reports, QA/QC information, and associated raw data for 10 percent of the reference data as required by the QAPP (Tetra Tech 2005).

QA/QC criteria were reviewed in accordance with EPA guidance (EPA 2004) and the QAPP (Tetra Tech 2005). The cursory review for total metals consisted of evaluating the following requirements, as applicable:

- Holding times

- Initial and continuing calibrations
- Laboratory blank results
- Laboratory control sample (LCS) and laboratory control sample duplicates (LCSD) results
- Matrix spike (MS) and matrix spike duplicate (MSD) results
- Serial dilutions results

In addition to QA/QC criteria described above, the following criteria were reviewed during full validation:

- ICP interference check samples (ICS)
- Target analyte identification and quantitation
- Quantitation limit verification

Section 3.0 presents the results of the both the cursory review and full validation.

During data validation, worksheets were produced for each SDG that identify any QA/QC issues resulting in data qualification. Data validation findings were written in 13 individual data validation reports (one for each SDG). Data qualifiers were assigned to the results in the electronic database in accordance with EPA guidelines (EPA 2004). In addition to data validation qualifiers, comment codes were added to the database to indicate the primary reason for the validation qualifier. Table 1 defines data validation qualifiers and comment codes that are applied to the data set. Details about specific QC issues can be found in the individual SDG data validation reports and accompanying validation worksheets provided in the Appendix.

The overall objective of data validation is to ensure that the quality of the reference data set is adequate for the intended use, as defined by the QAPP (Tetra Tech 2005) for the PARCC parameters. Table 2 provides the QC criteria as defined by the QAPP. PARCC parameters were assessed by completing the following tasks:

- Reviewing precision and accuracy of laboratory QC data
- Reviewing the overall analytical process, including holding time, calibration, analytical or matrix performance, and analyte identification and quantitation
- Assigning qualifiers to affected data when QA/QC criteria were not achieved
- Reviewing and summarizing implications of the frequency and severity of qualifiers in the validated data

Prior to the XRF demonstration, soil and sediment samples were collected from nine locations across the U.S. and then blended, dried, sieved, and homogenized in the characterization laboratory to produce a set of 326 reference samples. Each of these samples were subsequently analyzed by both the reference laboratory and all participating technology vendors. As such, 326 prepared soil/sediment samples were delivered to Shealy for the measurement of total metals. The analytical program included the following analyses and methods:

- Total metal for 22 analytes by inductively coupled plasma atomic emission spectroscopy (ICP-AES) according to EPA Methods 3050B/6010B (EPA 1996)
- Total mercury by cold vapor atomic absorption spectroscopy (CVAA) according to EPA Method 7471A (EPA 1996)

3.0 DATA VALIDATION RESULTS

The parameters listed in Section 2.0 were evaluated during cursory review and full validation of analytical reports for all methods, as applicable. Each of the validation components discussed in this section is summarized as follows:

- Acceptable – All criteria were met and no data were qualified on that basis
- Acceptable with qualification – Most criteria were met, but at least one data point was qualified as estimated because of issues related to the review component

Since no data were rejected, all data were determined to be either acceptable or acceptable with qualification. Sections 3.1 through 3.9 discuss each review component and the results of each. Tables that summarize the data validation findings follow Section 6.0 of this DVSR. Only qualified data are included in the tables. No reference laboratory data were rejected during the validation process. As such, all results are acceptable with the qualification noted in the sections that follow.

3.1 Holding Time

Acceptable. The technical holding times were defined as the maximum time allowable between sample collection and, as applicable, sample extraction, preparation, or analysis. The holding times used for validation purposes were recommended in the specific analytical methods (EPA 1996) and were specified in the QAPP (Tetra Tech 2005).

Because the soil and sediment samples were prepared prior to submission to the reference laboratory, and because the preparation included drying to remove moisture, no chemical or physical (for example ice) preservation was required. The holding time for sample digestion was 180 days for the ICP-AES analyses and 28 days for mercury. All sample digestions and analyses were conducted within the specified holding times. No data were qualified based on holding time exceedances. This fact contributes to the high technical quality of the reference data.

3.2 Calibration

Acceptable. Laboratory instrument calibration requirements were established to ensure that analytical instruments could produce acceptable qualitative and quantitative data for all target analytes. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of an analytical run, while producing a linear curve. Continuing calibration demonstrates that the instrument is capable of repeating the performance established during the initial calibration (EPA 1996).

For total metal analyses (ICP-AES and CVAA), initial calibration review included evaluating criteria for the curve's correlation coefficient and initial calibration verification (ICV) percent recoveries. The ICV percent recoveries verify that the analytical system is operating within the established calibration criteria at the beginning of an analytical run. The continuing calibration review included evaluation of the criteria for continuing calibration verification (CCV) percent recoveries. The CCV percent recoveries verify that the analytical system is operating within the established calibration throughout the analytical run.

All ICV and CCV percent recoveries associated with the reference data were within acceptable limits of 90 to 110 percent. As such, no data were qualified or rejected because of calibration exceedances. This fact contributes to the high technical quality of the data.

3.3 Laboratory Blanks

Acceptable with qualification. No field blanks were required by the QAPP, since samples were prepared after collection and before submission to the reference laboratory. However, laboratory blanks were prepared and analyzed to evaluate the existence and magnitude of contamination resulting from laboratory activities. Blanks prepared and analyzed in the laboratory consisted of calibration and preparation blanks. If a problem with any blank existed, all associated data were carefully evaluated to assess whether the sample data were affected. At a minimum, calibration blanks were analyzed for every 10 analyses conducted on each instrument. Preparation blanks were prepared at a frequency of one per preparation batch per matrix or every 20 samples, whichever is greater (EPA 1996).

When laboratory blank contamination was identified, sample results were compared to the practical quantitation limit (PQL) and the maximum blank value as required by the validation guidelines (EPA 2004). Most of the blank detections were positive results (i.e. greater than the method detection limit [MDL]), but less than the PQL. In these instances, if associated sample results were also less than the PQL, they were qualified as undetected (U); with the comment code "b." In these same instances, if the associated sample results were greater than the PQL, the reviewer used professional judgment to determine if the sample results were adversely affected. If so, then the results were qualified as estimated with the potential for being biased high (J+). If not, then no qualification was required.

In a few cases, the maximum blank value exceeded the PQL. In these cases, all associated sample results less than the PQL were qualified as undetected (U) with the comment code "b." In cases where the associated sample results were greater than the PQL, but less than the blank concentration, the results were also qualified as undetected (U); with the comment code "b." If the associated sample results were greater than both the PQL and the blank value, the reviewer used professional judgment to determine if sample results were adversely affected. If so, then the results were qualified as estimated with the potential for being biased high (J+); with the comment code "b." Sample results significantly above the blank were not qualified.

In addition to laboratory blank contamination, negative drift greater than the magnitude of the PQL was observed in some laboratory blanks. Associated sample data were qualified as undetected (U) if the results were less than the PQL. Professional judgement was used to determine if the negative drift adversely affected associated sample results greater than the PQL. If so, then sample results were qualified as estimated with the potential for being biased low (J-) due to the negative drift of the instrument baseline; with the comment code "b."

Of all target analyte data, 2.6 percent of the data was qualified as undetected because of laboratory blank contamination (U, b), and less than 1 percent of the data was qualified as estimated (either J+, b or J-, b). The low occurrence of results affected by blank contamination indicates that the general quality of the analytical data was not significantly compromised by blank contamination. Table 3 provides all results that were qualified based on laboratory blanks.

3.4 Laboratory Control Samples

Acceptable. LCSs and LCSDs were prepared and analyzed with each batch of 20 or fewer samples of the same matrix. All percent recoveries were within the QC limits of 80 to 120 percent; all relative percent differences (RPD) between the LCD and LCSD values were less than the criterion of 20 percent. No data were qualified or rejected on the basis of LCS/LCSD results. This fact contributes to the high technical quality of the data.

3.5 Matrix Spike Samples

Acceptable with qualification. MS and MSD samples were prepared and analyzed with each batch of 20 or fewer samples of the same matrix. All percent recoveries were within the QC limits of 75 to 125 percent, and all RPDs between the MS and MSD values were less than the criterion of 25 percent, except as discussed in the following paragraphs.

Sample results affected by MS and MSD percent recoveries issues were qualified as estimated and either biased high (J+) if the recoveries were greater than 125 percent; or qualified as estimated and biased low (J-) if the recoveries were less than 75 percent. In at least one case, the MS was higher than 125 percent and the MSD was lower than 75 percent; the associated results were qualified as estimated (J) with no distinction for potential bias. All data qualified on the basis of MS and MSD recovery were also assigned the comment code "e." Of all target analyte data, less than 1 percent was qualified as estimated and biased high (J+, e), while about 8 percent of the data were qualified as estimated and biased low (J-, e). Antimony and silver were the most frequently qualified sample results. Based on experience, antimony and silver soil recoveries are frequently low using the selected methods. Table 4 provides the results that were qualified based on MS/MSD results.

The precision between MS and MSD results were generally acceptable. If the RPD between MS and MSD results were greater than 25 percent, the data were already qualified based on exceedance of the acceptance window for recovery. Therefore, no additional qualification was required for MS/MSD precision.

No data were rejected on the basis of MS/MSD results. The relatively low occurrence of data qualification due to MS/MSD recoveries and RPDs contribute to the high technical quality of the data.

3.6 Serial Dilution Results

Acceptable with qualification. Serial dilutions were conducted and analyzed by Shealy at a frequency of 1 per batch of 20 samples. The serial dilution analysis can evaluate whether matrix interference exists and whether the accuracy of the analytical data is affected. For all target analyte data, less than 1 percent of the data was qualified as estimated and biased high (J+, j), while about 2 percent of the data were qualified as estimated and biased low (J-, j). Serial dilution results are used to determine whether characteristics of the digest matrix, such as viscosity or the presence of analytes at high concentrations, may interfere with the detected analytes. Qualifiers were applied to cases where interference was suspected. However, the low incidence of apparent matrix interference contributes to the high technical quality of the data. Table 5 provides the results that were qualified based on MS/MSD results.

3.7 ICP Interference Check Samples

Acceptable. ICP results for each ICS were evaluated. The ICS verifies the validity of the laboratory's inter-element and background correction factors. High levels of certain elements (including aluminum, calcium, iron, and magnesium) can affect sample results if the inter-element and background correction factors have not been optimized. Incorrect correction factors may result in false positives, false negatives, or biased results. All ICS recoveries were within QC limits of 80 to 120 percent, and no significant biases were observed due to potential spectral interference. No data were qualified or rejected because of ICS criteria violations. This fact contributes to the high technical quality of the data.

3.8 Target Analyte Identification and Quantitation

Acceptable Identification is determined by measuring the characteristic wavelength of energy emitted by the analyte (ICP) or absorbed by the analyte (CVAA). External calibration standards are used to quantify the analyte concentration in the sample digest. Sample digest concentrations are converted to soil units (milligrams per kilogram) and corrected for percent moisture. For 10 percent of the samples, results were recalculated to verify the accuracy of reporting. All results were correctly calculated by the laboratory, except for one mercury result, whose miscalculation was the result of an error in entering the dilution factor. Shealy immediately resolved this error and corrected reports were provided. Since the result was corrected, no qualification was required. No other reporting errors were observed.

For inorganic analyses, analytical instruments can make reliable qualitative identification of analytes at concentrations below the PQL. Detected results below the PQL are considered quantitatively uncertain. Sample results below the PQL were reported by the laboratory with a "J" qualifier. No additional qualification was required.

3.9 Quantitation Limit Verification

Acceptable. Reference laboratory quantitation limits were specified in the QAPP (Tetra Tech 2005). Circumstances that affected quantitation were limited and included dilution and percent moisture factors. Since the samples were prepared prior to submission to the reference laboratory, moisture content was very low and had little impact on quantitation limits. The laboratory did correct all quantitation limits for moisture content. Due to the presence of percent-level analytes in some samples, dilutions were required. However, the required PQLs for the reference laboratory were high enough that even with dilution and moisture content factors applied, the reporting limits did not exceed those of the XRF instruments. This allows for effective comparison of results between the reference laboratory and XRF instruments.

4.0 PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS, AND COMPARABILITY EVALUATION SUMMARY

All analytical data were reviewed for PARCC parameters to validate reference data. The following sections discuss the overall data quality, including the PARCC parameters, as determined by the data validation.

4.1 Precision

Precision is a measure of the reproducibility of an experimental value without considering a true or referenced value. The primary indicators of precision were the MS/MSD RPD and LCS/LCSD RPD between the duplicate results. Precision criteria of less than 20 percent RPD for LCS/LCSD and 25 percent for MS/MSD were generally met for all duplicate pairs. No data were qualified based on duplicate precision of MS/MSD or LCS/LCSD pairs that were not already qualified for other reasons. Such low occurrence of laboratory precision problems supports the validity, usability, and defensibility of the data.

4.2 Accuracy

Accuracy assesses the proximity of an experimental value to a true or referenced value. The primary accuracy indicators were the recoveries of MS and LCS spikes. Accuracy is expressed as percent recovery. Overall, about 8 percent of the data was qualified as estimated and no data were rejected because of accuracy problems. The low frequency of accuracy problems supports the validity, usability, and defensibility of the data.

4.3 Representativeness

Representativeness refers to how well sample data accurately reflect true environmental conditions. The QAPP was carefully designed to ensure that actual environmental samples be collected by choosing representative sites across the US from which sample material was collected. The blending and homogenization was executed according to the approved QAPP (Tetra Tech 2005).

4.4 Completeness

Completeness is defined as the percentage of measurements that are considered to be valid. The validity of sample results is evaluated through the data validation process. Sample results that are rejected and any missing analyses are considered incomplete. Data that are qualified as estimated (J) or undetected estimated (UJ) are considered valid and usable. Data qualified as rejected (R) are considered unusable for all purposes. Since no data were rejected in this data set, a completeness of 100 percent was achieved. A total of 4,238 target analyte results were evaluated. The completeness goal stated in the QAPP (Tetra Tech 2005) was 90 percent.

4.5 Comparability

Comparability is a qualitative parameter that expresses the confidence with which one data set may be compared to another. Widely-accepted SW-846 methods were used for this project. It is recognized that direct comparison of the reference laboratory data (using ICP-AES and CVAA techniques) to the XRF measurements may result in discrepancies due to differences in the preparation and measurement techniques; however, the reference laboratory data is expected to provide an acceptable basis for comparison to XRF measurement results in accordance with the project objectives.

Comparability of the data was also achieved by producing full data packages, by using a homogenous matrix, standard quantitation limits, standardized data validation procedures, and by evaluating the PARCC parameters uniformly. In addition, the use of specified and well-documented analyses, approved laboratories, and the standardized process of data review and validation have resulted in a high degree of comparability for the data.

5.0 CONCLUSIONS FOR DATA QUALITY AND DATA USABILITY

Although some qualifiers were added to the data, a final review of the data set with respect to the data quality parameters discussed in Section 4.0 indicates that the data are of overall good quality. No analytical data were rejected. The data quality is generally consistent with project objectives for producing data of suitable quality for comparison to XRF data. All supporting documentation and data are available upon request, including cursory review and full validation reports as well as the electronic database that contains sample results.

6.0 REFERENCES

Tetra Tech EM, Inc. (Tetra Tech). 2005. “Demonstration and Quality Assurance Project Plan, XRF Technologies for Measuring Trace Elements in Soil and Sediment.” March.

U.S. Environmental Protection Agency (EPA). 1996. “Test Methods for Evaluating Solid Waste”, Third Edition (SW-846). With promulgated revisions. December.

EPA. 2004. “USEPA Contract Laboratory Program National Functional Guidelines For Inorganic Data Review”. October.

TABLES

TABLE 1: DATA VALIDATION QUALIFIERS AND COMMENT CODES

Qualifier	Definition
No Qualifier	Indicates that the data are acceptable both qualitatively and quantitatively.
U	Indicates compound was analyzed for but not detected above the concentration listed. The value listed is the sample quantitation limit.
J	Indicates an estimated concentration value. The result is considered qualitatively acceptable, but quantitatively unreliable.
J+	The result is an estimated quantity, but the result may be biased high.
J-	The result is an estimated quantity, but the result may be biased low.
UJ	Indicates an estimated quantitation limit. The compound was analyzed for, but was considered non-detected.
R	The data are unusable (compound may or may not be present). Resampling and reanalysis is necessary for verification.

Comment Code	Definition
a	Surrogate recovery exceeded (not applicable to this data set)
b	Laboratory method blank and common blank contamination
c	Calibration criteria exceeded
d	Duplicate precision criteria exceeded
e	Matrix spike or laboratory control sample recovery exceeded
f	Field blank contamination (not applicable to this data set)
g	Quantification below reporting limit
h	Holding time exceeded
i	Internal standard criteria exceeded (not applicable to this data set)
j	Other qualification (will be specified in report)

TABLE 2: QC CRITERIA

Parameter	Method	QC Check	Frequency	Criterion	Corrective Action
Reference Method					
Target Metals (12 ICP metals and Hg)	3050B/6010B and 7471A	Method and instrument blanks	One per analytical batch of 20 or less	Less than the reporting limit	1. Check calculations 2. Assess and eliminate source of contamination 3. Reanalyze blank 4. Inform Tetra Tech project manager 5. Flag affected results
		MS/MSD	One per analytical batch of 20 or less	75 to 125 percent recovery RPD ≤ 25	1. Check calculations 2. Check LCS/LCSD and digest duplicate results to determine whether they meet criterion 3. Inform Tetra Tech project manager 4. Flag affected results
		LCS/LCSD	One per analytical batch of 20 or less	80 to 120 percent recovery RPD ≤ 20	1. Check calculations 2. Check instrument operating conditions and adjust as necessary 3. Check MS/MSD and digest duplicate results to determine whether they meet criterion 4. Inform Tetra Tech project manager 5. Redigest and reanalyze the entire batch of samples 6. Flag affected results
		Performance audit samples	One per analytical batch of 20 or less	Within acceptance limits	1. Evaluated by Tetra Tech QA chemist 2. Inform laboratory and recommend changes 3. Flag affected results
Percent moisture		Laboratory duplicates	One per analytical batch of 20 or less	RPD ≤ 20	1. Check calculations 2. Reanalyze sample batch 3. Inform Tetra Tech project manager 4. Flag affected results

TABLE 3: DATA QUALIFICATION: LABORATORY METHOD BLANK CONTAMINATION

Sample ID	Analyte	Result	Unit	Validation Qualifier	Comment Code
AS-SO-04-XX	Selenium	6.2	mg/kg	U	b
AS-SO-06-XX	Antimony	2.4	mg/kg	UJ	b, e
AS-SO-10-XX	Selenium	1.1	mg/kg	U	b
AS-SO-11-XX	Selenium	1.1	mg/kg	U	b
AS-SO-13-XX	Antimony	2.4	mg/kg	UJ	b, e
BN-SO-18-XX	Silver	0.94	mg/kg	U	b
BN-SO-28-XX	Silver	0.77	mg/kg	U	b
BN-SO-31-XX	Silver	0.97	mg/kg	U	b
BN-SO-35-XX	Silver	0.85	mg/kg	U	b
KP-SE-01-XX	Mercury	0.053	mg/kg	U	b
KP-SE-11-XX	Mercury	0.079	mg/kg	U	b
KP-SE-12-XX	Mercury	0.06	mg/kg	U	b
KP-SE-14-XX	Mercury	0.065	mg/kg	U	b
KP-SE-17-XX	Mercury	0.082	mg/kg	U	b
KP-SE-19-XX	Mercury	0.044	mg/kg	U	b
KP-SE-25-XX	Mercury	0.096	mg/kg	U	b
KP-SE-25-XX	Selenium	0.26	mg/kg	U	b
KP-SE-28-XX	Mercury	0.056	mg/kg	U	b
KP-SE-30-XX	Mercury	0.1	mg/kg	U	b
KP-SE-30-XX	Selenium	0.24	mg/kg	U	b
KP-SO-02-XX	Mercury	0.043	mg/kg	U	b
KP-SO-02-XX	Selenium	0.42	mg/kg	U	b
KP-SO-03-XX	Cadmium	0.074	mg/kg	U	b
KP-SO-03-XX	Mercury	0.044	mg/kg	U	b
KP-SO-04-XX	Cadmium	0.046	mg/kg	U	b
KP-SO-04-XX	Mercury	0.018	mg/kg	U	b
KP-SO-04-XX	Selenium	0.28	mg/kg	U	b
KP-SO-05-XX	Cadmium	0.13	mg/kg	U	b
KP-SO-05-XX	Mercury	0.044	mg/kg	U	b
KP-SO-05-XX	Selenium	0.24	mg/kg	U	b
KP-SO-06-XX	Arsenic	0.73	mg/kg	J-	b
KP-SO-06-XX	Mercury	0.059	mg/kg	U	b
KP-SO-07-XX	Arsenic	2	mg/kg	J-	b
KP-SO-07-XX	Mercury	0.027	mg/kg	U	b
KP-SO-07-XX	Selenium	0.21	mg/kg	U	b
KP-SO-09-XX	Cadmium	0.094	mg/kg	U	b
KP-SO-09-XX	Mercury	0.046	mg/kg	U	b

TABLE 3: DATA QUALIFICATION: LABORATORY METHOD BLANK CONTAMINATION (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Comment Code
KP-SO-10-XX	Arsenic	0.7	mg/kg	J-	b
KP-SO-10-XX	Mercury	0.028	mg/kg	U	b
KP-SO-10-XX	Selenium	0.22	mg/kg	U	b
KP-SO-13-XX	Arsenic	1.4	mg/kg	J-	b
KP-SO-13-XX	Cadmium	0.045	mg/kg	U	b
KP-SO-13-XX	Mercury	0.037	mg/kg	U	b
KP-SO-15-XX	Arsenic	0.76	mg/kg	J-	b
KP-SO-15-XX	Mercury	0.029	mg/kg	U	b
KP-SO-16-XX	Cadmium	0.063	mg/kg	U	b
KP-SO-16-XX	Mercury	0.016	mg/kg	U	b
KP-SO-18-XX	Arsenic	0.56	mg/kg	J-	b
KP-SO-18-XX	Mercury	0.016	mg/kg	U	b
KP-SO-20-XX	Arsenic	1.5	mg/kg	J-	b
KP-SO-20-XX	Mercury	0.03	mg/kg	U	b
KP-SO-21-XX	Cadmium	0.098	mg/kg	U	b
KP-SO-21-XX	Mercury	0.042	mg/kg	U	b
KP-SO-22-XX	Arsenic	0.7	mg/kg	J-	b
KP-SO-22-XX	Mercury	0.027	mg/kg	U	b
KP-SO-23-XX	Cadmium	0.048	mg/kg	U	b
KP-SO-23-XX	Mercury	0.017	mg/kg	U	b
KP-SO-24-XX	Arsenic	1.4	mg/kg	J-	b
KP-SO-24-XX	Mercury	0.017	mg/kg	U	b
KP-SO-26-XX	Cadmium	0.061	mg/kg	U	b
KP-SO-26-XX	Mercury	0.013	mg/kg	U	b
KP-SO-26-XX	Selenium	0.22	mg/kg	U	b
KP-SO-27-XX	Arsenic	1.3	mg/kg	J-	b
KP-SO-27-XX	Cadmium	0.05	mg/kg	U	b
KP-SO-27-XX	Mercury	0.021	mg/kg	U	b
KP-SO-29-XX	Arsenic	1.5	mg/kg	J-	b
KP-SO-29-XX	Mercury	0.013	mg/kg	U	b
KP-SO-31-XX	Mercury	0.017	mg/kg	U	b
KP-SO-32-XX	Arsenic	1.6	mg/kg	J-	b
KP-SO-32-XX	Cadmium	0.045	mg/kg	U	b
KP-SO-32-XX	Mercury	0.014	mg/kg	U	b
LV-SE-02-XX	Mercury	0.02	mg/kg	U	b
LV-SE-10-XX	Mercury	0.023	mg/kg	U	b
LV-SE-11-XX	Selenium	1.3	mg/kg	U	b

TABLE 3: DATA QUALIFICATION: LABORATORY METHOD BLANK CONTAMINATION (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Comment Code
LV-SE-14-XX	Mercury	0.056	mg/kg	U	b
LV-SE-21-XX	Mercury	0.048	mg/kg	U	b
LV-SE-24-XX	Mercury	0.053	mg/kg	U	b
LV-SE-29-XX	Selenium	1.2	mg/kg	U	b
LV-SE-32-XX	Mercury	0.052	mg/kg	U	b
RF-SE-07-XX	Mercury	0.091	mg/kg	U	b
RF-SE-08-XX	Silver	0.39	mg/kg	U	b
RF-SE-10-XX	Silver	0.34	mg/kg	U	b
RF-SE-12-XX	Mercury	0.099	mg/kg	U	b
RF-SE-23-XX	Copper	0.2	mg/kg	U	b
RF-SE-23-XX	Zinc	0.6	mg/kg	U	b
RF-SE-33-XX	Silver	0.33	mg/kg	U	b
RF-SE-36-XX	Mercury	0.081	mg/kg	U	b
RF-SE-36-XX	Selenium	1	mg/kg	U	b
RF-SE-45-XX	Cadmium	0.52	mg/kg	U	b
RF-SE-53-XX	Cadmium	0.57	mg/kg	U	b
SB-SO-03-XX	Antimony	1.2	mg/kg	UJ	b, e
SB-SO-12-XX	Silver	2.1	mg/kg	UJ	b
SB-SO-13-XX	Silver	2.2	mg/kg	UJ	b
SB-SO-15-XX	Silver	1.6	mg/kg	UJ	b
SB-SO-17-XX	Silver	2.3	mg/kg	UJ	b, e
SB-SO-18-XX	Antimony	1.2	mg/kg	UJ	b, e
SB-SO-30-XX	Selenium	1.3	mg/kg	J+	b
SB-SO-32-XX	Silver	0.1	mg/kg	UJ	b, e
SB-SO-37-XX	Silver	2	mg/kg	UJ	b
SB-SO-46-XX	Silver	2.2	mg/kg	UJ	b, e
SB-SO-48-XX	Silver	0.1	mg/kg	UJ	b, e
SB-SO-53-XX	Antimony	1.2	mg/kg	UJ	b, e
TL-SE-01-XX	Mercury	0.074	mg/kg	U	b
TL-SE-03-XX	Mercury	0.32	mg/kg	J-	b
TL-SE-03-XX	Silver	0.94	mg/kg	U	b
TL-SE-04-XX	Mercury	0.26	mg/kg	J-	b
TL-SE-10-XX	Mercury	0.19	mg/kg	J-	b
TL-SE-11-XX	Mercury	0.021	mg/kg	U	b
TL-SE-12-XX	Mercury	0.22	mg/kg	J-	b
TL-SE-14-XX	Mercury	0.08	mg/kg	U	b
TL-SE-15-XX	Mercury	0.28	mg/kg	J-	b

TABLE 3: DATA QUALIFICATION: LABORATORY METHOD BLANK CONTAMINATION (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Comment Code
TL-SE-15-XX	Silver	1	mg/kg	U	b
TL-SE-18-XX	Mercury	0.025	mg/kg	U	b
TL-SE-19-XX	Mercury	0.32	mg/kg	J-	b
TL-SE-19-XX	Silver	1.1	mg/kg	U	b
TL-SE-20-XX	Mercury	0.26	mg/kg	J-	b
TL-SE-22-XX	Mercury	0.082	mg/kg	U	b
TL-SE-23-XX	Mercury	0.41	mg/kg	J-	b
TL-SE-23-XX	Silver	1.3	mg/kg	U	b
TL-SE-24-XX	Mercury	0.26	mg/kg	J-	b
TL-SE-24-XX	Silver	1.3	mg/kg	U	b
TL-SE-25-XX	Mercury	0.44	mg/kg	J-	b
TL-SE-25-XX	Silver	0.94	mg/kg	U	b
TL-SE-26-XX	Mercury	0.24	mg/kg	J-	b
TL-SE-27-XX	Mercury	0.02	mg/kg	U	b
TL-SE-29-XX	Mercury	0.076	mg/kg	U	b
TL-SE-31-XX	Mercury	0.57	mg/kg	J-	b
TL-SE-31-XX	Silver	1.2	mg/kg	U	b
WS-SO-06-XX	Mercury	0.07	mg/kg	U	b
WS-SO-08-XX	Mercury	0.063	mg/kg	U	b
WS-SO-10-XX	Mercury	0.058	mg/kg	U	b
WS-SO-12-XX	Mercury	0.068	mg/kg	UJ	b, e
WS-SO-17-XX	Mercury	0.069	mg/kg	UJ	b, e
WS-SO-20-XX	Mercury	0.06	mg/kg	U	b
WS-SO-23-XX	Mercury	0.05	mg/kg	U	b
WS-SO-30-XX	Mercury	0.069	mg/kg	UJ	b, e
WS-SO-31-XX	Selenium	1.2	mg/kg	U	b
WS-SO-35-XX	Mercury	0.071	mg/kg	UJ	b, e

Notes:
mg/kg = Milligrams per kilogram
b = Data were qualified based on blank contamination
e = Data were additionally qualified based on matrix spike/matrix spike duplicate exceedances
J+ = Result is estimated and potentially biased high
J- = Result is estimated and potentially biased low
UJ = Result is undetected at estimated quantitation limits

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
AS-SO-01-XX	Antimony	3.8	mg/kg	J-	e
AS-SO-02-XX	Antimony	<2.6	mg/kg	UJ	e
AS-SO-03-XX	Mercury	3.7	mg/kg	J-	e
AS-SO-03-XX	Silver	480	mg/kg	J-	e
AS-SO-04-XX	Antimony	<6.4	mg/kg	UJ	e
AS-SO-05-XX	Mercury	2.5	mg/kg	J-	e
AS-SO-05-XX	Silver	330	mg/kg	J-	e
AS-SO-06-XX	Antimony	2.4	mg/kg	UJ	b, e
AS-SO-07-XX	Antimony	3.6	mg/kg	J-	e
AS-SO-08-XX	Mercury	2.5	mg/kg	J-	e
AS-SO-08-XX	Silver	280	mg/kg	J-	e
AS-SO-09-XX	Antimony	<2.6	mg/kg	UJ	e
AS-SO-10-XX	Antimony	1.9	mg/kg	J-	e
AS-SO-11-XX	Antimony	3.7	mg/kg	J-	e
AS-SO-12-XX	Antimony	<2.6	mg/kg	UJ	e
AS-SO-13-XX	Antimony	2.4	mg/kg	UJ	b, e
BN-SO-01-XX	Antimony	<1.3	mg/kg	UJ	e
BN-SO-01-XX	Silver	<1.3	mg/kg	UJ	e
BN-SO-05-XX	Antimony	160	mg/kg	J-	e
BN-SO-07-XX	Antimony	110	mg/kg	J-	e
BN-SO-07-XX	Silver	990	mg/kg	J+	e
BN-SO-09-XX	Antimony	750	mg/kg	J-	e
BN-SO-09-XX	Silver	100	mg/kg	J-	e
BN-SO-10-XX	Antimony	<1.3	mg/kg	UJ	e
BN-SO-10-XX	Silver	<1.3	mg/kg	UJ	e
BN-SO-11-XX	Antimony	4	mg/kg	J-	e
BN-SO-11-XX	Silver	140	mg/kg	J-	e
BN-SO-12-XX	Antimony	750	mg/kg	J-	e
BN-SO-12-XX	Silver	210	mg/kg	J-	e
BN-SO-14-XX	Antimony	3.5	mg/kg	J-	e
BN-SO-14-XX	Silver	140	mg/kg	J-	e
BN-SO-15-XX	Antimony	<1.3	mg/kg	UJ	e
BN-SO-15-XX	Silver	<1.3	mg/kg	UJ	e
BN-SO-16-XX	Antimony	120	mg/kg	J-	e
BN-SO-16-XX	Arsenic	1100	mg/kg	J+	e
BN-SO-19-XX	Antimony	150	mg/kg	J-	e
BN-SO-21-XX	Antimony	150	mg/kg	J-	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
BN-SO-21-XX	Arsenic	1300	mg/kg	J+	e
BN-SO-23-XX	Antimony	<1.2	mg/kg	UJ	e
BN-SO-23-XX	Silver	130	mg/kg	J-	e
BN-SO-24-XX	Antimony	810	mg/kg	J-	e
BN-SO-24-XX	Silver	140	mg/kg	J-	e
BN-SO-25-XX	Antimony	82	mg/kg	J-	e, j
BN-SO-25-XX	Arsenic	700	mg/kg	J	e, j
BN-SO-26-XX	Antimony	150	mg/kg	J-	e
BN-SO-29-XX	Antimony	150	mg/kg	J-	e
BN-SO-32-XX	Antimony	160	mg/kg	J-	e
BN-SO-33-XX	Antimony	100	mg/kg	J-	e
CN-SO-01-XX	Antimony	13	mg/kg	J-	e
CN-SO-02-XX	Mercury	270	mg/kg	J-	e
CN-SO-03-XX	Mercury	34	mg/kg	J-	e
CN-SO-04-XX	Antimony	13	mg/kg	J-	e
CN-SO-05-XX	Mercury	280	mg/kg	J-	e
CN-SO-06-XX	Mercury	40	mg/kg	J-	e
CN-SO-07-XX	Mercury	36	mg/kg	J-	e
CN-SO-08-XX	Antimony	15	mg/kg	J-	e
CN-SO-09-XX	Mercury	260	mg/kg	J-	e
CN-SO-10-XX	Antimony	13	mg/kg	J-	e
CN-SO-11-XX	Antimony	17	mg/kg	J-	e
KP-SE-01-XX	Lead	310	mg/kg	J-	e
KP-SE-01-XX	Silver	<0.26	mg/kg	UJ	e
KP-SE-08-XX	Lead	300	mg/kg	J-	e
KP-SE-08-XX	Silver	<0.27	mg/kg	UJ	e
KP-SE-11-XX	Lead	310	mg/kg	J-	e
KP-SE-11-XX	Silver	<0.27	mg/kg	UJ	e
KP-SE-12-XX	Lead	320	mg/kg	J-	e
KP-SE-12-XX	Silver	<0.26	mg/kg	UJ	e
KP-SE-14-XX	Lead	680	mg/kg	J-	e, j
KP-SE-14-XX	Silver	<0.26	mg/kg	UJ	e
KP-SE-17-XX	Lead	300	mg/kg	J-	e
KP-SE-17-XX	Silver	<0.27	mg/kg	UJ	e
KP-SE-25-XX	Lead	310	mg/kg	J-	e
KP-SE-25-XX	Silver	<0.27	mg/kg	UJ	e
KP-SE-30-XX	Lead	300	mg/kg	J-	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
KP-SE-30-XX	Silver	<0.27	mg/kg	UJ	e
KP-SO-04-XX	Antimony	94	mg/kg	J+	e
KP-SO-06-XX	Antimony	8.1	mg/kg	J+	e
KP-SO-07-XX	Antimony	17	mg/kg	J+	e
KP-SO-10-XX	Antimony	6.1	mg/kg	J+	e
KP-SO-13-XX	Antimony	16	mg/kg	J+	e
KP-SO-15-XX	Antimony	6.3	mg/kg	J+	e
KP-SO-16-XX	Antimony	93	mg/kg	J+	e
KP-SO-18-XX	Antimony	6.7	mg/kg	J+	e
KP-SO-20-XX	Antimony	19	mg/kg	J+	e
KP-SO-22-XX	Antimony	8.3	mg/kg	J+	e
KP-SO-23-XX	Antimony	86	mg/kg	J+	e
KP-SO-24-XX	Antimony	17	mg/kg	J+	e
KP-SO-26-XX	Antimony	90	mg/kg	J+	e
KP-SO-27-XX	Antimony	15	mg/kg	J+	e
KP-SO-29-XX	Antimony	18	mg/kg	J+	e
KP-SO-32-XX	Antimony	16	mg/kg	J+	e
LV-SE-01-XX	Antimony	<1.5	mg/kg	UJ	e
LV-SE-02-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-02-XX	Lead	20	mg/kg	J-	e
LV-SE-02-XX	Silver	<1.3	mg/kg	UJ	e
LV-SE-05-XX	Mercury	2.6	mg/kg	J-	e
LV-SE-06-XX	Mercury	610	mg/kg	J-	e
LV-SE-07-XX	Antimony	<6.7	mg/kg	UJ	e
LV-SE-08-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-09-XX	Lead	14	mg/kg	J-	e
LV-SE-10-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-10-XX	Lead	25	mg/kg	J-	e
LV-SE-10-XX	Silver	<1.3	mg/kg	UJ	e
LV-SE-11-XX	Antimony	<1.4	mg/kg	UJ	e
LV-SE-12-XX	Lead	19	mg/kg	J-	e
LV-SE-13-XX	Mercury	640	mg/kg	J-	e
LV-SE-14-XX	Antimony	<1.5	mg/kg	UJ	e
LV-SE-15-XX	Antimony	290	mg/kg	J+	e
LV-SE-15-XX	Silver	300	mg/kg	J-	e
LV-SE-16-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-17-XX	Antimony	280	mg/kg	J+	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
LV-SE-17-XX	Lead	17	mg/kg	J-	e
LV-SE-17-XX	Silver	200	mg/kg	J-	e
LV-SE-18-XX	Antimony	<6.7	mg/kg	UJ	e
LV-SE-19-XX	Lead	17	mg/kg	J-	e
LV-SE-20-XX	Antimony	140	mg/kg	J+	e
LV-SE-20-XX	Silver	75	mg/kg	J-	e
LV-SE-21-XX	Antimony	<1.5	mg/kg	UJ	e
LV-SE-22-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-22-XX	Lead	22	mg/kg	J-	e
LV-SE-22-XX	Silver	<1.3	mg/kg	UJ	e
LV-SE-23-XX	Antimony	<6.6	mg/kg	UJ	e
LV-SE-24-XX	Antimony	<1.5	mg/kg	UJ	e
LV-SE-25-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-25-XX	Lead	23	mg/kg	J-	e
LV-SE-25-XX	Silver	<1.3	mg/kg	UJ	e
LV-SE-26-XX	Lead	25	mg/kg	J-	e
LV-SE-27-XX	Lead	16	mg/kg	J-	e
LV-SE-28-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-29-XX	Antimony	<1.4	mg/kg	UJ	e
LV-SE-30-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-31-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-31-XX	Lead	49	mg/kg	J-	e
LV-SE-31-XX	Silver	<1.3	mg/kg	UJ	e
LV-SE-32-XX	Antimony	<1.4	mg/kg	UJ	e
LV-SE-33-XX	Lead	21	mg/kg	J-	e
LV-SE-35-XX	Antimony	<1.3	mg/kg	UJ	e
LV-SE-35-XX	Lead	22	mg/kg	J-	e
LV-SE-35-XX	Silver	<1.3	mg/kg	UJ	e
LV-SE-36-XX	Lead	21	mg/kg	J-	e
LV-SE-38-XX	Lead	15	mg/kg	J-	e
LV-SE-39-XX	Lead	22	mg/kg	J-	e
LV-SE-41-XX	Mercury	610	mg/kg	J-	e
LV-SE-42-XX	Lead	22	mg/kg	J-	e
LV-SE-43-XX	Antimony	160	mg/kg	J+	e
LV-SE-43-XX	Silver	60	mg/kg	J-	e
LV-SE-45-XX	Antimony	<6.7	mg/kg	UJ	e
LV-SE-47-XX	Antimony	<1.3	mg/kg	UJ	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
LV-SE-48-XX	Antimony	<6.6	mg/kg	UJ	e
LV-SE-50-XX	Lead	24	mg/kg	J-	e
LV-SE-51-XX	Antimony	210	mg/kg	J+	e
LV-SE-51-XX	Silver	250	mg/kg	J-	e
LV-SO-03-XX	Mercury	48	mg/kg	J-	e
LV-SO-03-XX	Silver	210	mg/kg	J-	e
LV-SO-04-XX	Mercury	130	mg/kg	J-	e
LV-SO-04-XX	Silver	<1.2	mg/kg	UJ	e
LV-SO-34-XX	Mercury	130	mg/kg	J-	e
LV-SO-34-XX	Silver	<1.2	mg/kg	UJ	e
LV-SO-37-XX	Mercury	130	mg/kg	J-	e
LV-SO-40-XX	Mercury	46	mg/kg	J-	e
LV-SO-40-XX	Silver	210	mg/kg	J-	e
LV-SO-49-XX	Mercury	52	mg/kg	J-	e
LV-SO-49-XX	Silver	220	mg/kg	J-	e
RF-SE-02-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-03-XX	Antimony	<1.2	mg/kg	UJ	e
RF-SE-04-XX	Antimony	3.2	mg/kg	J+	e
RF-SE-04-XX	Silver	12	mg/kg	J-	e
RF-SE-05-XX	Antimony	4.1	mg/kg	J+	e
RF-SE-05-XX	Silver	7.4	mg/kg	J-	e
RF-SE-06-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-13-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-14-XX	Antimony	4.4	mg/kg	J+	e
RF-SE-14-XX	Silver	13	mg/kg	J-	e
RF-SE-15-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-19-XX	Antimony	3.7	mg/kg	J+	e
RF-SE-19-XX	Silver	14	mg/kg	J-	e
RF-SE-22-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-24-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-25-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-26-XX	Antimony	2.2	mg/kg	J+	e
RF-SE-26-XX	Silver	7.2	mg/kg	J-	e
RF-SE-27-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-28-XX	Antimony	<1.2	mg/kg	UJ	e
RF-SE-30-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-31-XX	Antimony	<1.3	mg/kg	UJ	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
RF-SE-32-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-34-XX	Antimony	2.9	mg/kg	J+	e
RF-SE-34-XX	Silver	10	mg/kg	J-	e
RF-SE-38-XX	Antimony	<1.2	mg/kg	UJ	e
RF-SE-39-XX	Antimony	2.9	mg/kg	J+	e
RF-SE-39-XX	Silver	8.2	mg/kg	J-	e
RF-SE-42-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-43-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-44-XX	Antimony	2.7	mg/kg	J+	e
RF-SE-44-XX	Silver	7.2	mg/kg	J-	e
RF-SE-45-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-49-XX	Antimony	<1.2	mg/kg	UJ	e
RF-SE-52-XX	Antimony	3.4	mg/kg	J+	e
RF-SE-52-XX	Silver	11	mg/kg	J-	e
RF-SE-53-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-55-XX	Antimony	<1.2	mg/kg	UJ	e
RF-SE-56-XX	Antimony	3.5	mg/kg	J+	e
RF-SE-56-XX	Silver	8.3	mg/kg	J-	e
RF-SE-57-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-58-XX	Antimony	<1.3	mg/kg	UJ	e
RF-SE-59-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-01-XX	Antimony	180	mg/kg	J	e
SB-SO-02-XX	Antimony	44	mg/kg	J-	e, j
SB-SO-02-XX	Silver	<1.2	mg/kg	UJ	e
SB-SO-03-XX	Antimony	1.2	mg/kg	UJ	b, e
SB-SO-04-XX	Silver	<1.3	mg/kg	UJ	e
SB-SO-05-XX	Antimony	1.6	mg/kg	J-	e
SB-SO-06-XX	Antimony	1.7	mg/kg	J-	e
SB-SO-07-XX	Antimony	45	mg/kg	J	e
SB-SO-08-XX	Antimony	5.4	mg/kg	J-	e
SB-SO-09-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-09-XX	Silver	160	mg/kg	J-	e
SB-SO-10-XX	Antimony	62	mg/kg	J	e
SB-SO-11-XX	Antimony	5.7	mg/kg	J-	e
SB-SO-12-XX	Antimony	620	mg/kg	J	e
SB-SO-13-XX	Antimony	430	mg/kg	J	e
SB-SO-14-XX	Antimony	4.1	mg/kg	J-	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
SB-SO-15-XX	Antimony	600	mg/kg	J-	j, e
SB-SO-16-XX	Antimony	170	mg/kg	J	e
SB-SO-17-XX	Antimony	800	mg/kg	J+	e
SB-SO-17-XX	Silver	2.3	mg/kg	UJ	b, e
SB-SO-18-XX	Antimony	1.2	mg/kg	UJ	b, e
SB-SO-19-XX	Antimony	310	mg/kg	J	e
SB-SO-20-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-20-XX	Silver	140	mg/kg	J-	e
SB-SO-21-XX	Antimony	4.9	mg/kg	J	e
SB-SO-22-XX	Antimony	10	mg/kg	J	e, j
SB-SO-23-XX	Antimony	48	mg/kg	J-	e
SB-SO-23-XX	Silver	<0.26	mg/kg	UJ	e
SB-SO-24-XX	Antimony	180	mg/kg	J	e
SB-SO-25-XX	Antimony	6.8	mg/kg	J+	e
SB-SO-26-XX	Antimony	61	mg/kg	J	e
SB-SO-27-XX	Antimony	6.7	mg/kg	J+	e
SB-SO-28-XX	Antimony	42	mg/kg	J-	e
SB-SO-28-XX	Silver	<0.26	mg/kg	UJ	e
SB-SO-29-XX	Silver	<1.2	mg/kg	UJ	e
SB-SO-30-XX	Antimony	3.2	mg/kg	J-	e
SB-SO-31-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-31-XX	Silver	160	mg/kg	J-	e, j
SB-SO-32-XX	Antimony	46	mg/kg	J-	e
SB-SO-32-XX	Silver	0.1	mg/kg	UJ	b, e
SB-SO-33-XX	Antimony	350	mg/kg	J	e
SB-SO-33-XX	Silver	2	mg/kg	J	e
SB-SO-34-XX	Silver	<1.3	mg/kg	UJ	e
SB-SO-35-XX	Antimony	6	mg/kg	J+	e
SB-SO-36-XX	Silver	<1.2	mg/kg	UJ	e
SB-SO-37-XX	Antimony	340	mg/kg	J	e
SB-SO-38-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-39-XX	Antimony	4.7	mg/kg	J-	e
SB-SO-40-XX	Antimony	2.2	mg/kg	J-	e
SB-SO-41-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-42-XX	Antimony	4.6	mg/kg	J-	e
SB-SO-43-XX	Antimony	40	mg/kg	J-	e
SB-SO-43-XX	Silver	<0.26	mg/kg	UJ	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
SB-SO-44-XX	Antimony	6.8	mg/kg	J+	e
SB-SO-45-XX	Antimony	180	mg/kg	J	e
SB-SO-45-XX	Silver	2.1	mg/kg	J-	e
SB-SO-46-XX	Antimony	740	mg/kg	J+	e
SB-SO-46-XX	Silver	2.2	mg/kg	UJ	b, e
SB-SO-47-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-48-XX	Antimony	39	mg/kg	J-	e
SB-SO-48-XX	Silver	0.1	mg/kg	UJ	b, e
SB-SO-49-XX	Silver	<1.2	mg/kg	UJ	e
SB-SO-50-XX	Antimony	57	mg/kg	J	e
SB-SO-51-XX	Antimony	<1.3	mg/kg	UJ	e
SB-SO-52-XX	Antimony	150	mg/kg	J	e
SB-SO-53-XX	Antimony	1.2	mg/kg	UJ	b, e
SB-SO-54-XX	Lead	5.2	mg/kg	J-	e
SB-SO-54-XX	Silver	<0.5	mg/kg	UJ	e
SB-SO-55-XX	Antimony	340	mg/kg	J	e
SB-SO-55-XX	Silver	2.2	mg/kg	J	e
SB-SO-56-XX	Silver	<1.2	mg/kg	UJ	e
TL-SE-01-XX	Antimony	<1.2	mg/kg	UJ	e
TL-SE-01-XX	Lead	48	mg/kg	J-	e
TL-SE-01-XX	Silver	5.7	mg/kg	J-	e
TL-SE-05-XX	Antimony	100	mg/kg	J+	e
TL-SE-05-XX	Silver	180	mg/kg	J-	e
TL-SE-09-XX	Antimony	100	mg/kg	J+	e
TL-SE-09-XX	Silver	170	mg/kg	J-	e
TL-SE-11-XX	Antimony	<1.2	mg/kg	UJ	e
TL-SE-11-XX	Lead	54	mg/kg	J-	e
TL-SE-11-XX	Silver	5.5	mg/kg	J-	e
TL-SE-13-XX	Antimony	95	mg/kg	J+	j, e
TL-SE-13-XX	Silver	160	mg/kg	J	j, e
TL-SE-14-XX	Antimony	<1.2	mg/kg	UJ	e
TL-SE-14-XX	Lead	50	mg/kg	J-	e
TL-SE-14-XX	Silver	5.7	mg/kg	J-	e
TL-SE-18-XX	Antimony	<1.2	mg/kg	UJ	e
TL-SE-18-XX	Lead	46	mg/kg	J-	e
TL-SE-18-XX	Silver	6.3	mg/kg	J-	e
TL-SE-22-XX	Antimony	<1.2	mg/kg	UJ	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
TL-SE-22-XX	Lead	54	mg/kg	J-	e
TL-SE-22-XX	Silver	6.5	mg/kg	J-	e
TL-SE-27-XX	Antimony	<1.2	mg/kg	UJ	e
TL-SE-27-XX	Lead	51	mg/kg	J-	e
TL-SE-27-XX	Silver	7.8	mg/kg	J-	e
TL-SE-29-XX	Antimony	<1.2	mg/kg	UJ	e
TL-SE-29-XX	Lead	51	mg/kg	J-	e
TL-SE-29-XX	Silver	5.9	mg/kg	J-	e
WS-SO-01-XX	Antimony	41	mg/kg	J-	e
WS-SO-01-XX	Mercury	5.8	mg/kg	J	e, j
WS-SO-01-XX	Silver	69	mg/kg	J-	e
WS-SO-02-XX	Antimony	130	mg/kg	J-	e
WS-SO-02-XX	Silver	150	mg/kg	J-	e
WS-SO-03-XX	Antimony	8.9	mg/kg	J-	e
WS-SO-03-XX	Mercury	0.86	mg/kg	J-	e
WS-SO-04-XX	Antimony	45	mg/kg	J-	e
WS-SO-04-XX	Silver	76	mg/kg	J-	e
WS-SO-05-XX	Antimony	8.6	mg/kg	J-	e
WS-SO-05-XX	Silver	0.76	mg/kg	J-	e
WS-SO-07-XX	Silver	400	mg/kg	J-	e
WS-SO-09-XX	Antimony	7.1	mg/kg	J-	e
WS-SO-09-XX	Mercury	0.89	mg/kg	J-	e
WS-SO-10-XX	Silver	<1.3	mg/kg	UJ	e
WS-SO-11-XX	Silver	340	mg/kg	J-	e
WS-SO-12-XX	Antimony	<1.3	mg/kg	UJ	e
WS-SO-12-XX	Mercury	0.068	mg/kg	UJ	b, e
WS-SO-13-XX	Antimony	200	mg/kg	J-	e
WS-SO-13-XX	Silver	170	mg/kg	J-	e
WS-SO-14-XX	Antimony	8.4	mg/kg	J-	e
WS-SO-14-XX	Mercury	0.74	mg/kg	J-	e
WS-SO-15-XX	Antimony	48	mg/kg	J-	e
WS-SO-15-XX	Silver	90	mg/kg	J-	e
WS-SO-16-XX	Antimony	110	mg/kg	J-	e
WS-SO-16-XX	Silver	150	mg/kg	J-	e
WS-SO-17-XX	Antimony	<1.3	mg/kg	UJ	e
WS-SO-17-XX	Mercury	0.069	mg/kg	UJ	b, e
WS-SO-18-XX	Antimony	130	mg/kg	J-	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Validation Code
WS-SO-18-XX	Silver	140	mg/kg	J-	e
WS-SO-19-XX	Antimony	150	mg/kg	J-	e
WS-SO-19-XX	Silver	160	mg/kg	J-	e
WS-SO-20-XX	Silver	<1.3	mg/kg	UJ	e
WS-SO-21-XX	Antimony	120	mg/kg	J-	e
WS-SO-21-XX	Silver	150	mg/kg	J-	e
WS-SO-22-XX	Antimony	41	mg/kg	J-	e
WS-SO-22-XX	Silver	72	mg/kg	J-	e
WS-SO-23-XX	Silver	<1.3	mg/kg	UJ	e
WS-SO-24-XX	Antimony	97	mg/kg	J-	e
WS-SO-24-XX	Silver	140	mg/kg	J-	e
WS-SO-25-XX	Silver	450	mg/kg	J-	e
WS-SO-26-XX	Antimony	7.6	mg/kg	J-	e
WS-SO-26-XX	Mercury	0.83	mg/kg	J-	e
WS-SO-27-XX	Antimony	<1.3	mg/kg	UJ	e
WS-SO-27-XX	Mercury	0.11	mg/kg	J-	e
WS-SO-28-XX	Antimony	120	mg/kg	J-	e
WS-SO-28-XX	Silver	130	mg/kg	J-	e
WS-SO-29-XX	Antimony	120	mg/kg	J-	e
WS-SO-29-XX	Silver	140	mg/kg	J-	e
WS-SO-30-XX	Antimony	1.2	mg/kg	J-	e
WS-SO-30-XX	Mercury	0.069	mg/kg	UJ	b, e
WS-SO-31-XX	Antimony	7.2	mg/kg	J-	e
WS-SO-31-XX	Mercury	0.85	mg/kg	J-	e
WS-SO-32-XX	Antimony	190	mg/kg	J-	e
WS-SO-32-XX	Silver	190	mg/kg	J-	e
WS-SO-33-XX	Antimony	6.9	mg/kg	J-	e
WS-SO-33-XX	Mercury	0.87	mg/kg	J-	e
WS-SO-34-XX	Antimony	45	mg/kg	J-	e
WS-SO-34-XX	Silver	78	mg/kg	J-	e
WS-SO-35-XX	Antimony	<1.3	mg/kg	UJ	e
WS-SO-35-XX	Mercury	0.071	mg/kg	UJ	b, e
WS-SO-36-XX	Antimony	120	mg/kg	J-	e
WS-SO-36-XX	Silver	120	mg/kg	J-	e
WS-SO-37-XX	Antimony	120	mg/kg	J-	e
WS-SO-37-XX	Silver	140	mg/kg	J-	e

TABLE 4: DATA QUALIFICATION: MATRIX SPIKE RECOVERY EXCEEDANCES (Continued)

Notes:
< = Less than
mg/kg = Milligram per kilogram
b = Data were qualified based on blank contamination
e = Data were additionally qualified based on matrix spike/matrix spike duplicate exceedances
j = Data were additionally qualified based on serial dilution exceedances
J = Result is estimated and biased could not be determined
J+ = Result is estimated and potentially biased high
J- = Result is estimated and potentially biased low
UJ = Result is undetected at estimated quantitation limit

TABLE 5: DATA QUALIFICATION: SERIAL DILUTION EXCEEDANCES

Sample ID	Analyte	Result	Unit	Validation Qualifier	Comment Code
AS-SO-09-XX	Arsenic	25	mg/kg	J-	j
AS-SO-09-XX	Cadmium	100	mg/kg	J-	j
AS-SO-09-XX	Chromium	390	mg/kg	J-	j
AS-SO-09-XX	Copper	250	mg/kg	J-	j
AS-SO-09-XX	Iron	94000	mg/kg	J-	j
AS-SO-09-XX	Lead	3200	mg/kg	J-	j
AS-SO-09-XX	Nickel	170	mg/kg	J-	j
AS-SO-09-XX	Silver	9.6	mg/kg	J-	j
AS-SO-09-XX	Vanadium	65	mg/kg	J-	j
AS-SO-09-XX	Zinc	6800	mg/kg	J-	j
BN-SO-11-XX	Mercury	24	mg/kg	J-	j
BN-SO-25-XX	Antimony	82	mg/kg	J-	e, j
BN-SO-25-XX	Arsenic	700	mg/kg	J	e, j
BN-SO-25-XX	Cadmium	370	mg/kg	J-	j
BN-SO-25-XX	Chromium	64	mg/kg	J-	j
BN-SO-25-XX	Copper	930	mg/kg	J-	j
BN-SO-25-XX	Iron	16000	mg/kg	J-	j
BN-SO-25-XX	Lead	5400	mg/kg	J-	j
BN-SO-25-XX	Nickel	88	mg/kg	J-	j
BN-SO-25-XX	Selenium	19	mg/kg	J-	j
BN-SO-25-XX	Silver	48	mg/kg	J-	j
BN-SO-25-XX	Vanadium	28	mg/kg	J-	j
BN-SO-25-XX	Zinc	2900	mg/kg	J-	j
KP-SE-14-XX	Antimony	11	mg/kg	J-	j
KP-SE-14-XX	Chromium	46	mg/kg	J-	j
KP-SE-14-XX	Copper	2.7	mg/kg	J+	j
KP-SE-14-XX	Iron	520	mg/kg	J-	j
KP-SE-14-XX	Lead	680	mg/kg	J-	e, j
KP-SE-14-XX	Nickel	23	mg/kg	J-	j
LV-SE-29-XX	Lead	7.2	mg/kg	J+	j
LV-SE-29-XX	Mercury	1.5	mg/kg	J-	j
LV-SE-35-XX	Arsenic	31	mg/kg	J-	j
LV-SE-35-XX	Chromium	74	mg/kg	J-	j
LV-SE-35-XX	Iron	24000	mg/kg	J-	j
LV-SE-35-XX	Nickel	170	mg/kg	J-	j
LV-SE-35-XX	Vanadium	55	mg/kg	J-	j
LV-SE-35-XX	Zinc	67	mg/kg	J-	j
LV-SO-34-XX	Antimony	870	mg/kg	J-	j

TABLE 5: DATA QUALIFICATIONS: SERIAL DILUTION EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Comment Code
LV-SO-34-XX	Arsenic	110	mg/kg	J-	j
LV-SO-34-XX	Cadmium	2300	mg/kg	J-	j
LV-SO-34-XX	Chromium	2200	mg/kg	J-	j
LV-SO-34-XX	Iron	20000	mg/kg	J-	j
LV-SO-34-XX	Lead	3700	mg/kg	J-	j
LV-SO-34-XX	Nickel	1900	mg/kg	J-	j
LV-SO-34-XX	Selenium	220	mg/kg	J-	j
LV-SO-34-XX	Vanadium	230	mg/kg	J-	j
LV-SO-34-XX	Zinc	48	mg/kg	J-	j
RF-SE-16-XX	Antimony	85	mg/kg	J-	j
RF-SE-16-XX	Arsenic	72	mg/kg	J-	j
RF-SE-16-XX	Cadmium	310	mg/kg	J-	j
RF-SE-16-XX	Chromium	820	mg/kg	J-	j
RF-SE-16-XX	Copper	73	mg/kg	J-	j
RF-SE-16-XX	Iron	16000	mg/kg	J-	j
RF-SE-16-XX	Lead	24	mg/kg	J-	j
RF-SE-16-XX	Nickel	1700	mg/kg	J-	j
RF-SE-16-XX	Silver	130	mg/kg	J-	j
RF-SE-16-XX	Vanadium	32	mg/kg	J-	j
RF-SE-16-XX	Zinc	760	mg/kg	J-	j
RF-SE-24-XX	Arsenic	130	mg/kg	J+	j
RF-SE-24-XX	Cadmium	6.5	mg/kg	J+	j
RF-SE-24-XX	Chromium	74	mg/kg	J+	j
RF-SE-24-XX	Copper	860	mg/kg	J+	j
RF-SE-24-XX	Iron	24000	mg/kg	J+	j
RF-SE-24-XX	Lead	410	mg/kg	J+	j
RF-SE-24-XX	Nickel	170	mg/kg	J+	j
RF-SE-24-XX	Silver	3.8	mg/kg	J+	j
RF-SE-24-XX	Vanadium	46	mg/kg	J+	j
RF-SE-24-XX	Zinc	1400	mg/kg	J-	j
SB-SO-02-XX	Antimony	44	mg/kg	J-	e, j
SB-SO-02-XX	Arsenic	23	mg/kg	J-	j
SB-SO-02-XX	Lead	22	mg/kg	J-	j
SB-SO-02-XX	Mercury	130	mg/kg	J+	j
SB-SO-15-XX	Antimony	600	mg/kg	J-	j, e
SB-SO-15-XX	Arsenic	170	mg/kg	J-	j
SB-SO-15-XX	Chromium	91	mg/kg	J-	j
SB-SO-15-XX	Copper	30	mg/kg	J-	j
SB-SO-15-XX	Iron	51000	mg/kg	J-	j

TABLE 5: DATA QUALIFICATIONS: SERIAL DILUTION EXCEEDANCES (Continued)

Sample ID	Analyte	Result	Unit	Validation Qualifier	Comment Code
SB-SO-15-XX	Lead	40	mg/kg	J-	j
SB-SO-15-XX	Nickel	100	mg/kg	J-	j
SB-SO-15-XX	Vanadium	52	mg/kg	J-	j
SB-SO-15-XX	Zinc	36	mg/kg	J-	j
SB-SO-22-XX	Antimony	10	mg/kg	J	e, j
SB-SO-22-XX	Zinc	64	mg/kg	J-	j
SB-SO-31-XX	Arsenic	8	mg/kg	J-	j
SB-SO-31-XX	Nickel	3200	mg/kg	J-	j
SB-SO-31-XX	Selenium	28	mg/kg	J-	j
SB-SO-31-XX	Silver	160	mg/kg	J-	e, j
SB-SO-31-XX	Zinc	3900	mg/kg	J-	j
TL-SE-13-XX	Antimony	95	mg/kg	J+	j, e
TL-SE-13-XX	Chromium	36	mg/kg	J+	j
TL-SE-13-XX	Copper	4400	mg/kg	J+	j
TL-SE-13-XX	Iron	22000	mg/kg	J+	j
TL-SE-13-XX	Lead	1100	mg/kg	J+	j
TL-SE-13-XX	Silver	160	mg/kg	J	j, e
TL-SE-13-XX	Vanadium	59	mg/kg	J+	j
WS-SO-01-XX	Mercury	5.8	mg/kg	J	e, j
WS-SO-33-XX	Arsenic	450	mg/kg	J-	j
WS-SO-33-XX	Cadmium	11	mg/kg	J-	j
WS-SO-33-XX	Chromium	120	mg/kg	J-	j
WS-SO-33-XX	Copper	150	mg/kg	J-	j
WS-SO-33-XX	Iron	28000	mg/kg	J-	j
WS-SO-33-XX	Lead	3700	mg/kg	J-	j
WS-SO-33-XX	Nickel	65	mg/kg	J-	j
WS-SO-33-XX	Silver	13	mg/kg	J-	j
WS-SO-33-XX	Vanadium	53	mg/kg	J-	j
WS-SO-33-XX	Zinc	830	mg/kg	J-	j

Notes:
mg/kg = Milligram per kilogram
e = Data were additionally qualified based on matrix spike/matrix spike duplicate exceedances
j = Data were qualified based on serial dilution exceedances
J = Result is estimated and biased could not be determined
J+ = Result is estimated and potentially biased high
J- = Result is estimated and potentially biased low

APPENDIX D

DEVELOPER AND REFERENCE LABORATORY DATA

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
1	KP-SO-06-XX	Reference Laboratory	8.1 J+	1 J-	0.1 U	290	26	1,400	620
1	KP-SO-10-XX	Reference Laboratory	6.1 J+	1 J-	0.1 U	300	26	1,600	560
1	KP-SO-15-XX	Reference Laboratory	6.3 J+	1 J-	0.1 U	340	26	1,600	510
1	KP-SO-18-XX	Reference Laboratory	6.7 J+	1 J-	0.1 U	250	24	1,200	500
1	KP-SO-22-XX	Reference Laboratory	8.3 J+	1 J-	0.1 U	260	29	1,300	650
1	KP-SO-06-RI	Rigaku, Inc.	289	85	866	198	37	3,882	358
1	KP-SO-10-RI	Rigaku, Inc.	325	116	893	246	43	3,883	399
1	KP-SO-15-RI	Rigaku, Inc.	303	101	913	227	40	3,880	357
1	KP-SO-18-RI	Rigaku, Inc.	310	105	885	212	42	3,892	360
1	KP-SO-22-RI	Rigaku, Inc.	366	124	957	212	41	3,968	359
2	KP-SO-07-XX	Reference Laboratory	17 J+	2 J-	0.1 U	170	48	990	1,200
2	KP-SO-13-XX	Reference Laboratory	16 J+	1 J-	0.045 U	180	52	980	1,200
2	KP-SO-20-XX	Reference Laboratory	19 J+	2 J-	0.1 U	160	46	910	1,300
2	KP-SO-24-XX	Reference Laboratory	17 J+	1 J-	0.1 U	160	49	900	1,100
2	KP-SO-27-XX	Reference Laboratory	15 J+	1 J-	0.05 U	170	45	970	1,200
2	KP-SO-29-XX	Reference Laboratory	18 J+	2 J-	0.1 U	150	42	870	1,200
2	KP-SO-32-XX	Reference Laboratory	16 J+	2 J-	0.045 U	180	50	970	1,200
2	KP-SO-07-RI	Rigaku, Inc.	420	102	854	91	65	3,569	792
2	KP-SO-13-RI	Rigaku, Inc.	510	102	971	81	64	3,526	747
2	KP-SO-20-RI	Rigaku, Inc.	459	82	899	142	60	3,603	777
2	KP-SO-24-RI	Rigaku, Inc.	467	98	908	89	62	3,637	804
2	KP-SO-27-RI	Rigaku, Inc.	399	117	885	156	58	3,576	760
2	KP-SO-29-RI	Rigaku, Inc.	447	108	871	91	51	3,537	789
2	KP-SO-32-RI	Rigaku, Inc.	457	107	885	154	57	3,606	790
3	KP-SO-04-XX	Reference Laboratory	94 J+	3	0.046 U	180	200	1,300	5,800
3	KP-SO-16-XX	Reference Laboratory	93 J+	3	0.063 U	200	230	1,400	6,100
3	KP-SO-23-XX	Reference Laboratory	86 J+	3	0.048 U	180	190	1,300	5,300
3	KP-SO-26-XX	Reference Laboratory	90 J+	4	0.061 U	210	230	1,500	6,500
3	KP-SO-31-XX	Reference Laboratory	88	28	0.1 U	140	200	1,100	5,700
3	KP-SO-04-RI	Rigaku, Inc.	1,011	126	765	129	186	3,642	3,280
3	KP-SO-16-RI	Rigaku, Inc.	1,106	145	779	74	183	3,584	3,259
3	KP-SO-23-RI	Rigaku, Inc.	1,042	120	764	123	183	3,626	3,269
3	KP-SO-26-RI	Rigaku, Inc.	1,125	104	777	137	192	3,639	3,392
3	KP-SO-31-RI	Rigaku, Inc.	1,184	148	810	125	182	3,665	3,379

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
1	KP-SO-06-XX	Reference Laboratory	0.06 U	140	0.25 U	0.25 U	2 J	11
1	KP-SO-10-XX	Reference Laboratory	0.03 U	150	0.22 U	0.25 U	2 J	12
1	KP-SO-15-XX	Reference Laboratory	0.03 U	170	0.25 U	0.25 U	2 J	15
1	KP-SO-18-XX	Reference Laboratory	0.02 U	120	0.25 U	0.25 U	2 J	11
1	KP-SO-22-XX	Reference Laboratory	0.03 U	130	0.25 U	0.25 U	2 J	11
1	KP-SO-06-RI	Rigaku, Inc.	71	122	16	302	19	36
1	KP-SO-10-RI	Rigaku, Inc.	58	128	19	306	18	38
1	KP-SO-15-RI	Rigaku, Inc.	62	127	14	301	21	34
1	KP-SO-18-RI	Rigaku, Inc.	69	133	16	316	25	31
1	KP-SO-22-RI	Rigaku, Inc.	70	121	16	321	19	45
2	KP-SO-07-XX	Reference Laboratory	0.03 U	87	0.21 U	0.25 U	1 J	26
2	KP-SO-13-XX	Reference Laboratory	0.04 U	90	0.25 U	0.25 U	1 J	24
2	KP-SO-20-XX	Reference Laboratory	0.03 U	79	0.25 U	0.25 U	1 J	25
2	KP-SO-24-XX	Reference Laboratory	0.02 U	78	0.25 U	0.25 U	1 J	22
2	KP-SO-27-XX	Reference Laboratory	0.02 U	87	0.25 U	0.25 U	1 J	24
2	KP-SO-29-XX	Reference Laboratory	0.01 U	73	0.25 U	0.25 U	1 J	22
2	KP-SO-32-XX	Reference Laboratory	0.01 U	88	0.51	0.25 U	1 J	24
2	KP-SO-07-RI	Rigaku, Inc.	68	94	15	290	25	40
2	KP-SO-13-RI	Rigaku, Inc.	50	86	15	326	15	35
2	KP-SO-20-RI	Rigaku, Inc.	62	94	17	310	24	57
2	KP-SO-24-RI	Rigaku, Inc.	62	90	16	305	28	44
2	KP-SO-27-RI	Rigaku, Inc.	66	90	15	301	18	41
2	KP-SO-29-RI	Rigaku, Inc.	63	93	17	294	24	41
2	KP-SO-32-RI	Rigaku, Inc.	64	96	18	308	22	47
3	KP-SO-04-XX	Reference Laboratory	0.02 U	93	0.28 U	0.16 J	1 J	45
3	KP-SO-16-XX	Reference Laboratory	0.02 U	100	0.25 U	0.16 J	1 J	47
3	KP-SO-23-XX	Reference Laboratory	0.02 U	91	0.25 U	0.13 J	1 J	41
3	KP-SO-26-XX	Reference Laboratory	0.01 U	110	0.22 U	0.17 J	1 J	52
3	KP-SO-31-XX	Reference Laboratory	0.02 U	68	0.25 U	0.4	2 J	38
3	KP-SO-04-RI	Rigaku, Inc.	61	81	17	260	25	57
3	KP-SO-16-RI	Rigaku, Inc.	48	81	19	271	15	55
3	KP-SO-23-RI	Rigaku, Inc.	59	78	18	262	18	53
3	KP-SO-26-RI	Rigaku, Inc.	52	88	16	267	20	59
3	KP-SO-31-RI	Rigaku, Inc.	42	82	20	273	14	58

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
4	KP-SO-02-XX	Reference Laboratory	410	10	0.1	6	780	1,700	18,000
4	KP-SO-03-XX	Reference Laboratory	360	9	0.074 U	5	670	1,600	19,000
4	KP-SO-05-XX	Reference Laboratory	410	12	0.13 U	6	780	2,000	24,000
4	KP-SO-09-XX	Reference Laboratory	420	11	0.094 U	5	780	1,800	22,000
4	KP-SO-21-XX	Reference Laboratory	370	10	0.098 U	5	700	1,700	19,000
4	KP-SO-02-RI	Rigaku, Inc.	2,230	166	588	-8	539	3,679	10,300
4	KP-SO-03-RI	Rigaku, Inc.	2,237	120	598	31	590	3,686	10,425
4	KP-SO-05-RI	Rigaku, Inc.	2,056	140	578	-13	573	3,666	10,700
4	KP-SO-09-RI	Rigaku, Inc.	2,034	136	581	7	545	3,637	10,389
4	KP-SO-21-RI	Rigaku, Inc.	2,049	131	565	9	580	3,663	10,432
5	WS-SO-06-XX	Reference Laboratory	1.3 U	48	1.9	120	50	28,000	110
5	WS-SO-08-XX	Reference Laboratory	1.3	45	2	120	47	26,000	71
5	WS-SO-12-XX	Reference Laboratory	1.3 UJ	43	1.8	110	45	25,000	65
5	WS-SO-17-XX	Reference Laboratory	1.3 UJ	47	1.9	120	49	28,000	70
5	WS-SO-27-XX	Reference Laboratory	1.3 UJ	49	2	120	51	28,000	72
5	WS-SO-30-XX	Reference Laboratory	1.2 J-	51	2	130	53	29,000	81
5	WS-SO-35-XX	Reference Laboratory	1.3 UJ	49	2	130	51	28,000	74
5	WS-SO-06-RI	Rigaku, Inc.	147	75	600	113	42	15,860	6
5	WS-SO-08-RI	Rigaku, Inc.	164	52	602	83	42	15,925	4
5	WS-SO-12-RI	Rigaku, Inc.	135	66	587	65	50	15,982	-3
5	WS-SO-17-RI	Rigaku, Inc.	162	50	613	115	38	15,770	16
5	WS-SO-27-RI	Rigaku, Inc.	176	32	598	118	37	15,837	6
5	WS-SO-30-RI	Rigaku, Inc.	168	69	601	89	39	15,943	6
5	WS-SO-35-RI	Rigaku, Inc.	158	61	620	105	42	15,895	6
6	WS-SO-03-XX	Reference Laboratory	8.9 J-	500	12	140	170	32,000	4,300
6	WS-SO-05-XX	Reference Laboratory	8.6 J-	440	12	140	160	31,000	4,000
6	WS-SO-09-XX	Reference Laboratory	7.1 J-	480	12	130	160	30,000	4,000
6	WS-SO-14-XX	Reference Laboratory	8.4 J-	430	11	120	150	28,000	3,700
6	WS-SO-26-XX	Reference Laboratory	7.6 J-	520	12	140	160	30,000	4,000
6	WS-SO-31-XX	Reference Laboratory	7.2 J-	520	12	140	170	32,000	4,200
6	WS-SO-33-XX	Reference Laboratory	6.9 J-	450 J-	11 J-	120 J-	150 J-	28,000 J-	3,700 J-
6	WS-SO-03-RI	Rigaku, Inc.	441	199	565	94	102	16,124	1,996
6	WS-SO-05-RI	Rigaku, Inc.	445	230	579	98	94	16,250	2,026
6	WS-SO-09-RI	Rigaku, Inc.	413	186	576	115	98	16,184	1,979
6	WS-SO-14-RI	Rigaku, Inc.	466	240	566	132	98	16,132	1,974
6	WS-SO-26-RI	Rigaku, Inc.	468	241	593	103	101	16,212	1,979
6	WS-SO-31-RI	Rigaku, Inc.	479	211	578	129	97	16,183	1,967
6	WS-SO-33-RI	Rigaku, Inc.	480	184	592	115	101	16,200	2,028

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
4	KP-SO-02-XX	Reference Laboratory	0.04 U	4	0.42 U	0.82	0 J	100
4	KP-SO-03-XX	Reference Laboratory	0.04 U	3	0.25 U	0.73	0 J	92
4	KP-SO-05-XX	Reference Laboratory	0.04 U	4	0.24 U	0.82	0 J	110
4	KP-SO-09-XX	Reference Laboratory	0.05 U	3	0.25 U	0.84	0 J	110
4	KP-SO-21-XX	Reference Laboratory	0.04 U	4	0.25 U	0.76	0 J	100
4	KP-SO-02-RI	Rigaku, Inc.	54	32	20	212	28	91
4	KP-SO-03-RI	Rigaku, Inc.	47	31	18	200	24	91
4	KP-SO-05-RI	Rigaku, Inc.	52	33	20	198	21	91
4	KP-SO-09-RI	Rigaku, Inc.	53	37	21	206	26	90
4	KP-SO-21-RI	Rigaku, Inc.	44	33	21	203	25	95
5	WS-SO-06-XX	Reference Laboratory	0.07 U	61	1.3 U	0.93 J	56	230
5	WS-SO-08-XX	Reference Laboratory	0.06 U	58	1.3 U	0.86 J	52	220
5	WS-SO-12-XX	Reference Laboratory	0.07 UJ	55	1.3 U	0.94 J	49	210
5	WS-SO-17-XX	Reference Laboratory	0.07 UJ	59	1.3 U	0.89 J	56	230
5	WS-SO-27-XX	Reference Laboratory	0.11 J-	61	1.3 U	0.9 J	57	230
5	WS-SO-30-XX	Reference Laboratory	0.07 UJ	65	1.3 U	1 J	58	240
5	WS-SO-35-XX	Reference Laboratory	0.07 UJ	62	1.3 U	1 J	57	240
5	WS-SO-06-RI	Rigaku, Inc.	26	44	8	204	63	146
5	WS-SO-08-RI	Rigaku, Inc.	28	39	9	208	77	146
5	WS-SO-12-RI	Rigaku, Inc.	24	41	7	199	75	146
5	WS-SO-17-RI	Rigaku, Inc.	29	38	7	207	74	149
5	WS-SO-27-RI	Rigaku, Inc.	23	41	7	204	84	141
5	WS-SO-30-RI	Rigaku, Inc.	23	44	7	210	57	140
5	WS-SO-35-RI	Rigaku, Inc.	29	39	8	219	78	151
6	WS-SO-03-XX	Reference Laboratory	0.86 J-	75	1.6	15	58	930
6	WS-SO-05-XX	Reference Laboratory	0.76 J-	71	1.3 U	15	57	900
6	WS-SO-09-XX	Reference Laboratory	0.89 J-	70	1.3 U	14	56	870
6	WS-SO-14-XX	Reference Laboratory	0.74 J-	64	1.3 U	13	50	820
6	WS-SO-26-XX	Reference Laboratory	0.83 J-	70	1.3 U	14	56	900
6	WS-SO-31-XX	Reference Laboratory	0.85 J-	72	1.2 U	15	60	950
6	WS-SO-33-XX	Reference Laboratory	0.87 J-	65 J-	1.3 U	13 J-	53 J-	830 J-
6	WS-SO-03-RI	Rigaku, Inc.	23	45	9	188	74	399
6	WS-SO-05-RI	Rigaku, Inc.	30	43	7	197	81	395
6	WS-SO-09-RI	Rigaku, Inc.	31	49	6	193	57	418
6	WS-SO-14-RI	Rigaku, Inc.	29	48	8	202	70	399
6	WS-SO-26-RI	Rigaku, Inc.	26	47	10	199	69	396
6	WS-SO-31-RI	Rigaku, Inc.	24	39	7	196	63	396
6	WS-SO-33-RI	Rigaku, Inc.	30	40	7	198	66	406

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
7	WS-SO-01-XX	Reference Laboratory	41 J-	1900	47	100	590	32,000	18,000
7	WS-SO-04-XX	Reference Laboratory	45 J-	2000	50	94	640	34,000	20,000
7	WS-SO-15-XX	Reference Laboratory	48 J-	2300	56	82	720	37,000	24,000
7	WS-SO-22-XX	Reference Laboratory	41 J-	1900	47	84	620	33,000	17,000
7	WS-SO-34-XX	Reference Laboratory	45 J-	2000	50	91	660	36,000	22,000
7	WS-SO-01-RI	Rigaku, Inc.	813	866	425	137	392	17,607	9,601
7	WS-SO-04-RI	Rigaku, Inc.	877	828	427	112	396	17,625	9,652
7	WS-SO-15-RI	Rigaku, Inc.	901	841	445	88	379	17,579	9,764
7	WS-SO-22-RI	Rigaku, Inc.	952	848	434	120	378	17,542	9,554
7	WS-SO-34-RI	Rigaku, Inc.	845	838	434	106	379	17,569	9,666
8	WS-SO-02-XX	Reference Laboratory	130 J-	4200	98	49	1300	44,000	35,000
8	WS-SO-16-XX	Reference Laboratory	110 J-	3900	91	59	1300	42,000	24,000
8	WS-SO-18-XX	Reference Laboratory	130 J-	4100	95	63	1300	44,000	37,000
8	WS-SO-21-XX	Reference Laboratory	120 J-	3900	90	43	1200	40,000	43,000
8	WS-SO-24-XX	Reference Laboratory	97 J-	3600	81	54	1100	38,000	27,000
8	WS-SO-29-XX	Reference Laboratory	120 J-	3800	90	51	1200	40,000	42,000
8	WS-SO-37-XX	Reference Laboratory	120 J-	4100	95	63	1300	42,000	26,000
8	WS-SO-02-RI	Rigaku, Inc.	389	1,541	338	129	744	20,249	17,432
8	WS-SO-16-RI	Rigaku, Inc.	364	1,544	336	130	740	20,082	17,151
8	WS-SO-18-RI	Rigaku, Inc.	522	1,558	326	180	735	19,895	17,246
8	WS-SO-21-RI	Rigaku, Inc.	466	1,485	336	139	745	19,866	17,269
8	WS-SO-24-RI	Rigaku, Inc.	309	1,548	312	158	731	20,151	17,209
8	WS-SO-29-RI	Rigaku, Inc.	531	1,522	330	101	745	20,030	17,210
8	WS-SO-37-RI	Rigaku, Inc.	568	1,564	317	129	734	20,159	17,313
9	WS-SO-13-XX	Reference Laboratory	200 J-	5800	150	53	1800	47,000	45,000
9	WS-SO-19-XX	Reference Laboratory	150 J-	5000	130	66	1500	39,000	24,000
9	WS-SO-28-XX	Reference Laboratory	120 J-	4200	100	54	1200	33,000	30,000
9	WS-SO-32-XX	Reference Laboratory	190 J-	5500	140	54	1700	44,000	30,000
9	WS-SO-36-XX	Reference Laboratory	120 J-	3800	92	51	1100	30,000	45,000
9	WS-SO-13-RI	Rigaku, Inc.	101	2,007	303	152	975	19,879	20,959
9	WS-SO-19-RI	Rigaku, Inc.	139	2,004	304	152	966	20,134	20,926
9	WS-SO-28-RI	Rigaku, Inc.	270	2,006	306	156	956	19,964	21,260
9	WS-SO-32-RI	Rigaku, Inc.	304	2,028	308	147	957	20,163	20,967
9	WS-SO-36-RI	Rigaku, Inc.	223	2,032	301	113	970	20,164	21,151

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
7	WS-SO-01-XX	Reference Laboratory	5.8 J	66	1.3 U	69 J-	42	3,000
7	WS-SO-04-XX	Reference Laboratory	6.5	62	1.3 U	76 J-	44	3,100
7	WS-SO-15-XX	Reference Laboratory	5.8	58	1.3 U	90 J-	52	3,400
7	WS-SO-22-XX	Reference Laboratory	4.8	57	1.3 U	72 J-	44	3,000
7	WS-SO-34-XX	Reference Laboratory	5.4	60	1.3 U	78 J-	47	3,200
7	WS-SO-01-RI	Rigaku, Inc.	22	46	14	146	60	1,501
7	WS-SO-04-RI	Rigaku, Inc.	20	51	11	152	73	1,473
7	WS-SO-15-RI	Rigaku, Inc.	19	46	10	154	71	1,473
7	WS-SO-22-RI	Rigaku, Inc.	23	45	13	148	67	1,487
7	WS-SO-34-RI	Rigaku, Inc.	22	47	12	146	60	1,484
8	WS-SO-02-XX	Reference Laboratory	17	57	1.3 U	150 J-	36	6,000
8	WS-SO-16-XX	Reference Laboratory	15	60	1.1 J	150 J-	35	5,700
8	WS-SO-18-XX	Reference Laboratory	17	62	1.9	140 J-	36	5,900
8	WS-SO-21-XX	Reference Laboratory	14	51	1.6	150 J-	33	5,500
8	WS-SO-24-XX	Reference Laboratory	16	54	2.1	140 J-	30	5,200
8	WS-SO-29-XX	Reference Laboratory	15	55	1.7	140 J-	33	5,500
8	WS-SO-37-XX	Reference Laboratory	14	63	3	140 J-	34	5,800
8	WS-SO-02-RI	Rigaku, Inc.	21	55	15	112	51	2,557
8	WS-SO-16-RI	Rigaku, Inc.	17	57	18	116	67	2,536
8	WS-SO-18-RI	Rigaku, Inc.	21	53	16	114	59	2,551
8	WS-SO-21-RI	Rigaku, Inc.	27	58	17	119	58	2,512
8	WS-SO-24-RI	Rigaku, Inc.	17	51	16	113	63	2,529
8	WS-SO-29-RI	Rigaku, Inc.	16	51	17	113	61	2,544
8	WS-SO-37-RI	Rigaku, Inc.	15	52	18	117	56	2,535
9	WS-SO-13-XX	Reference Laboratory	11	75	3.7	170 J-	24	9,000
9	WS-SO-19-XX	Reference Laboratory	12	74	3.7	160 J-	20	7,700
9	WS-SO-28-XX	Reference Laboratory	11	59	2.3	130 J-	16	6,100
9	WS-SO-32-XX	Reference Laboratory	11	73	3.7	190 J-	23	8,500
9	WS-SO-36-XX	Reference Laboratory	13	55	1.7	120 J-	15	5,700
9	WS-SO-13-RI	Rigaku, Inc.	20	65	21	109	50	3,978
9	WS-SO-19-RI	Rigaku, Inc.	28	69	20	106	51	4,001
9	WS-SO-28-RI	Rigaku, Inc.	17	62	20	105	54	3,938
9	WS-SO-32-RI	Rigaku, Inc.	18	65	22	104	60	3,978
9	WS-SO-36-RI	Rigaku, Inc.	23	71	20	106	56	4,005

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
10	BN-SO-01-XX	Reference Laboratory	1.3 UJ	38	0.94	120	32	24,000	63
10	BN-SO-10-XX	Reference Laboratory	1.3 UJ	50	1.2	110	35	24,000	140
10	BN-SO-15-XX	Reference Laboratory	1.3 UJ	34	0.82	110	29	22,000	56
10	BN-SO-18-XX	Reference Laboratory	1.3 U	37	0.89	110	29	22,000	59
10	BN-SO-28-XX	Reference Laboratory	1.5	35	0.87	100	28	22,000	58
10	BN-SO-31-XX	Reference Laboratory	1.3	41	1	140	33	26,000	65
10	BN-SO-35-XX	Reference Laboratory	1.4	37	0.98	120	30	23,000	60
10	BN-SO-01-RI	Rigaku, Inc.	203	34	645	55	29	13,872	-17
10	BN-SO-10-RI	Rigaku, Inc.	198	69	642	96	27	13,866	-15
10	BN-SO-15-RI	Rigaku, Inc.	213	49	665	81	29	13,934	-21
10	BN-SO-18-RI	Rigaku, Inc.	184	46	624	60	23	14,018	-14
10	BN-SO-28-RI	Rigaku, Inc.	219	62	658	103	23	13,841	-11
10	BN-SO-31-RI	Rigaku, Inc.	251	47	733	59	21	13,882	-10
10	BN-SO-35-RI	Rigaku, Inc.	207	30	662	101	25	13,915	-11
11	BN-SO-02-XX	Reference Laboratory	11	140	50	90	170	28,000	840
11	BN-SO-04-XX	Reference Laboratory	9.1	120	42	79	140	24,000	700
11	BN-SO-17-XX	Reference Laboratory	9.3	110	39	79	140	23,000	680
11	BN-SO-22-XX	Reference Laboratory	7.3	98	34	65	110	20,000	590
11	BN-SO-27-XX	Reference Laboratory	9.6	110	39	78	130	24,000	660
11	BN-SO-02-RI	Rigaku, Inc.	241	75	640	125	92	13,783	303
11	BN-SO-04-RI	Rigaku, Inc.	252	67	643	52	92	13,700	332
11	BN-SO-17-RI	Rigaku, Inc.	252	77	648	69	95	13,691	310
11	BN-SO-22-RI	Rigaku, Inc.	285	88	683	79	90	13,741	321
11	BN-SO-27-RI	Rigaku, Inc.	288	76	663	45	94	13,692	318
12	BN-SO-03-XX	Reference Laboratory	65	620	290	120	840	25,000	4,700
12	BN-SO-06-XX	Reference Laboratory	60	600	280	94	810	24,000	4,500
12	BN-SO-08-XX	Reference Laboratory	57	570	270	100	750	22,000	4,300
12	BN-SO-13-XX	Reference Laboratory	65	320	150	98	410	17,000	2,400
12	BN-SO-20-XX	Reference Laboratory	57	540	260	88	730	22,000	4,100
12	BN-SO-30-XX	Reference Laboratory	64	630	300	100	860	26,000	4,800
12	BN-SO-34-XX	Reference Laboratory	68	630	290	110	830	25,000	4,700
12	BN-SO-03-RI	Rigaku, Inc.	538	315	672	146	488	14,067	2,193
12	BN-SO-06-RI	Rigaku, Inc.	559	310	666	43	481	14,026	2,184
12	BN-SO-08-RI	Rigaku, Inc.	558	298	674	100	495	13,942	2,185
12	BN-SO-13-RI	Rigaku, Inc.	626	316	684	98	493	14,050	2,178
12	BN-SO-20-RI	Rigaku, Inc.	523	301	662	77	516	13,973	2,147
12	BN-SO-30-RI	Rigaku, Inc.	585	304	675	72	493	13,924	2,199
12	BN-SO-34-RI	Rigaku, Inc.	563	296	660	93	489	14,105	2,176

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
10	BN-SO-01-XX	Reference Laboratory	0.13	63	1.3 U	1.3 UJ	55	92
10	BN-SO-10-XX	Reference Laboratory	0.14	54	1.2 J	1.3 UJ	55	110
10	BN-SO-15-XX	Reference Laboratory	0.15	58	1.3 U	1.3 UJ	49	89
10	BN-SO-18-XX	Reference Laboratory	0.13	59	1.3	0.94 U	46	88
10	BN-SO-28-XX	Reference Laboratory	0.16	54	1.3 U	0.77 U	48	81
10	BN-SO-31-XX	Reference Laboratory	0.14	71	1.3 U	0.97 U	54	94
10	BN-SO-35-XX	Reference Laboratory	0.15	63	1.2 J	0.85 U	50	87
10	BN-SO-01-RI	Rigaku, Inc.	29	41	6	221	70	66
10	BN-SO-10-RI	Rigaku, Inc.	23	44	7	221	73	72
10	BN-SO-15-RI	Rigaku, Inc.	27	43	5	224	70	86
10	BN-SO-18-RI	Rigaku, Inc.	25	49	5	224	54	63
10	BN-SO-28-RI	Rigaku, Inc.	21	43	5	226	68	72
10	BN-SO-31-RI	Rigaku, Inc.	25	41	7	241	71	87
10	BN-SO-35-RI	Rigaku, Inc.	36	45	8	227	66	72
11	BN-SO-02-XX	Reference Laboratory	0.37	54	4.3	7.6	60	470
11	BN-SO-04-XX	Reference Laboratory	0.36	48	2.9	6.5	50	400
11	BN-SO-17-XX	Reference Laboratory	0.39	47	2.7	6.3	49	390
11	BN-SO-22-XX	Reference Laboratory	0.37	40	2.8	5.4	43	330
11	BN-SO-27-XX	Reference Laboratory	0.38	46	3.7	6.1	52	380
11	BN-SO-02-RI	Rigaku, Inc.	27	40	9	223	60	230
11	BN-SO-04-RI	Rigaku, Inc.	30	45	7	223	58	220
11	BN-SO-17-RI	Rigaku, Inc.	35	38	8	216	57	221
11	BN-SO-22-RI	Rigaku, Inc.	23	41	6	236	77	232
11	BN-SO-27-RI	Rigaku, Inc.	19	37	7	234	57	223
12	BN-SO-03-XX	Reference Laboratory	1.6	100	17	42	48	2,300
12	BN-SO-06-XX	Reference Laboratory	2	92	15	41	48	2,300
12	BN-SO-08-XX	Reference Laboratory	2	94	14	38	39	2,200
12	BN-SO-13-XX	Reference Laboratory	1.6	71	9.2	21	37	1,200
12	BN-SO-20-XX	Reference Laboratory	1.6	84	14	37	44	2,100
12	BN-SO-30-XX	Reference Laboratory	1.6	99	17	44	50	2,400
12	BN-SO-34-XX	Reference Laboratory	2	100	17	42	49	2,300
12	BN-SO-03-RI	Rigaku, Inc.	17	59	11	200	60	1,200
12	BN-SO-06-RI	Rigaku, Inc.	22	55	11	197	54	1,212
12	BN-SO-08-RI	Rigaku, Inc.	25	53	11	201	74	1,211
12	BN-SO-13-RI	Rigaku, Inc.	20	59	11	208	63	1,218
12	BN-SO-20-RI	Rigaku, Inc.	30	64	14	196	62	1,247
12	BN-SO-30-RI	Rigaku, Inc.	34	58	11	212	64	1,213
12	BN-SO-34-RI	Rigaku, Inc.	32	59	12	197	60	1,216

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
13	BN-SO-07-XX	Reference Laboratory	110 J-	990 J+	520	82	1,400	23,000	6,900
13	BN-SO-16-XX	Reference Laboratory	120 J-	1,100 J+	570	86	1,500	25,000	8,100
13	BN-SO-21-XX	Reference Laboratory	150 J-	1,300 J+	660	110	1,700	30,000	8,900
13	BN-SO-25-XX	Reference Laboratory	82 J-	700 J	370 J-	64 J-	930 J-	16,000 J-	5,400 J-
13	BN-SO-33-XX	Reference Laboratory	100 J-	1,100	640	100	1,600	27,000	8,000
13	BN-SO-07-RI	Rigaku, Inc.	786	467	700	74	870	13,940	3,698
13	BN-SO-16-RI	Rigaku, Inc.	871	475	741	101	875	14,102	3,735
13	BN-SO-21-RI	Rigaku, Inc.	715	482	708	81	859	13,924	3,705
13	BN-SO-25-RI	Rigaku, Inc.	805	500	722	59	895	13,960	3,730
13	BN-SO-33-RI	Rigaku, Inc.	824	511	741	54	870	14,054	3,715
14	BN-SO-05-XX	Reference Laboratory	160 J-	1,600	850	86	2,200	26,000	12,000
14	BN-SO-19-XX	Reference Laboratory	150 J-	1,600	860	79	2,200	26,000	12,000
14	BN-SO-26-XX	Reference Laboratory	150 J-	1,700	900	82	2,400	27,000	12,000
14	BN-SO-29-XX	Reference Laboratory	150 J-	1,600	880	86	2,300	26,000	12,000
14	BN-SO-32-XX	Reference Laboratory	160 J-	1,600	860	84	2,300	26,000	12,000
14	BN-SO-05-RI	Rigaku, Inc.	800	705	695	86	1,336	14,228	5,477
14	BN-SO-19-RI	Rigaku, Inc.	927	713	719	120	1,303	14,345	5,496
14	BN-SO-26-RI	Rigaku, Inc.	967	711	729	79	1,326	14,305	5,559
14	BN-SO-29-RI	Rigaku, Inc.	901	685	714	115	1,300	14,132	5,501
14	BN-SO-32-RI	Rigaku, Inc.	894	695	719	81	1,314	14,401	5,584
15	CN-SO-01-XX	Reference Laboratory	13 J-	13	21	190	700	38,000	1,200
15	CN-SO-04-XX	Reference Laboratory	13 J-	11	21	200	680	37,000	1,200
15	CN-SO-08-XX	Reference Laboratory	15 J-	15	25	210	740	43,000	1,300
15	CN-SO-10-XX	Reference Laboratory	13 J-	13	22	200	760	39,000	1,200
15	CN-SO-11-XX	Reference Laboratory	17 J-	16	30	240	860	47,000	1,600
15	CN-SO-01-RI	Rigaku, Inc.	335	42	664	185	368	18,032	514
15	CN-SO-04-RI	Rigaku, Inc.	323	17	635	205	405	18,122	513
15	CN-SO-08-RI	Rigaku, Inc.	378	43	664	158	364	18,393	505
15	CN-SO-10-RI	Rigaku, Inc.	341	35	641	188	383	18,522	531
15	CN-SO-11-RI	Rigaku, Inc.	330	38	640	146	385	18,265	518

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
13	BN-SO-07-XX	Reference Laboratory	3.4	120	26	70	41	4,000
13	BN-SO-16-XX	Reference Laboratory	3.4	130	29	77	44	4,400
13	BN-SO-21-XX	Reference Laboratory	3.6	160	35	88	52	5,100
13	BN-SO-25-XX	Reference Laboratory	3.8	88 J-	19 J-	48 J-	28 J-	2,900 J-
13	BN-SO-33-XX	Reference Laboratory	4	150	34	81	48	5,100
13	BN-SO-07-RI	Rigaku, Inc.	29	68	15	195	70	2,193
13	BN-SO-16-RI	Rigaku, Inc.	34	70	16	207	60	2,187
13	BN-SO-21-RI	Rigaku, Inc.	31	76	14	191	59	2,174
13	BN-SO-25-RI	Rigaku, Inc.	29	74	17	190	64	2,204
13	BN-SO-33-RI	Rigaku, Inc.	30	73	17	199	57	2,169
14	BN-SO-05-XX	Reference Laboratory	5	160	48	110	39	6,700
14	BN-SO-19-XX	Reference Laboratory	5	160	48	120	39	6,700
14	BN-SO-26-XX	Reference Laboratory	5.4	160	49	120	40	7,000
14	BN-SO-29-XX	Reference Laboratory	5.4	160	48	120	41	6,800
14	BN-SO-32-XX	Reference Laboratory	5.4	160	48	120	39	6,700
14	BN-SO-05-RI	Rigaku, Inc.	18	78	16	175	57	3,096
14	BN-SO-19-RI	Rigaku, Inc.	21	80	19	177	56	3,077
14	BN-SO-26-RI	Rigaku, Inc.	18	79	18	184	59	3,118
14	BN-SO-29-RI	Rigaku, Inc.	25	80	20	178	63	3,074
14	BN-SO-32-RI	Rigaku, Inc.	27	81	18	175	58	3,146
15	CN-SO-01-XX	Reference Laboratory	0.13	240	2.2	12	21	3,100
15	CN-SO-04-XX	Reference Laboratory	0.14	240	1.5	12	22	2,900
15	CN-SO-08-XX	Reference Laboratory	0.16	280	1.3 U	15	26	3,200
15	CN-SO-10-XX	Reference Laboratory	0.12	240	1.9	14	22	3,000
15	CN-SO-11-XX	Reference Laboratory	0.15	320	1.3 U	16	27	3,500
15	CN-SO-01-RI	Rigaku, Inc.	27	123	9	227	71	1,671
15	CN-SO-04-RI	Rigaku, Inc.	32	122	7	228	75	1,628
15	CN-SO-08-RI	Rigaku, Inc.	40	127	7	239	68	1,690
15	CN-SO-10-RI	Rigaku, Inc.	37	126	7	232	70	1,658
15	CN-SO-11-RI	Rigaku, Inc.	35	125	8	232	62	1,689

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
16	AS-SO-02-XX	Reference Laboratory	2.6 UJ	18	50	180	140	48,000	1,600
16	AS-SO-06-XX	Reference Laboratory	2.4 UJ	19	52	190	130	52,000	1,600
16	AS-SO-10-XX	Reference Laboratory	1.9 J-	18	48	180	110	45,000	1,400
16	AS-SO-11-XX	Reference Laboratory	3.7 J-	22	63	230	150	52,000	2,100
16	AS-SO-13-XX	Reference Laboratory	2.4 UJ	20	57	200	150	52,000	1,700
16	AS-SO-02-RI	Rigaku, Inc.	247	7	518	147	62	18,017	607
16	AS-SO-06-RI	Rigaku, Inc.	229	-13	523	105	56	17,814	636
16	AS-SO-10-RI	Rigaku, Inc.	234	1	534	123	64	17,877	639
16	AS-SO-11-RI	Rigaku, Inc.	259	-11	519	154	64	17,923	629
16	AS-SO-13-RI	Rigaku, Inc.	226	8	515	135	66	18,167	646
17	AS-SO-01-XX	Reference Laboratory	3.8 J-	26	100	420	250	100,000	3,200
17	AS-SO-04-XX	Reference Laboratory	6.4 UJ	22	110	480	260	110,000	3,300
17	AS-SO-07-XX	Reference Laboratory	3.6 J-	21	97	380	240	88,000	2,900
17	AS-SO-09-XX	Reference Laboratory	2.6 UJ	25 J-	100 J-	390 J-	250 J-	94,000 J-	3,200 J-
17	AS-SO-12-XX	Reference Laboratory	2.6 UJ	29	120	440	270	93,000	3,300
17	AS-SO-01-RI	Rigaku, Inc.	169	-47	400	248	77	28,556	994
17	AS-SO-04-RI	Rigaku, Inc.	140	-42	406	256	96	28,250	992
17	AS-SO-07-RI	Rigaku, Inc.	142	-61	406	233	91	28,106	1,014
17	AS-SO-09-RI	Rigaku, Inc.	154	-35	406	255	82	28,894	991
17	AS-SO-12-RI	Rigaku, Inc.	115	-42	368	294	89	28,910	966
18	SB-SO-03-XX	Reference Laboratory	1.2 UJ	9	0.51 U	150	48	38,000	18
18	SB-SO-06-XX	Reference Laboratory	1.7 J-	8	0.51 U	140	44	35,000	16
18	SB-SO-14-XX	Reference Laboratory	4.1 J-	9	0.51 U	150	46	37,000	17
18	SB-SO-38-XX	Reference Laboratory	1.3 UJ	10	0.51 U	150	57	37,000	18
18	SB-SO-41-XX	Reference Laboratory	1.3 UJ	9	0.51 U	160	58	40,000	19
18	SB-SO-47-XX	Reference Laboratory	1.3 UJ	8	0.51 U	140	44	34,000	16
18	SB-SO-51-XX	Reference Laboratory	1.3 UJ	9	0.51 U	160	50	40,000	18
18	SB-SO-03-RI	Rigaku, Inc.	241	14	640	152	29	20,833	-46
18	SB-SO-06-RI	Rigaku, Inc.	200	19	597	144	31	20,593	-54
18	SB-SO-14-RI	Rigaku, Inc.	191	23	585	151	32	20,649	-51
18	SB-SO-38-RI	Rigaku, Inc.	211	21	609	180	31	20,656	-63
18	SB-SO-41-RI	Rigaku, Inc.	187	15	589	151	28	20,630	-41
18	SB-SO-47-RI	Rigaku, Inc.	184	24	601	154	31	20,564	-39
18	SB-SO-51-RI	Rigaku, Inc.	183	6	590	146	32	20,716	-55

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
16	AS-SO-02-XX	Reference Laboratory	0.76	91	2.6 U	4.5	42	3,300
16	AS-SO-06-XX	Reference Laboratory	0.74	93	2.6 U	4.8	44	3,500
16	AS-SO-10-XX	Reference Laboratory	0.78	84	1.1 U	4.4	42	3,000
16	AS-SO-11-XX	Reference Laboratory	0.72	120	1.1 U	5.6	54	3,800
16	AS-SO-13-XX	Reference Laboratory	0.79	100	3	5.2	50	3,800
16	AS-SO-02-RI	Rigaku, Inc.	14	49	3	181	61	1,447
16	AS-SO-06-RI	Rigaku, Inc.	15	40	3	181	56	1,475
16	AS-SO-10-RI	Rigaku, Inc.	5	49	3	174	52	1,441
16	AS-SO-11-RI	Rigaku, Inc.	14	49	1	179	63	1,457
16	AS-SO-13-RI	Rigaku, Inc.	7	45	2	170	57	1,509
17	AS-SO-01-XX	Reference Laboratory	1.4	180	2.6 U	9.3	66	6,900
17	AS-SO-04-XX	Reference Laboratory	1.3	200	6.2 U	12	72	7,400
17	AS-SO-07-XX	Reference Laboratory	1.4	160	2.7	8.9	63	6,300
17	AS-SO-09-XX	Reference Laboratory	1.4	170 J-	2.6 U	9.6 J-	65 J-	6,800 J-
17	AS-SO-12-XX	Reference Laboratory	1.4	190	2.6 U	3.2	73	7,500
17	AS-SO-01-RI	Rigaku, Inc.	-12	57	-4	135	70	2,628
17	AS-SO-04-RI	Rigaku, Inc.	-11	59	-2	133	57	2,696
17	AS-SO-07-RI	Rigaku, Inc.	-16	61	-3	135	56	2,725
17	AS-SO-09-RI	Rigaku, Inc.	-14	62	-2	135	52	2,602
17	AS-SO-12-RI	Rigaku, Inc.	-11	56	-1	123	62	2,698
18	SB-SO-03-XX	Reference Laboratory	62	210	1.3 U	1.3 U	67	90
18	SB-SO-06-XX	Reference Laboratory	55	200	1.3 U	1.3 U	63	82
18	SB-SO-14-XX	Reference Laboratory	55	210	1.3 U	1.3 U	66	95
18	SB-SO-38-XX	Reference Laboratory	56	210	1.3 U	1.3 U	68	91
18	SB-SO-41-XX	Reference Laboratory	54	230	1.3 U	1.3 U	71	96
18	SB-SO-47-XX	Reference Laboratory	58	200	1.3 U	1.3 U	62	82
18	SB-SO-51-XX	Reference Laboratory	54	230	1.3 U	1.3 U	74	93
18	SB-SO-03-RI	Rigaku, Inc.	48	107	6	216	117	63
18	SB-SO-06-RI	Rigaku, Inc.	47	99	6	208	116	62
18	SB-SO-14-RI	Rigaku, Inc.	37	98	4	199	110	63
18	SB-SO-38-RI	Rigaku, Inc.	46	100	7	210	111	63
18	SB-SO-41-RI	Rigaku, Inc.	45	100	5	204	113	62
18	SB-SO-47-RI	Rigaku, Inc.	38	106	7	204	118	61
18	SB-SO-51-RI	Rigaku, Inc.	48	97	7	209	148	63

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
19	SB-SO-05-XX	Reference Laboratory	1.6 J-	9	0.51 U	140	46	35,000	16
19	SB-SO-18-XX	Reference Laboratory	1.2 UJ	10	0.51 U	150	46	38,000	17
19	SB-SO-30-XX	Reference Laboratory	3.2 J-	7	0.51 U	94	27	22,000	10
19	SB-SO-40-XX	Reference Laboratory	2.2 J-	9	0.51 U	120	40	33,000	15
19	SB-SO-53-XX	Reference Laboratory	1.2 UJ	10	0.51 U	140	44	37,000	17
19	SB-SO-05-RI	Rigaku, Inc.	212	4	608	158	24	20,004	-52
19	SB-SO-18-RI	Rigaku, Inc.	209	16	605	137	25	19,723	-61
19	SB-SO-30-RI	Rigaku, Inc.	231	21	618	161	30	19,809	-47
19	SB-SO-40-RI	Rigaku, Inc.	236	-9	623	146	28	19,764	-40
19	SB-SO-53-RI	Rigaku, Inc.	241	35	645	125	27	19,905	-50
20	SB-SO-08-XX	Reference Laboratory	5.4 J-	13	0.51 U	120	39	32,000	17
20	SB-SO-11-XX	Reference Laboratory	5.7 J-	13	0.51 U	140	46	36,000	20
20	SB-SO-21-XX	Reference Laboratory	4.9 J	13	0.51 U	130	43	34,000	18
20	SB-SO-39-XX	Reference Laboratory	4.7 J-	13	0.51 U	140	46	34,000	19
20	SB-SO-42-XX	Reference Laboratory	4.6 J-	13	0.51 U	140	45	35,000	18
20	SB-SO-08-RI	Rigaku, Inc.	172	27	581	117	28	18,535	-42
20	SB-SO-11-RI	Rigaku, Inc.	179	11	600	123	30	18,371	-38
20	SB-SO-21-RI	Rigaku, Inc.	192	4	578	135	78	19,571	-66
20	SB-SO-39-RI	Rigaku, Inc.	194	11	586	135	24	18,504	-31
20	SB-SO-42-RI	Rigaku, Inc.	183	7	578	112	28	18,441	-40
21	SB-SO-22-XX	Reference Laboratory	10 J	18	0.51 U	120	37	29,000	22
21	SB-SO-25-XX	Reference Laboratory	6.8 J+	18	0.51 U	120	37	29,000	22
21	SB-SO-27-XX	Reference Laboratory	6.7 J+	18	0.51 U	120	37	29,000	22
21	SB-SO-35-XX	Reference Laboratory	6 J+	17	0.51 U	110	35	28,000	21
21	SB-SO-44-XX	Reference Laboratory	6.8 J+	18	0.51 U	120	37	29,000	22
21	SB-SO-22-RI	Rigaku, Inc.	157	28	591	132	32	15,830	-39
21	SB-SO-25-RI	Rigaku, Inc.	181	16	625	122	31	15,907	-35
21	SB-SO-27-RI	Rigaku, Inc.	143	14	578	149	32	15,846	-39
21	SB-SO-35-RI	Rigaku, Inc.	128	21	552	135	31	15,679	-51
21	SB-SO-44-RI	Rigaku, Inc.	139	12	574	164	26	15,749	-57

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
19	SB-SO-05-XX	Reference Laboratory	540	200	1.3 U	1.3 U	61	80
19	SB-SO-18-XX	Reference Laboratory	280	210	1.3 U	1.3 U	70	84
19	SB-SO-30-XX	Reference Laboratory	290	120	1.3 J+	1.3 U	43	50
19	SB-SO-40-XX	Reference Laboratory	280	180	1.3 U	1.3 U	58	74
19	SB-SO-53-XX	Reference Laboratory	270	200	1.3 U	1.3 U	64	81
19	SB-SO-05-RI	Rigaku, Inc.	148	91	6	212	114	54
19	SB-SO-18-RI	Rigaku, Inc.	134	99	4	212	98	62
19	SB-SO-30-RI	Rigaku, Inc.	160	92	6	219	95	52
19	SB-SO-40-RI	Rigaku, Inc.	160	95	5	218	107	61
19	SB-SO-53-RI	Rigaku, Inc.	125	97	7	218	142	55
20	SB-SO-08-XX	Reference Laboratory	730	180	1.3 U	1.3 U	57	70
20	SB-SO-11-XX	Reference Laboratory	810	200	1.3 U	1.3 U	66	84
20	SB-SO-21-XX	Reference Laboratory	740	190	1.3 U	1.3 U	58	75
20	SB-SO-39-XX	Reference Laboratory	790	200	1.3 U	1.3 U	62	77
20	SB-SO-42-XX	Reference Laboratory	740	200	1.3 U	1.3 U	65	78
20	SB-SO-08-RI	Rigaku, Inc.	358	96	4	201	124	58
20	SB-SO-11-RI	Rigaku, Inc.	345	93	4	202	141	61
20	SB-SO-21-RI	Rigaku, Inc.	32	1,366	14	218	134	1,865
20	SB-SO-39-RI	Rigaku, Inc.	346	91	5	212	118	56
20	SB-SO-42-RI	Rigaku, Inc.	341	89	7	200	159	54
21	SB-SO-22-XX	Reference Laboratory	3300	160	1.3 U	1.3 U	52	64 J-
21	SB-SO-25-XX	Reference Laboratory	3000	160	1.3 U	1.3 U	54	63
21	SB-SO-27-XX	Reference Laboratory	3100	170	1.3 U	1.3 U	54	65
21	SB-SO-35-XX	Reference Laboratory	3100	160	1.3 U	1.3 U	50	62
21	SB-SO-44-XX	Reference Laboratory	3000	170	1.3 U	1.3 U	53	64
21	SB-SO-22-RI	Rigaku, Inc.	803	83	5	204	140	55
21	SB-SO-25-RI	Rigaku, Inc.	787	85	7	209	125	53
21	SB-SO-27-RI	Rigaku, Inc.	755	81	6	194	121	51
21	SB-SO-35-RI	Rigaku, Inc.	773	90	6	196	121	55
21	SB-SO-44-RI	Rigaku, Inc.	760	89	6	194	195	50

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
22	SB-SO-23-XX	Reference Laboratory	48 J-	37	0.1 U	21	7	4,500	36
22	SB-SO-28-XX	Reference Laboratory	42 J-	36	0.1 U	21	7	4,400	36
22	SB-SO-32-XX	Reference Laboratory	46 J-	40	0.1 U	23	7.6	4,900	40
22	SB-SO-43-XX	Reference Laboratory	40 J-	35	0.1 U	20	6.7	4,200	34
22	SB-SO-48-XX	Reference Laboratory	39 J-	36	0.1 U	21	6.9	4,500	36
22	SB-SO-23-RI	Rigaku, Inc.	113	-6	703	77	11	4,597	-1
22	SB-SO-28-RI	Rigaku, Inc.	89	-3	608	110	22	4,931	-4
22	SB-SO-32-RI	Rigaku, Inc.	56	65	517	103	19	4,800	-1
22	SB-SO-43-RI	Rigaku, Inc.	61	84	547	110	25	4,798	2
22	SB-SO-48-RI	Rigaku, Inc.	56	84	538	76	21	4,797	-14
23	SB-SO-02-XX	Reference Laboratory	44 J-	23 J-	0.5 U	130	43	35,000	22 J-
23	SB-SO-07-XX	Reference Laboratory	45 J	22	0.5 U	120	38	35,000	23
23	SB-SO-10-XX	Reference Laboratory	62 J	26	0.5 U	140	44	41,000	27
23	SB-SO-26-XX	Reference Laboratory	61 J	30	0.5 U	160	50	46,000	31
23	SB-SO-50-XX	Reference Laboratory	57 J	27	0.5 U	140	46	42,000	28
23	SB-SO-02-RI	Rigaku, Inc.	182	16	571	117	32	21,148	-64
23	SB-SO-07-RI	Rigaku, Inc.	230	20	600	125	26	21,733	-49
23	SB-SO-10-RI	Rigaku, Inc.	198	17	569	146	24	21,449	-57
23	SB-SO-26-RI	Rigaku, Inc.	-47	-196	46	-124	-37	4,098	-234
23	SB-SO-50-RI	Rigaku, Inc.	218	40	596	198	30	21,439	-50
24	SB-SO-01-XX	Reference Laboratory	180 J	65	0.5 U	140	46	47,000	30
24	SB-SO-16-XX	Reference Laboratory	170 J	64	0.5 U	140	45	47,000	30
24	SB-SO-24-XX	Reference Laboratory	180 J	66	0.5 U	150	49	49,000	32
24	SB-SO-45-XX	Reference Laboratory	180 J	63	0.5 U	140	45	47,000	30
24	SB-SO-52-XX	Reference Laboratory	150 J	62	0.5 U	140	47	46,000	29
24	SB-SO-01-RI	Rigaku, Inc.	260	36	604	140	28	22,448	-48
24	SB-SO-16-RI	Rigaku, Inc.	235	42	578	178	22	22,611	-49
24	SB-SO-24-RI	Rigaku, Inc.	233	42	596	171	28	22,572	-45
24	SB-SO-45-RI	Rigaku, Inc.	216	23	558	129	28	22,432	-48
24	SB-SO-52-RI	Rigaku, Inc.	245	29	564	129	26	22,574	-54

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
22	SB-SO-23-XX	Reference Laboratory	8500	26	0.22 J	0.26 UJ	13	8
22	SB-SO-28-XX	Reference Laboratory	8800	26	0.26 U	0.26 UJ	13	8
22	SB-SO-32-XX	Reference Laboratory	8900	28	0.36	0.1 UJ	14	9
22	SB-SO-43-XX	Reference Laboratory	7600	24	0.26 U	0.26 UJ	13	8
22	SB-SO-48-XX	Reference Laboratory	8200	25	0.26 U	0.1 UJ	13	8
22	SB-SO-23-RI	Rigaku, Inc.	2,552	35	8	231	160	28
22	SB-SO-28-RI	Rigaku, Inc.	2,712	39	8	209	196	32
22	SB-SO-32-RI	Rigaku, Inc.	2,621	33	11	179	164	31
22	SB-SO-43-RI	Rigaku, Inc.	2,651	36	7	184	322	29
22	SB-SO-48-RI	Rigaku, Inc.	2,681	36	9	179	315	32
23	SB-SO-02-XX	Reference Laboratory	130 J+	180	1.2 U	1.2 UJ	59	88
23	SB-SO-07-XX	Reference Laboratory	270	170	1.4	1.6	53	86
23	SB-SO-10-XX	Reference Laboratory	220	200	2.8	1.8	59	100
23	SB-SO-26-XX	Reference Laboratory	260	220	3.4	1.8	68	110
23	SB-SO-50-XX	Reference Laboratory	200	200	2.9	1.8	61	100
23	SB-SO-02-RI	Rigaku, Inc.	76	88	4	196	103	70
23	SB-SO-07-RI	Rigaku, Inc.	75	94	4	206	111	66
23	SB-SO-10-RI	Rigaku, Inc.	70	91	5	202	102	61
23	SB-SO-26-RI	Rigaku, Inc.	-88	2	-22	11	8	-9
23	SB-SO-50-RI	Rigaku, Inc.	72	96	5	205	154	59
24	SB-SO-01-XX	Reference Laboratory	400	190	1.8	2.3	65	95
24	SB-SO-16-XX	Reference Laboratory	480	190	1.9	2.2	65	97
24	SB-SO-24-XX	Reference Laboratory	420	200	2.5	2.3	67	95
24	SB-SO-45-XX	Reference Laboratory	450	190	2.8	2.1 J-	63	93
24	SB-SO-52-XX	Reference Laboratory	430	190	1.8	2.2	64	90
24	SB-SO-01-RI	Rigaku, Inc.	105	83	4	208	107	60
24	SB-SO-16-RI	Rigaku, Inc.	100	80	5	199	113	60
24	SB-SO-24-RI	Rigaku, Inc.	108	81	6	205	112	59
24	SB-SO-45-RI	Rigaku, Inc.	105	85	3	193	135	54
24	SB-SO-52-RI	Rigaku, Inc.	111	86	5	202	135	59

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
25	SB-SO-13-XX	Reference Laboratory	430 J	160	1 U	140	46	61,000	36
25	SB-SO-19-XX	Reference Laboratory	310 J	100	0.5 U	100	32	42,000	25
25	SB-SO-33-XX	Reference Laboratory	350 J	110	0.5 U	100	33	45,000	28
25	SB-SO-37-XX	Reference Laboratory	340 J	130	1 U	120	39	51,000	31
25	SB-SO-55-XX	Reference Laboratory	340 J	120	0.5 U	120	37	49,000	29
25	SB-SO-13-RI	Rigaku, Inc.	322	46	570	144	22	25,192	-54
25	SB-SO-19-RI	Rigaku, Inc.	329	48	574	123	27	25,518	-58
25	SB-SO-33-RI	Rigaku, Inc.	296	45	552	146	27	25,443	-52
25	SB-SO-37-RI	Rigaku, Inc.	272	55	565	110	25	25,224	-60
25	SB-SO-55-RI	Rigaku, Inc.	308	52	594	106	23	25,157	-53
26	SB-SO-12-XX	Reference Laboratory	620 J	190	1 U	100	33	55,000	43
26	SB-SO-15-XX	Reference Laboratory	600 J-	170 J-	1 U	91 J-	30 J-	51,000 J-	40 J-
26	SB-SO-17-XX	Reference Laboratory	800 J+	210	1 U	110	37	61,000	48
26	SB-SO-46-XX	Reference Laboratory	740 J+	190	1 U	120	35	57,000	47
26	SB-SO-54-XX	Reference Laboratory	280	31	0.2 U	25	5.8	8,600	5 J-
26	SB-SO-12-RI	Rigaku, Inc.	327	60	535	156	21	28,010	-60
26	SB-SO-15-RI	Rigaku, Inc.	368	59	534	185	18	28,182	-59
26	SB-SO-17-RI	Rigaku, Inc.	353	56	546	140	16	27,967	-62
26	SB-SO-46-RI	Rigaku, Inc.	338	39	546	129	21	27,861	-61
26	SB-SO-54-RI	Rigaku, Inc.	358	56	561	105	19	28,180	-62
27	KP-SE-08-XX	Reference Laboratory	6.2	3	0.11 U	88	3.8	840	300 J-
27	KP-SE-11-XX	Reference Laboratory	5.6	3	0.11 U	96	4.1	940	310 J-
27	KP-SE-17-XX	Reference Laboratory	4.9	3	0.11 U	98	4.1	940	300 J-
27	KP-SE-25-XX	Reference Laboratory	6	3	0.11 U	99	4.3	960	310 J-
27	KP-SE-30-XX	Reference Laboratory	5.7	3	0.11 U	83	3.6	830	300 J-
27	KP-SE-08-RI	Rigaku, Inc.	234	151	881	69	24	3,769	346
27	KP-SE-11-RI	Rigaku, Inc.	184	119	787	88	22	3,754	357
27	KP-SE-17-RI	Rigaku, Inc.	249	148	935	76	24	3,754	355
27	KP-SE-25-RI	Rigaku, Inc.	250	161	940	65	21	3,743	343
27	KP-SE-30-RI	Rigaku, Inc.	249	156	940	60	18	3,725	357

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
25	SB-SO-13-XX	Reference Laboratory	850	180	4.4	2.2 UJ	74	70
25	SB-SO-19-XX	Reference Laboratory	740	120	2.5	1.8	51	51
25	SB-SO-33-XX	Reference Laboratory	870	130	3	2 J	52	56
25	SB-SO-37-XX	Reference Laboratory	790	150	2.5 U	2 UJ	63	58
25	SB-SO-55-XX	Reference Laboratory	900	140	2.5	2.2 J	61	60
25	SB-SO-13-RI	Rigaku, Inc.	161	72	3	203	121	52
25	SB-SO-19-RI	Rigaku, Inc.	175	70	3	201	127	44
25	SB-SO-33-RI	Rigaku, Inc.	161	72	2	201	102	44
25	SB-SO-37-RI	Rigaku, Inc.	155	69	5	187	120	48
25	SB-SO-55-RI	Rigaku, Inc.	160	73	3	209	157	46
26	SB-SO-12-XX	Reference Laboratory	1,400	110	2.5 U	2.1 UJ	59	42
26	SB-SO-15-XX	Reference Laboratory	1,100	100 J-	3.4	1.6 UJ	52 J-	36 J-
26	SB-SO-17-XX	Reference Laboratory	1,200	120	2.8	2.3 UJ	60	42
26	SB-SO-46-XX	Reference Laboratory	670	120	2.6	2.2 UJ	57	41
26	SB-SO-54-XX	Reference Laboratory	560	20	0.5 U	0.5 UJ	11	6
26	SB-SO-12-RI	Rigaku, Inc.	218	60	1	192	134	37
26	SB-SO-15-RI	Rigaku, Inc.	225	59	2	198	123	36
26	SB-SO-17-RI	Rigaku, Inc.	202	54	0	192	128	36
26	SB-SO-46-RI	Rigaku, Inc.	227	53	2	200	154	37
26	SB-SO-54-RI	Rigaku, Inc.	236	55	2	192	154	40
27	KP-SE-08-XX	Reference Laboratory	0.09 U	42	0.27 U	0.27 UJ	4	5
27	KP-SE-11-XX	Reference Laboratory	0.08 U	46	0.43	0.27 UJ	4	6
27	KP-SE-17-XX	Reference Laboratory	0.08 U	47	0.27 U	0.27 UJ	4	5
27	KP-SE-25-XX	Reference Laboratory	0.1 U	47	0.26 U	0.27 UJ	4	5
27	KP-SE-30-XX	Reference Laboratory	0.1 U	39	0.24 U	0.27 UJ	4	5
27	KP-SE-08-RI	Rigaku, Inc.	69	70	20	289	25	36
27	KP-SE-11-RI	Rigaku, Inc.	78	69	18	260	22	32
27	KP-SE-17-RI	Rigaku, Inc.	77	64	20	304	25	38
27	KP-SE-25-RI	Rigaku, Inc.	74	65	20	303	21	33
27	KP-SE-30-RI	Rigaku, Inc.	73	58	21	302	34	33

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
28	KP-SE-01-XX	Reference Laboratory	3.2	2	0.1 U	34	2.2	480	310 J-
28	KP-SE-12-XX	Reference Laboratory	3.1	2	0.1 U	42	2.5	510	320 J-
28	KP-SE-14-XX	Reference Laboratory	11 J-	2	0.1 U	46 J-	2.7 J+	520 J-	680 J-
28	KP-SE-19-XX	Reference Laboratory	3	2	0.1 U	44	2.3	510	330
28	KP-SE-28-XX	Reference Laboratory	3.3	2	0.1 U	45	2.3	520	320
28	KP-SE-01-RI	Rigaku, Inc.	301	126	974	33	23	3,454	352
28	KP-SE-12-RI	Rigaku, Inc.	273	147	906	26	25	3,507	340
28	KP-SE-14-RI	Rigaku, Inc.	306	143	957	67	19	3,392	321
28	KP-SE-19-RI	Rigaku, Inc.	282	116	950	-3	16	3,396	329
28	KP-SE-28-RI	Rigaku, Inc.	243	104	891	48	18	3,444	342
29	TL-SE-04-XX	Reference Laboratory	1.2 U	10	0.5 U	62	1,900	42,000	32
29	TL-SE-10-XX	Reference Laboratory	1.2 U	10	0.5 U	64	2,000	43,000	35
29	TL-SE-12-XX	Reference Laboratory	1.2 U	10	0.5 U	66	2,100	44,000	34
29	TL-SE-15-XX	Reference Laboratory	1.2 U	9	0.5 U	54	1,800	36,000	28
29	TL-SE-20-XX	Reference Laboratory	1.2 U	10	0.5 U	64	2,000	42,000	32
29	TL-SE-24-XX	Reference Laboratory	1.2 U	11	0.5 U	67	2,100	43,000	37
29	TL-SE-26-XX	Reference Laboratory	1.2 U	10	0.5 U	62	2,000	40,000	34
29	TL-SE-04-RI	Rigaku, Inc.	112	-31	478	54	923	21,259	-57
29	TL-SE-10-RI	Rigaku, Inc.	119	-14	493	76	922	21,398	-68
29	TL-SE-12-RI	Rigaku, Inc.	116	-25	481	65	909	21,337	-79
29	TL-SE-15-RI	Rigaku, Inc.	114	-14	479	93	922	21,444	-55
29	TL-SE-20-RI	Rigaku, Inc.	127	-24	483	74	942	21,349	-61
29	TL-SE-24-RI	Rigaku, Inc.	147	-21	505	64	963	21,685	-62
29	TL-SE-26-RI	Rigaku, Inc.	136	-16	510	77	930	21,391	-72
30	TL-SE-03-XX	Reference Laboratory	2.5 U	9	1 U	91	1,600	63,000	12
30	TL-SE-19-XX	Reference Laboratory	2.5 U	10	1 U	96	1,700	66,000	13
30	TL-SE-23-XX	Reference Laboratory	2.5 U	9	1 U	92	1,600	64,000	12
30	TL-SE-25-XX	Reference Laboratory	2.5 U	10	1 U	91	1,600	62,000	11
30	TL-SE-31-XX	Reference Laboratory	2.5 U	10	1 U	110	1,800	74,000	13
30	TL-SE-03-RI	Rigaku, Inc.	69	-37	383	83	689	29,357	-107
30	TL-SE-19-RI	Rigaku, Inc.	71	-16	401	100	675	29,326	-93
30	TL-SE-23-RI	Rigaku, Inc.	67	-42	417	118	678	29,328	-104
30	TL-SE-25-RI	Rigaku, Inc.	62	-44	413	113	657	29,513	-101
30	TL-SE-31-RI	Rigaku, Inc.	64	-26	393	91	682	29,358	-91

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
28	KP-SE-01-XX	Reference Laboratory	0.05 U	16	0.26 U	0.26 UJ	2 J	6
28	KP-SE-12-XX	Reference Laboratory	0.06 U	20	0.26 U	0.26 UJ	2 J	8
28	KP-SE-14-XX	Reference Laboratory	0.07 U	23 J-	0.26 U	0.26 UJ	3 J	7
28	KP-SE-19-XX	Reference Laboratory	0.04 U	22	0.26 U	0.26 U	2 J	7
28	KP-SE-28-XX	Reference Laboratory	0.06 U	22	0.26 U	0.26 U	2 J	6
28	KP-SE-01-RI	Rigaku, Inc.	70	45	20	318	22	31
28	KP-SE-12-RI	Rigaku, Inc.	60	44	17	308	30	55
28	KP-SE-14-RI	Rigaku, Inc.	69	42	17	341	30	30
28	KP-SE-19-RI	Rigaku, Inc.	66	46	20	316	20	35
28	KP-SE-28-RI	Rigaku, Inc.	69	50	18	295	22	30
29	TL-SE-04-XX	Reference Laboratory	0.26 J-	71	1.2 U	1.3	95	160
29	TL-SE-10-XX	Reference Laboratory	0.19 J-	72	1.2 U	1.2 U	95	160
29	TL-SE-12-XX	Reference Laboratory	0.22 J-	75	1.2 U	1.2 U	100	170
29	TL-SE-15-XX	Reference Laboratory	0.28 J-	63	1.2 U	1 U	84	140
29	TL-SE-20-XX	Reference Laboratory	0.26 J-	74	1.2 U	1.2 U	100	160
29	TL-SE-24-XX	Reference Laboratory	0.26 J-	77	1.2 U	1.3 U	100	170
29	TL-SE-26-XX	Reference Laboratory	0.24 J-	70	1.2 U	1.2 U	96	160
29	TL-SE-04-RI	Rigaku, Inc.	10	44	1	166	136	93
29	TL-SE-10-RI	Rigaku, Inc.	4	44	3	173	128	91
29	TL-SE-12-RI	Rigaku, Inc.	7	43	-1	166	139	91
29	TL-SE-15-RI	Rigaku, Inc.	-1	45	1	161	140	93
29	TL-SE-20-RI	Rigaku, Inc.	5	41	2	164	149	90
29	TL-SE-24-RI	Rigaku, Inc.	16	41	1	183	148	99
29	TL-SE-26-RI	Rigaku, Inc.	1	48	2	175	145	89
30	TL-SE-03-XX	Reference Laboratory	0.32 J-	110	2.5 U	0.94 U	140	200
30	TL-SE-19-XX	Reference Laboratory	0.32 J-	120	2.5 U	1.1 U	150	210
30	TL-SE-23-XX	Reference Laboratory	0.41 J-	110	2.5 U	1.3 U	150	200
30	TL-SE-25-XX	Reference Laboratory	0.44 J-	110	2.5 U	0.94 U	150	200
30	TL-SE-31-XX	Reference Laboratory	0.57 J-	130	2.5 U	1.2 U	170	230
30	TL-SE-03-RI	Rigaku, Inc.	-17	50	-1	140	173	89
30	TL-SE-19-RI	Rigaku, Inc.	-7	51	-2	141	187	85
30	TL-SE-23-RI	Rigaku, Inc.	-7	48	-3	141	204	87
30	TL-SE-25-RI	Rigaku, Inc.	-10	49	-1	146	193	91
30	TL-SE-31-RI	Rigaku, Inc.	-8	54	0	139	192	89

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
31	TL-SE-01-XX	Reference Laboratory	1.2 UJ	9	0.5 U	110	1,400	19,000	48 J-
31	TL-SE-11-XX	Reference Laboratory	1.2 UJ	15	0.5 U	140	1,600	28,000	54 J-
31	TL-SE-14-XX	Reference Laboratory	1.2 UJ	10	0.27 J	110	1,500	18,000	50 J-
31	TL-SE-18-XX	Reference Laboratory	1.2 UJ	10	0.5 U	150	1,300	24,000	46 J-
31	TL-SE-22-XX	Reference Laboratory	1.2 UJ	11	0.5 U	150	1,700	26,000	54 J-
31	TL-SE-27-XX	Reference Laboratory	1.2 UJ	10	0.28 J	130	1,500	19,000	51 J-
31	TL-SE-29-XX	Reference Laboratory	1.2 UJ	11	0.22 J	140	1,600	23,000	51 J-
31	TL-SE-01-RI	Rigaku, Inc.	184	6	549	96	697	17,602	-55
31	TL-SE-11-RI	Rigaku, Inc.	144	-26	522	83	708	18,031	-61
31	TL-SE-14-RI	Rigaku, Inc.	182	-12	544	110	713	18,509	-48
31	TL-SE-18-RI	Rigaku, Inc.	164	6	526	88	726	18,075	-54
31	TL-SE-22-RI	Rigaku, Inc.	167	-15	533	110	724	18,371	-47
31	TL-SE-27-RI	Rigaku, Inc.	170	-24	537	134	689	18,594	-64
31	TL-SE-29-RI	Rigaku, Inc.	176	-15	529	117	703	18,315	-62
32	LV-SE-02-XX	Reference Laboratory	1.3 UJ	28	0.51 U	72	33	23,000	20 J-
32	LV-SE-10-XX	Reference Laboratory	1.3 UJ	34	0.51 U	84	42	28,000	25 J-
32	LV-SE-22-XX	Reference Laboratory	1.3 UJ	30	0.51 U	69	33	23,000	22 J-
32	LV-SE-25-XX	Reference Laboratory	1.3 UJ	31	0.51 U	74	36	25,000	23 J-
32	LV-SE-31-XX	Reference Laboratory	1.3 UJ	32	0.51 U	78	36	25,000	49 J-
32	LV-SE-35-XX	Reference Laboratory	1.3 UJ	31 J-	0.51 U	74 J-	35	24,000 J-	22 J-
32	LV-SE-50-XX	Reference Laboratory	2.5 U	29	1 U	74	34	24,000	24 J-
32	LV-SE-02-RI	Rigaku, Inc.	182	25	601	71	29	15,603	-30
32	LV-SE-10-RI	Rigaku, Inc.	182	37	615	65	24	15,490	-29
32	LV-SE-22-RI	Rigaku, Inc.	189	32	622	76	28	15,618	-45
32	LV-SE-25-RI	Rigaku, Inc.	213	44	653	88	29	15,568	-39
32	LV-SE-31-RI	Rigaku, Inc.	201	31	624	60	22	15,786	-39
32	LV-SE-35-RI	Rigaku, Inc.	195	42	619	69	24	15,585	-36
32	LV-SE-50-RI	Rigaku, Inc.	177	28	591	60	31	15,658	-44
33	LV-SE-12-XX	Reference Laboratory	2.6 U	190	1 U	55	34	72,000	19 J-
33	LV-SE-26-XX	Reference Laboratory	2.6 U	220	1 U	64	39	83,000	25 J-
33	LV-SE-33-XX	Reference Laboratory	2.6 U	170	1 U	52	31	66,000	21 J-
33	LV-SE-39-XX	Reference Laboratory	2.6 U	190	1 U	58	35	74,000	22 J-
33	LV-SE-42-XX	Reference Laboratory	2.7 U	170	1.1 U	50	30	65,000	22 J-
33	LV-SE-12-RI	Rigaku, Inc.	277	29	545	154	16	35,880	-88
33	LV-SE-26-RI	Rigaku, Inc.	302	47	544	96	15	35,793	-72
33	LV-SE-33-RI	Rigaku, Inc.	275	25	539	96	18	35,182	-83
33	LV-SE-39-RI	Rigaku, Inc.	303	33	529	101	14	35,840	-78
33	LV-SE-42-RI	Rigaku, Inc.	238	42	499	125	15	36,267	-81

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
31	TL-SE-01-XX	Reference Laboratory	0.07 U	180	1.2 U	5.7 J-	75	130
31	TL-SE-11-XX	Reference Laboratory	0.02 U	210	1.2 U	5.5 J-	85	140
31	TL-SE-14-XX	Reference Laboratory	0.08 U	180	1.2 U	5.7 J-	73	140
31	TL-SE-18-XX	Reference Laboratory	0.03 U	190	1.2 U	6.3 J-	70	120
31	TL-SE-22-XX	Reference Laboratory	0.08 U	210	1.2 U	6.5 J-	80	150
31	TL-SE-27-XX	Reference Laboratory	0.02 U	200	1.2 U	7.8 J-	67	140
31	TL-SE-29-XX	Reference Laboratory	0.08 U	200	1.2 U	5.9 J-	80	140
31	TL-SE-01-RI	Rigaku, Inc.	10	94	2	184	116	72
31	TL-SE-11-RI	Rigaku, Inc.	16	99	1	190	119	70
31	TL-SE-14-RI	Rigaku, Inc.	14	103	2	186	127	72
31	TL-SE-18-RI	Rigaku, Inc.	5	94	2	188	123	67
31	TL-SE-22-RI	Rigaku, Inc.	27	103	2	189	117	72
31	TL-SE-27-RI	Rigaku, Inc.	8	98	4	191	131	67
31	TL-SE-29-RI	Rigaku, Inc.	27	98	1	185	123	74
32	LV-SE-02-XX	Reference Laboratory	0.02 U	160	3.8	1.3 UJ	53	65
32	LV-SE-10-XX	Reference Laboratory	0.02 U	200	4.7	1.3 UJ	66	77
32	LV-SE-22-XX	Reference Laboratory	1.1	170	5.2	1.3 UJ	51	66
32	LV-SE-25-XX	Reference Laboratory	1	170	5.1	1.3 UJ	56	70
32	LV-SE-31-XX	Reference Laboratory	1	180	5.1	1.3 UJ	58	70
32	LV-SE-35-XX	Reference Laboratory	1.4	170 J-	5	1.3 UJ	55 J-	67 J-
32	LV-SE-50-XX	Reference Laboratory	1.2	170	3.3	2.5 U	57	65
32	LV-SE-02-RI	Rigaku, Inc.	34	75	7	216	82	51
32	LV-SE-10-RI	Rigaku, Inc.	31	75	6	213	83	55
32	LV-SE-22-RI	Rigaku, Inc.	32	75	8	218	87	53
32	LV-SE-25-RI	Rigaku, Inc.	31	74	7	225	87	79
32	LV-SE-31-RI	Rigaku, Inc.	35	74	5	209	84	53
32	LV-SE-35-RI	Rigaku, Inc.	28	73	9	216	80	63
32	LV-SE-50-RI	Rigaku, Inc.	30	79	8	209	92	49
33	LV-SE-12-XX	Reference Laboratory	5.6	71	3	2.6 U	72	66
33	LV-SE-26-XX	Reference Laboratory	6	83	6.1	2.6 U	86	75
33	LV-SE-33-XX	Reference Laboratory	6.8	66	2.8	2.6 U	67	59
33	LV-SE-39-XX	Reference Laboratory	8	74	5.1	2.6 U	74	66
33	LV-SE-42-XX	Reference Laboratory	4.3	67	3.4	2.7 U	64	57
33	LV-SE-12-RI	Rigaku, Inc.	5	41	2	182	88	44
33	LV-SE-26-RI	Rigaku, Inc.	3	39	1	188	104	42
33	LV-SE-33-RI	Rigaku, Inc.	6	38	0	192	103	49
33	LV-SE-39-RI	Rigaku, Inc.	2	44	2	184	92	42
33	LV-SE-42-RI	Rigaku, Inc.	3	33	2	166	93	42

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
34	LV-SE-09-XX	Reference Laboratory	6.7 U	450	2.7 U	48	34	150,000	14 J-
34	LV-SE-19-XX	Reference Laboratory	6.7 U	500	2.7 U	55	37	160,000	17 J-
34	LV-SE-27-XX	Reference Laboratory	6.7 U	530	2.7 U	56	39	180,000	16 J-
34	LV-SE-36-XX	Reference Laboratory	6.7 U	550	2.7 U	60	40	180,000	21 J-
34	LV-SE-38-XX	Reference Laboratory	6.7 U	480	2.7 U	52	36	160,000	15 J-
34	LV-SE-09-RI	Rigaku, Inc.	169	63	392	173	6	66,112	-122
34	LV-SE-19-RI	Rigaku, Inc.	177	31	383	176	7	66,611	-122
34	LV-SE-27-RI	Rigaku, Inc.	255	37	400	169	2	65,189	-130
34	LV-SE-36-RI	Rigaku, Inc.	204	60	375	207	4	66,642	-118
34	LV-SE-38-RI	Rigaku, Inc.	-30	-59	274	55	-15	41,849	-172
35	LV-SE-07-XX	Reference Laboratory	6.7 UJ	780	2.7 U	57	48	200,000	11
35	LV-SE-18-XX	Reference Laboratory	6.7 UJ	800	2.7 U	61	49	210,000	11
35	LV-SE-23-XX	Reference Laboratory	6.6 UJ	660	2.6 U	53	40	170,000	8
35	LV-SE-45-XX	Reference Laboratory	6.7 UJ	650	2.7 U	50	40	170,000	8
35	LV-SE-48-XX	Reference Laboratory	6.6 UJ	680	2.6 U	52	42	180,000	9
35	LV-SE-07-RI	Rigaku, Inc.	191	73	332	217	0	85,976	-147
35	LV-SE-18-RI	Rigaku, Inc.	144	91	336	200	1	84,794	-138
35	LV-SE-23-RI	Rigaku, Inc.	147	87	328	234	1	86,198	-150
35	LV-SE-45-RI	Rigaku, Inc.	242	65	349	226	4	85,141	-143
35	LV-SE-48-RI	Rigaku, Inc.	117	96	312	210	-1	86,120	-142
36	LV-SE-01-XX	Reference Laboratory	1.5 UJ	6	0.76	4	18	1,100	17
36	LV-SE-14-XX	Reference Laboratory	1.5 UJ	5	0.74	4	16	980	14
36	LV-SE-21-XX	Reference Laboratory	1.5 UJ	7	0.84	4	19	970	18
36	LV-SE-24-XX	Reference Laboratory	1.5 UJ	5	0.68	4	15	840	14
36	LV-SE-32-XX	Reference Laboratory	1.4 UJ	6	0.87	4	16	860	14
36	LV-SE-01-RI	Rigaku, Inc.	44	-15	473	-74	6	3,040	-80
36	LV-SE-14-RI	Rigaku, Inc.	38	1	481	-45	1	3,040	-80
36	LV-SE-21-RI	Rigaku, Inc.	43	-20	487	-52	-1	3,057	-82
36	LV-SE-24-RI	Rigaku, Inc.	42	-36	477	-61	-2	3,067	-83
36	LV-SE-32-RI	Rigaku, Inc.	42	-30	479	-61	1	3,055	-82

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
34	LV-SE-09-XX	Reference Laboratory	6	55	6.7 U	6.7 U	100	51 J
34	LV-SE-19-XX	Reference Laboratory	7.2	65	5.9 J	6.7 U	110	55 J
34	LV-SE-27-XX	Reference Laboratory	11	64	6.7 U	6.7 U	120	58 J
34	LV-SE-36-XX	Reference Laboratory	8.5	70	11	6.7 U	120	60 J
34	LV-SE-38-XX	Reference Laboratory	7.9	75	6.7 U	6.7 U	100	54 J
34	LV-SE-09-RI	Rigaku, Inc.	-23	25	-5	133	117	27
34	LV-SE-19-RI	Rigaku, Inc.	-16	26	-5	138	112	22
34	LV-SE-27-RI	Rigaku, Inc.	-18	19	-4	137	117	33
34	LV-SE-36-RI	Rigaku, Inc.	-20	20	-5	132	117	30
34	LV-SE-38-RI	Rigaku, Inc.	-56	13	-13	96	70	9
35	LV-SE-07-XX	Reference Laboratory	5.5	58	10	6.7 U	130	24 J
35	LV-SE-18-XX	Reference Laboratory	5.4	60	12	6.7 U	140	52 J
35	LV-SE-23-XX	Reference Laboratory	5	50 J	9.6	6.6 U	120	18 J
35	LV-SE-45-XX	Reference Laboratory	5.6	50 J	8.2	6.7 U	120	19 J
35	LV-SE-48-XX	Reference Laboratory	7.3	50 J	7.6	6.6 U	120	30 J
35	LV-SE-07-RI	Rigaku, Inc.	-29	18	-5	128	139	18
35	LV-SE-18-RI	Rigaku, Inc.	-31	19	-7	120	138	15
35	LV-SE-23-RI	Rigaku, Inc.	-32	18	-6	125	148	12
35	LV-SE-45-RI	Rigaku, Inc.	-27	19	-6	128	138	15
35	LV-SE-48-RI	Rigaku, Inc.	-35	16	-7	122	139	10
36	LV-SE-01-XX	Reference Laboratory	0.1 U	49	1.5 U	1.5 U	2 J	14 J
36	LV-SE-14-XX	Reference Laboratory	0.06 U	46	1.5 U	1.5 U	1 J	12 J
36	LV-SE-21-XX	Reference Laboratory	0.05 U	49	1.5 U	1.5 U	2 J	14 J
36	LV-SE-24-XX	Reference Laboratory	0.05 U	44	1.5 U	1.5 U	1 J	12 J
36	LV-SE-32-XX	Reference Laboratory	0.05 U	47	1.4 U	1.4 U	1 J	19
36	LV-SE-01-RI	Rigaku, Inc.	-3	26	-1	165	3	14
36	LV-SE-14-RI	Rigaku, Inc.	-6	25	1	164	11	8
36	LV-SE-21-RI	Rigaku, Inc.	-1	28	0	171	13	11
36	LV-SE-24-RI	Rigaku, Inc.	2	27	1	170	5	12
36	LV-SE-32-RI	Rigaku, Inc.	1	28	0	169	10	8

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
37	LV-SE-08-XX	Reference Laboratory	1.3 UJ	30	0.52 U	54	23	23,000	55
37	LV-SE-16-XX	Reference Laboratory	1.3 UJ	29	0.52 U	53	22	22,000	53
37	LV-SE-28-XX	Reference Laboratory	1.3 UJ	31	0.52 U	59	25	25,000	59
37	LV-SE-30-XX	Reference Laboratory	1.3 UJ	30	0.52 U	58	25	24,000	58
37	LV-SE-47-XX	Reference Laboratory	1.3 UJ	31	0.52 U	56	23	23,000	57
37	LV-SE-08-RI	Rigaku, Inc.	184	46	595	42	23	16,577	6
37	LV-SE-16-RI	Rigaku, Inc.	185	36	628	112	19	16,504	-13
37	LV-SE-28-RI	Rigaku, Inc.	211	4	651	64	25	16,469	-7
37	LV-SE-30-RI	Rigaku, Inc.	180	34	607	76	23	16,750	-6
37	LV-SE-47-RI	Rigaku, Inc.	165	34	576	33	25	16,509	-12
38	LV-SE-11-XX	Reference Laboratory	1.4 UJ	150	6.6	120	270	42,000	7
38	LV-SE-29-XX	Reference Laboratory	1.4 UJ	150	6.3	120	260	42,000	7 J+
38	LV-SE-44-XX	Reference Laboratory	1.4 U	140	6.1	120	250	40,000	8
38	LV-SE-46-XX	Reference Laboratory	0.88 U	110	5	92	200	32,000	6
38	LV-SE-52-XX	Reference Laboratory	1.4 U	160	6.8	130	280	44,000	8
38	LV-SE-11-RI	Rigaku, Inc.	193	55	551	79	144	22,687	-68
38	LV-SE-29-RI	Rigaku, Inc.	230	71	582	146	154	22,583	-70
38	LV-SE-44-RI	Rigaku, Inc.	201	40	556	118	143	22,794	-75
38	LV-SE-46-RI	Rigaku, Inc.	179	49	549	108	137	22,493	-68
38	LV-SE-52-RI	Rigaku, Inc.	220	81	573	129	140	22,459	-68
39	RF-SE-07-XX	Reference Laboratory	1.3 U	12	0.5 U	92	81	17,000	24
39	RF-SE-12-XX	Reference Laboratory	1.2 U	14	0.5 U	100	110	20,000	25
39	RF-SE-23-XX	Reference Laboratory	0.25 U	0 U	0.1 U	0 U	0.2 U	4 J	0 U
39	RF-SE-36-XX	Reference Laboratory	1.2 U	12	0.5 U	91	82	17,000	22
39	RF-SE-42-XX	Reference Laboratory	1.3 UJ	14	0.56	110	95	19,000	28
39	RF-SE-45-XX	Reference Laboratory	1.3 UJ	15	0.52 U	110	100	21,000	33
39	RF-SE-53-XX	Reference Laboratory	1.3 UJ	14	0.57 U	110	95	19,000	28
39	RF-SE-07-RI	Rigaku, Inc.	202	28	666	79	68	13,796	-38
39	RF-SE-12-RI	Rigaku, Inc.	202	15	627	106	75	14,275	-26
39	RF-SE-23-RI	Rigaku, Inc.	216	11	641	71	69	13,770	-26
39	RF-SE-36-RI	Rigaku, Inc.	191	33	648	77	60	13,504	-21
39	RF-SE-42-RI	Rigaku, Inc.	193	24	651	91	66	13,628	-24
39	RF-SE-45-RI	Rigaku, Inc.	222	-2	632	64	68	13,658	-29
39	RF-SE-53-RI	Rigaku, Inc.	228	-23	651	81	69	13,779	-37

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
37	LV-SE-08-XX	Reference Laboratory	5.2	110	4.8	1.3 U	44	61
37	LV-SE-16-XX	Reference Laboratory	5.4	110	5	1.3 U	42	59
37	LV-SE-28-XX	Reference Laboratory	5.4	120	5.8	1.3 U	48	65
37	LV-SE-30-XX	Reference Laboratory	6.3	120	5.6	1.3 U	48	66
37	LV-SE-47-XX	Reference Laboratory	4.9	120	4.2	1.3 U	45	65
37	LV-SE-08-RI	Rigaku, Inc.	31	70	9	206	85	64
37	LV-SE-16-RI	Rigaku, Inc.	36	72	8	217	89	53
37	LV-SE-28-RI	Rigaku, Inc.	37	68	9	215	86	55
37	LV-SE-30-RI	Rigaku, Inc.	24	74	9	208	87	60
37	LV-SE-47-RI	Rigaku, Inc.	34	69	7	201	86	54
38	LV-SE-11-XX	Reference Laboratory	2.8	870	1.3 U	1.4 U	35	200
38	LV-SE-29-XX	Reference Laboratory	1.5 J-	860	1.2 U	1.4 U	35	200
38	LV-SE-44-XX	Reference Laboratory	1.5	830	1.4 U	1.4 U	34	190
38	LV-SE-46-XX	Reference Laboratory	1.4	660	0.88 U	0.88 U	27	150
38	LV-SE-52-XX	Reference Laboratory	21	910	1.4 U	1.4 U	38	210
38	LV-SE-11-RI	Rigaku, Inc.	15	347	3	192	50	104
38	LV-SE-29-RI	Rigaku, Inc.	2	353	2	195	42	106
38	LV-SE-44-RI	Rigaku, Inc.	12	363	1	190	42	104
38	LV-SE-46-RI	Rigaku, Inc.	9	357	3	188	43	110
38	LV-SE-52-RI	Rigaku, Inc.	9	353	4	198	45	107
39	RF-SE-07-XX	Reference Laboratory	0.09 U	180	1.3 U	1.3 U	34	130
39	RF-SE-12-XX	Reference Laboratory	0.1 U	210	1.2 U	1.2 U	38	140
39	RF-SE-23-XX	Reference Laboratory	2.4	2 U	0.25 U	0.37	3 U	1 U
39	RF-SE-36-XX	Reference Laboratory	0.08 U	180	1 U	1.2 U	34	120
39	RF-SE-42-XX	Reference Laboratory	0.08 U	210	1.3 U	1.3 U	40	140
39	RF-SE-45-XX	Reference Laboratory	0.08 U	220	1.3 U	1.3 U	43	150
39	RF-SE-53-XX	Reference Laboratory	0.08 U	210	1.3 U	1.3 U	40	140
39	RF-SE-07-RI	Rigaku, Inc.	47	94	8	230	59	95
39	RF-SE-12-RI	Rigaku, Inc.	47	102	8	218	59	96
39	RF-SE-23-RI	Rigaku, Inc.	52	97	13	206	52	88
39	RF-SE-36-RI	Rigaku, Inc.	39	99	7	226	59	88
39	RF-SE-42-RI	Rigaku, Inc.	36	99	8	220	55	88
39	RF-SE-45-RI	Rigaku, Inc.	53	96	11	212	46	92
39	RF-SE-53-RI	Rigaku, Inc.	66	103	12	210	56	86

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
40	RF-SE-03-XX	Reference Laboratory	1.2 UJ	27	1.3	93	200	17,000	88
40	RF-SE-28-XX	Reference Laboratory	1.2 UJ	31	1.5	100	220	18,000	99
40	RF-SE-38-XX	Reference Laboratory	1.2 UJ	27	1.2	90	190	16,000	83
40	RF-SE-49-XX	Reference Laboratory	1.2 UJ	31	1.5	100	220	18,000	97
40	RF-SE-55-XX	Reference Laboratory	1.2 UJ	24	1.1	91	180	15,000	75
40	RF-SE-03-RI	Rigaku, Inc.	200	60	661	117	152	13,154	13
40	RF-SE-28-RI	Rigaku, Inc.	236	36	669	97	157	13,234	11
40	RF-SE-38-RI	Rigaku, Inc.	210	44	655	81	154	13,164	6
40	RF-SE-49-RI	Rigaku, Inc.	240	5	669	71	151	13,062	9
40	RF-SE-55-RI	Rigaku, Inc.	231	44	677	113	160	13,209	13
41	RF-SE-06-XX	Reference Laboratory	1.3 UJ	70	3.6	90	490	20,000	230
41	RF-SE-13-XX	Reference Laboratory	1.3 UJ	76	3.7	92	530	21,000	230
41	RF-SE-27-XX	Reference Laboratory	1.3 UJ	64	3.1	78	440	18,000	200
41	RF-SE-31-XX	Reference Laboratory	1.3 UJ	39	1.8	63	250	12,000	120
41	RF-SE-58-XX	Reference Laboratory	1.3 UJ	71	3.6	89	500	21,000	230
41	RF-SE-06-RI	Rigaku, Inc.	208	57	648	89	341	13,637	74
41	RF-SE-13-RI	Rigaku, Inc.	232	42	654	65	329	13,248	82
41	RF-SE-27-RI	Rigaku, Inc.	220	70	640	54	340	13,557	79
41	RF-SE-31-RI	Rigaku, Inc.	225	62	659	94	347	13,482	75
41	RF-SE-58-RI	Rigaku, Inc.	222	58	644	94	329	13,362	69
42	RF-SE-02-XX	Reference Laboratory	1.3 UJ	110	5.4	93	740	24,000	330
42	RF-SE-22-XX	Reference Laboratory	1.3 UJ	99	4.7	84	670	22,000	300
42	RF-SE-25-XX	Reference Laboratory	1.3 UJ	88	4	78	580	19,000	270
42	RF-SE-30-XX	Reference Laboratory	1.3 UJ	89	4.3	78	610	21,000	290
42	RF-SE-57-XX	Reference Laboratory	1.3 UJ	89	4.5	79	610	21,000	300
42	RF-SE-02-RI	Rigaku, Inc.	208	73	623	81	435	13,697	119
42	RF-SE-22-RI	Rigaku, Inc.	214	72	619	91	439	13,627	103
42	RF-SE-25-RI	Rigaku, Inc.	221	64	653	109	425	13,476	110
42	RF-SE-30-RI	Rigaku, Inc.	224	66	637	102	420	13,501	110
42	RF-SE-57-RI	Rigaku, Inc.	217	56	620	69	426	13,633	114

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
40	RF-SE-03-XX	Reference Laboratory	0.48	150	1.2 U	1.2 U	40	300
40	RF-SE-28-XX	Reference Laboratory	0.57	160	1.2 U	1.2 U	44	320
40	RF-SE-38-XX	Reference Laboratory	0.41	140	1.2 U	1.2 U	39	300
40	RF-SE-49-XX	Reference Laboratory	0.43	170	1.2 U	1.2 U	43	330
40	RF-SE-55-XX	Reference Laboratory	0.42	140	1.2 U	1.2 U	35	280
40	RF-SE-03-RI	Rigaku, Inc.	36	89	7	227	56	190
40	RF-SE-28-RI	Rigaku, Inc.	33	83	12	217	59	191
40	RF-SE-38-RI	Rigaku, Inc.	33	89	8	228	62	193
40	RF-SE-49-RI	Rigaku, Inc.	51	85	12	218	59	182
40	RF-SE-55-RI	Rigaku, Inc.	38	82	9	239	60	187
41	RF-SE-06-XX	Reference Laboratory	1.1	150	1.3 U	1.3 U	44	740
41	RF-SE-13-XX	Reference Laboratory	1.2	160	1.3 U	1.3	45	790
41	RF-SE-27-XX	Reference Laboratory	1.2	130	1.3 U	1.3 U	39	670
41	RF-SE-31-XX	Reference Laboratory	1.1	86	1.3 U	1.3 U	28	420
41	RF-SE-58-XX	Reference Laboratory	1.2	150	1.3 U	1.3 U	46	770
41	RF-SE-06-RI	Rigaku, Inc.	33	81	9	220	64	405
41	RF-SE-13-RI	Rigaku, Inc.	36	83	13	216	61	383
41	RF-SE-27-RI	Rigaku, Inc.	30	80	11	209	55	417
41	RF-SE-31-RI	Rigaku, Inc.	39	78	6	230	58	399
41	RF-SE-58-RI	Rigaku, Inc.	38	86	7	227	52	385
42	RF-SE-02-XX	Reference Laboratory	1.6	180	1.3 U	2.7	50	1,100
42	RF-SE-22-XX	Reference Laboratory	1.7	160	1.3 U	2.3	44	990
42	RF-SE-25-XX	Reference Laboratory	1.5	140	1.5	1.7	40	890
42	RF-SE-30-XX	Reference Laboratory	1.5	150	1.3 U	1.9	44	960
42	RF-SE-57-XX	Reference Laboratory	1.5	150	2	2.2	44	1,000
42	RF-SE-02-RI	Rigaku, Inc.	39	82	7	220	54	504
42	RF-SE-22-RI	Rigaku, Inc.	31	88	13	206	61	494
42	RF-SE-25-RI	Rigaku, Inc.	29	83	13	213	58	482
42	RF-SE-30-RI	Rigaku, Inc.	27	84	13	212	49	468
42	RF-SE-57-RI	Rigaku, Inc.	34	82	7	216	58	482

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
43	RF-SE-15-XX	Reference Laboratory	1.3 UJ	120	6.2	72	820	23,000	390
43	RF-SE-24-XX	Reference Laboratory	1.3 UJ	130 J+	6.5 J+	74 J+	860 J+	24,000 J+	410 J+
43	RF-SE-32-XX	Reference Laboratory	1.3 UJ	120	5.1	64	770	20,000	330
43	RF-SE-43-XX	Reference Laboratory	1.3 UJ	130	5.7	68	840	22,000	350
43	RF-SE-59-XX	Reference Laboratory	1.3 UJ	140	5.9	73	890	23,000	380
43	RF-SE-15-RI	Rigaku, Inc.	209	95	598	142	566	14,112	160
43	RF-SE-24-RI	Rigaku, Inc.	209	80	608	99	579	14,375	163
43	RF-SE-32-RI	Rigaku, Inc.	218	76	624	48	582	14,256	161
43	RF-SE-43-RI	Rigaku, Inc.	228	80	653	48	555	14,218	166
43	RF-SE-59-RI	Rigaku, Inc.	229	84	617	74	552	14,169	166
44	RF-SE-05-XX	Reference Laboratory	4.1 J+	160	9.1	69	1,000	26,000	450
44	RF-SE-26-XX	Reference Laboratory	2.2 J+	140	8.4	64	990	23,000	440
44	RF-SE-39-XX	Reference Laboratory	2.9 J+	160	9.3	73	1,100	26,000	490
44	RF-SE-44-XX	Reference Laboratory	2.7 J+	140	8.2	64	970	24,000	420
44	RF-SE-56-XX	Reference Laboratory	3.5 J+	180	9.6	75	1200	27,000	490
44	RF-SE-05-RI	Rigaku, Inc.	260	95	638	83	716	14,924	187
44	RF-SE-26-RI	Rigaku, Inc.	229	114	657	86	693	14,916	193
44	RF-SE-39-RI	Rigaku, Inc.	243	86	617	50	693	14,579	174
44	RF-SE-44-RI	Rigaku, Inc.	211	112	610	129	701	14,778	176
44	RF-SE-56-RI	Rigaku, Inc.	273	84	658	94	697	14,768	183
45	RF-SE-04-XX	Reference Laboratory	3.2 J+	230	12	42	1,500	27,000	730
45	RF-SE-14-XX	Reference Laboratory	4.4 J+	260	12	47	1,700	30,000	800
45	RF-SE-19-XX	Reference Laboratory	3.7 J+	250	13	48	1,700	30,000	800
45	RF-SE-34-XX	Reference Laboratory	2.9 J+	210	10	39	1,400	24,000	660
45	RF-SE-52-XX	Reference Laboratory	3.4 J+	220	11	42	1,500	26,000	720
45	RF-SE-04-RI	Rigaku, Inc.	252	119	611	65	947	15,229	327
45	RF-SE-14-RI	Rigaku, Inc.	207	160	604	64	956	15,099	331
45	RF-SE-19-RI	Rigaku, Inc.	212	154	591	91	946	15,270	326
45	RF-SE-34-RI	Rigaku, Inc.	274	127	627	23	933	15,283	310
45	RF-SE-52-RI	Rigaku, Inc.	220	148	600	109	952	15,259	316

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
43	RF-SE-15-XX	Reference Laboratory	2.6	160	1.4	3.6	45	1,300
43	RF-SE-24-XX	Reference Laboratory	2.3	170 J+	1.3 U	3.8 J+	46 J+	1,400 J-
43	RF-SE-32-XX	Reference Laboratory	2.8	140	1.3 U	4.2	36	1,100
43	RF-SE-43-XX	Reference Laboratory	2.7	150	1.3 U	4	40	1,200
43	RF-SE-59-XX	Reference Laboratory	0.09 U	160	1.3 U	4.5	42	1,300
43	RF-SE-15-RI	Rigaku, Inc.	22	90	12	202	64	637
43	RF-SE-24-RI	Rigaku, Inc.	21	96	11	202	68	665
43	RF-SE-32-RI	Rigaku, Inc.	27	85	6	209	58	649
43	RF-SE-43-RI	Rigaku, Inc.	14	89	12	208	64	639
43	RF-SE-59-RI	Rigaku, Inc.	39	84	8	213	62	627
44	RF-SE-05-XX	Reference Laboratory	2.6	150	3.1	7.4 J-	48	1,800
44	RF-SE-26-XX	Reference Laboratory	2.5	140	2.8	7.2 J-	42	1,700
44	RF-SE-39-XX	Reference Laboratory	2.2	150	2.6	8.2 J-	49	1,900
44	RF-SE-44-XX	Reference Laboratory	2.3	140	2.4	7.2 J-	44	1,600
44	RF-SE-56-XX	Reference Laboratory	2.2	160	1.8	8.3 J-	51	1,900
44	RF-SE-05-RI	Rigaku, Inc.	32	80	7	223	61	833
44	RF-SE-26-RI	Rigaku, Inc.	15	76	12	211	64	837
44	RF-SE-39-RI	Rigaku, Inc.	25	76	7	220	57	802
44	RF-SE-44-RI	Rigaku, Inc.	18	77	11	207	62	796
44	RF-SE-56-RI	Rigaku, Inc.	35	73	7	220	67	809
45	RF-SE-04-XX	Reference Laboratory	4.2	130	2.8	12 J-	46	2,400
45	RF-SE-14-XX	Reference Laboratory	4.7	140	3	13 J-	51	2,600
45	RF-SE-19-XX	Reference Laboratory	3.9	140	4.1	14 J-	52	2,700
45	RF-SE-34-XX	Reference Laboratory	4.5	120	1.9	10 J-	42	2,200
45	RF-SE-52-XX	Reference Laboratory	4.1	130	2	11 J-	47	2,300
45	RF-SE-04-RI	Rigaku, Inc.	37	76	6	207	55	1,083
45	RF-SE-14-RI	Rigaku, Inc.	3	75	12	204	52	1,066
45	RF-SE-19-RI	Rigaku, Inc.	-3	88	12	202	66	1,080
45	RF-SE-34-RI	Rigaku, Inc.	26	81	6	218	56	1,030
45	RF-SE-52-RI	Rigaku, Inc.	8	77	12	206	66	1,078

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
46	BN-SO-11-XX	Reference Laboratory	4 J-	2,900	720	820	120	23,000	56
46	BN-SO-14-XX	Reference Laboratory	3.5 J-	2,800	690	800	120	22,000	51
46	BN-SO-23-XX	Reference Laboratory	1.2 UJ	2,800	700	800	120	23,000	52
46	BN-SO-11-RI	Rigaku, Inc.	176	1,404	899	408	93	13,667	-30
46	BN-SO-14-RI	Rigaku, Inc.	168	1,371	880	442	88	13,694	-22
46	BN-SO-23-RI	Rigaku, Inc.	152	1,306	837	376	86	13,626	-34
47	BN-SO-09-XX	Reference Laboratory	750 J-	97	2,700	2,900	100	22,000	4,700
47	BN-SO-12-XX	Reference Laboratory	750 J-	89	2,600	2,800	96	21,000	4,500
47	BN-SO-24-XX	Reference Laboratory	810 J-	97	2,900	3,000	100	23,000	4,900
47	BN-SO-09-RI	Rigaku, Inc.	763	63	1,506	1,080	69	12,828	2,130
47	BN-SO-12-RI	Rigaku, Inc.	769	89	1,534	1,034	74	12,772	2,208
47	BN-SO-24-RI	Rigaku, Inc.	699	89	1,516	1,089	70	12,869	2,186
48	SB-SO-09-XX	Reference Laboratory	1.3 UJ	9	0.51 U	130	120	35,000	19
48	SB-SO-20-XX	Reference Laboratory	1.3 UJ	11	0.51 U	170	150	44,000	24
48	SB-SO-31-XX	Reference Laboratory	1.3 UJ	8 J-	0.51 U	140	130	38,000	21
48	SB-SO-09-RI	Rigaku, Inc.	169	0	563	137	78	19,548	-61
48	SB-SO-20-RI	Rigaku, Inc.	231	23	686	130	27	18,103	-49
48	SB-SO-31-RI	Rigaku, Inc.	202	7	601	147	87	19,821	-57
49	SB-SO-29-XX	Reference Laboratory	1.2 U	9	0.5 U	140	130	41,000	19
49	SB-SO-36-XX	Reference Laboratory	1.2 U	8	0.5 U	120	100	33,000	15
49	SB-SO-56-XX	Reference Laboratory	1.2 U	10	0.5 U	150	140	42,000	20
49	SB-SO-29-RI	Rigaku, Inc.	223	0	606	159	75	19,982	-53
49	SB-SO-36-RI	Rigaku, Inc.	215	10	589	142	81	20,196	-52
49	SB-SO-56-RI	Rigaku, Inc.	207	3	596	117	76	20,017	-59
50	SB-SO-04-XX	Reference Laboratory	940	13	2,800	2,800	100	38,000	21
50	SB-SO-34-XX	Reference Laboratory	980	12	2,500	2,500	91	34,000	18
50	SB-SO-49-XX	Reference Laboratory	700	12	2,500	2,400	89	33,000	18
50	SB-SO-04-RI	Rigaku, Inc.	323	18	1,717	1,224	70	18,689	-43
50	SB-SO-34-RI	Rigaku, Inc.	321	31	1,676	1,253	68	18,682	-38
50	SB-SO-49-RI	Rigaku, Inc.	302	8	1,688	1,288	68	18,764	-42

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
46	BN-SO-11-XX	Reference Laboratory	24 J-	2,900	140	140 J-	150	3,900
46	BN-SO-14-XX	Reference Laboratory	26	2,800	130	140 J-	150	3,800
46	BN-SO-23-XX	Reference Laboratory	31	2,800	130	130 J-	150	3,800
46	BN-SO-11-RI	Rigaku, Inc.	40	1,353	44	225	113	2,044
46	BN-SO-14-RI	Rigaku, Inc.	45	1,339	44	215	124	2,080
46	BN-SO-23-RI	Rigaku, Inc.	37	1,315	41	209	111	1,981
47	BN-SO-09-XX	Reference Laboratory	0.39	1,500	290	100 J-	340	81
47	BN-SO-12-XX	Reference Laboratory	0.34	1,400	290	210 J-	310	74
47	BN-SO-24-XX	Reference Laboratory	0.37	1,600	300	140 J-	350	81
47	BN-SO-09-RI	Rigaku, Inc.	17	639	87	214	199	59
47	BN-SO-12-RI	Rigaku, Inc.	23	641	83	215	185	63
47	BN-SO-24-RI	Rigaku, Inc.	19	625	84	224	183	58
48	SB-SO-09-XX	Reference Laboratory	30	2900	26	160 J-	120	3,600
48	SB-SO-20-XX	Reference Laboratory	10	3700	30	140 J-	160	4,500
48	SB-SO-31-XX	Reference Laboratory	32	3200 J-	28 J-	160 J-	140	3,900 J-
48	SB-SO-09-RI	Rigaku, Inc.	24	1,331	11	224	147	1,850
48	SB-SO-20-RI	Rigaku, Inc.	346	94	4	233	121	59
48	SB-SO-31-RI	Rigaku, Inc.	32	1,348	13	221	148	1,871
49	SB-SO-29-XX	Reference Laboratory	7.9 J	200	160	1.2 UJ	400	3,900
49	SB-SO-36-XX	Reference Laboratory	36	160	130	1.2 UJ	320	3,200
49	SB-SO-56-XX	Reference Laboratory	9	210	160	1.2 UJ	410	4,100
49	SB-SO-29-RI	Rigaku, Inc.	39	104	46	216	246	1,952
49	SB-SO-36-RI	Rigaku, Inc.	36	106	44	207	248	1,958
49	SB-SO-56-RI	Rigaku, Inc.	37	103	47	206	272	1,935
50	SB-SO-04-XX	Reference Laboratory	40	3,300	390	1.3 UJ	58	86
50	SB-SO-34-XX	Reference Laboratory	36	3,000	360	1.3 UJ	52	77
50	SB-SO-49-XX	Reference Laboratory	36	2,800	330	1.2 UJ	52	72
50	SB-SO-04-RI	Rigaku, Inc.	41	1,363	103	219	97	58
50	SB-SO-34-RI	Rigaku, Inc.	37	1,359	104	219	88	53
50	SB-SO-49-RI	Rigaku, Inc.	40	1,350	105	205	119	51

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
51	WS-SO-07-XX	Reference Laboratory	3.8	53	1.9	640	4,400	25,000	1,700
51	WS-SO-11-XX	Reference Laboratory	1.2 U	46	1.4	570	3,900	19,000	1,500
51	WS-SO-25-XX	Reference Laboratory	1.2 U	59	3.1	730	4,900	24,000	1,900
51	WS-SO-07-RI	Rigaku, Inc.	299	54	575	357	3,374	15,153	1,017
51	WS-SO-11-RI	Rigaku, Inc.	251	57	564	391	3,324	15,055	1,011
51	WS-SO-25-RI	Rigaku, Inc.	308	54	579	347	3,364	15,226	984
52	WS-SO-10-XX	Reference Laboratory	1.3 U	83	1.8	67	76	19,000	1,900
52	WS-SO-20-XX	Reference Laboratory	1.3 U	100	1.9	81	90	23,000	2,300
52	WS-SO-23-XX	Reference Laboratory	1.3 U	110	2.1	82	96	23,000	2,500
52	WS-SO-10-RI	Rigaku, Inc.	339	80	571	89	86	15,292	1,369
52	WS-SO-20-RI	Rigaku, Inc.	340	93	568	86	70	15,252	1,375
52	WS-SO-23-RI	Rigaku, Inc.	317	118	562	134	77	15,199	1,426
53	AS-SO-03-XX	Reference Laboratory	1.2 U	14	1,300	33	6,200	15,000	160
53	AS-SO-05-XX	Reference Laboratory	1.2 U	9	900	23	4,500	11,000	110
53	AS-SO-08-XX	Reference Laboratory	1.2 U	10	930	24	4,600	11,000	120
53	AS-SO-03-RI	Rigaku, Inc.	160	38	1,091	62	3,421	10,202	41
53	AS-SO-05-RI	Rigaku, Inc.	157	21	1,130	76	3,439	10,199	52
53	AS-SO-08-RI	Rigaku, Inc.	154	8	1,085	47	3,447	10,116	30
54	LV-SO-03-XX	Reference Laboratory	1.6	42	590	600	130	24,000	94
54	LV-SO-40-XX	Reference Laboratory	2.7	42	580	590	130	24,000	92
54	LV-SO-49-XX	Reference Laboratory	7.4	43	600	610	130	25,000	98
54	LV-SO-03-RI	Rigaku, Inc.	199	39	808	318	92	18,230	14
54	LV-SO-40-RI	Rigaku, Inc.	191	36	810	308	96	18,375	-8
54	LV-SO-49-RI	Rigaku, Inc.	194	32	824	313	94	18,292	3
55	LV-SO-04-XX	Reference Laboratory	860	120	2,400	2,300	98	22,000	4,000
55	LV-SO-34-XX	Reference Laboratory	870 J-	110 J-	2,300 J-	2,200 J-	87	20,000 J-	3,700 J-
55	LV-SO-37-XX	Reference Laboratory	590	84	1,700	1,600	66	16,000	2,800
55	LV-SO-04-RI	Rigaku, Inc.	819	102	1,482	1,135	70	17,094	2,288
55	LV-SO-34-RI	Rigaku, Inc.	720	83	1,472	1,094	78	16,931	2,192
55	LV-SO-37-RI	Rigaku, Inc.	778	94	1,473	1,137	75	17,016	2,264

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
51	WS-SO-07-XX	Reference Laboratory	0.26	260	1.2 U	400 J-	48	180
51	WS-SO-11-XX	Reference Laboratory	0.27	240	1.2 U	340 J-	43	160
51	WS-SO-25-XX	Reference Laboratory	0.25	300	1.2 U	450 J-	54	200
51	WS-SO-07-RI	Rigaku, Inc.	19	173	5	216	83	135
51	WS-SO-11-RI	Rigaku, Inc.	28	170	6	208	68	134
51	WS-SO-25-RI	Rigaku, Inc.	16	165	7	219	71	136
52	WS-SO-10-XX	Reference Laboratory	0.06 U	290	280	1.3 UJ	260	1,900
52	WS-SO-20-XX	Reference Laboratory	0.06 U	350	340	1.3 UJ	320	2,300
52	WS-SO-23-XX	Reference Laboratory	0.05 U	380	360	1.3 UJ	330	2,500
52	WS-SO-10-RI	Rigaku, Inc.	29	198	108	200	214	1,421
52	WS-SO-20-RI	Rigaku, Inc.	29	205	104	191	212	1,418
52	WS-SO-23-RI	Rigaku, Inc.	27	207	108	195	212	1,452
53	AS-SO-03-XX	Reference Laboratory	3.7 J-	520	200	480 J-	29	350
53	AS-SO-05-XX	Reference Laboratory	2.5 J-	370	140	330 J-	23	250
53	AS-SO-08-XX	Reference Laboratory	2.5 J-	380	140	280 J-	23	260
53	AS-SO-03-RI	Rigaku, Inc.	29	226	55	239	65	183
53	AS-SO-05-RI	Rigaku, Inc.	34	233	55	248	55	186
53	AS-SO-08-RI	Rigaku, Inc.	33	221	55	237	54	182
54	LV-SO-03-XX	Reference Laboratory	48 J-	2,000	120	210 J-	120	3,700
54	LV-SO-40-XX	Reference Laboratory	46 J-	1,900	120	210 J-	120	3,700
54	LV-SO-49-XX	Reference Laboratory	52 J-	2,000	120	220 J-	120	3,800
54	LV-SO-03-RI	Rigaku, Inc.	49	991	39	214	136	2,161
54	LV-SO-40-RI	Rigaku, Inc.	50	1,007	39	209	145	2,133
54	LV-SO-49-RI	Rigaku, Inc.	52	989	41	212	149	2,120
55	LV-SO-04-XX	Reference Laboratory	130 J-	2,000	230	1.2 UJ	260	53
55	LV-SO-34-XX	Reference Laboratory	130 J-	1,900 J-	220 J-	1.2 UJ	230 J-	48 J-
55	LV-SO-37-XX	Reference Laboratory	130 J-	1,400	170	1.2 U	180	37
55	LV-SO-04-RI	Rigaku, Inc.	89	995	71	201	212	51
55	LV-SO-34-RI	Rigaku, Inc.	87	974	73	196	198	50
55	LV-SO-37-RI	Rigaku, Inc.	87	993	74	196	222	51

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
56	CN-SO-03-XX	Reference Laboratory	22	87	63	17	72	15,000	130
56	CN-SO-06-XX	Reference Laboratory	20	91	64	18	74	16,000	130
56	CN-SO-07-XX	Reference Laboratory	20	90	63	19	72	17,000	130
56	CN-SO-03-RI	Rigaku, Inc.	193	104	638	62	68	12,600	52
56	CN-SO-06-RI	Rigaku, Inc.	194	72	677	30	62	12,004	43
56	CN-SO-07-RI	Rigaku, Inc.	205	101	668	52	71	12,449	46
57	CN-SO-02-XX	Reference Laboratory	230	19	820	290	140	22,000	490
57	CN-SO-05-XX	Reference Laboratory	130	6	630	26	160	23,000	25
57	CN-SO-09-XX	Reference Laboratory	120	6	580	21	140	19,000	23
57	CN-SO-02-RI	Rigaku, Inc.	190	44	858	42	112	12,591	-19
57	CN-SO-05-RI	Rigaku, Inc.	169	46	825	13	112	12,750	-26
57	CN-SO-09-RI	Rigaku, Inc.	186	10	828	64	98	12,514	-29
58	LV-SE-06-XX	Reference Laboratory	30	23	160	540	30	18,000	1,600
58	LV-SE-13-XX	Reference Laboratory	31	24	160	540	30	18,000	1,600
58	LV-SE-41-XX	Reference Laboratory	30	21	150	480	26	16,000	1,500
58	LV-SE-06-RI	Rigaku, Inc.	310	-8	652	299	22	14,762	996
58	LV-SE-13-RI	Rigaku, Inc.	367	3	668	301	30	14,849	1,013
58	LV-SE-41-RI	Rigaku, Inc.	430	1	662	309	23	14,832	1,008
59	LV-SE-05-XX	Reference Laboratory	92	20	440	840	39	16,000	14
59	LV-SE-20-XX	Reference Laboratory	140 J+	31	680	1,400	60	22,000	21
59	LV-SE-43-XX	Reference Laboratory	160 J+	24	550	1,100	47	19,000	17
59	LV-SE-05-RI	Rigaku, Inc.	225	30	857	558	43	15,135	-18
59	LV-SE-20-RI	Rigaku, Inc.	205	36	836	475	32	15,081	-30
59	LV-SE-43-RI	Rigaku, Inc.	203	15	879	473	38	15,079	-22
60	LV-SE-15-XX	Reference Laboratory	290 J+	32	1,300	83	2,300	22,000	18
60	LV-SE-17-XX	Reference Laboratory	280 J+	31	1,300	79	2,200	21,000	17 J-
60	LV-SE-51-XX	Reference Laboratory	210 J+	26	1,100	72	2,000	19,000	15
60	LV-SE-15-RI	Rigaku, Inc.	221	19	1,106	91	1,291	14,724	-32
60	LV-SE-17-RI	Rigaku, Inc.	194	13	1,044	67	1,312	14,853	-43
60	LV-SE-51-RI	Rigaku, Inc.	221	2	1,122	50	1,302	14,751	-34

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
56	CN-SO-03-XX	Reference Laboratory	34 J-	74	36	90	30	58
56	CN-SO-06-XX	Reference Laboratory	40 J-	76	38	94	32	59
56	CN-SO-07-XX	Reference Laboratory	36 J-	75	37	91	33	58
56	CN-SO-03-RI	Rigaku, Inc.	43	69	18	226	69	55
56	CN-SO-06-RI	Rigaku, Inc.	52	73	20	228	56	55
56	CN-SO-07-RI	Rigaku, Inc.	38	66	19	230	59	65
57	CN-SO-02-XX	Reference Laboratory	270 J-	530	190	68	160	1,900
57	CN-SO-05-XX	Reference Laboratory	280 J-	360	190	78	160	2,200
57	CN-SO-09-XX	Reference Laboratory	260 J-	330	170	74	140	2,100
57	CN-SO-02-RI	Rigaku, Inc.	140	183	55	216	117	1,159
57	CN-SO-05-RI	Rigaku, Inc.	134	186	51	205	117	1,191
57	CN-SO-09-RI	Rigaku, Inc.	136	187	51	211	119	1,135
58	LV-SE-06-XX	Reference Laboratory	610 J-	360	160	110	480	52
58	LV-SE-13-XX	Reference Laboratory	640 J-	360	160	110	470	51
58	LV-SE-41-XX	Reference Laboratory	610 J-	320	150	99	420	46
58	LV-SE-06-RI	Rigaku, Inc.	290	210	57	212	311	53
58	LV-SE-13-RI	Rigaku, Inc.	288	211	55	211	309	54
58	LV-SE-41-RI	Rigaku, Inc.	303	208	57	216	336	52
59	LV-SE-05-XX	Reference Laboratory	2.6 J-	400	340	49	340	1,800
59	LV-SE-20-XX	Reference Laboratory	2.8	660	500	75 J-	530	2,800
59	LV-SE-43-XX	Reference Laboratory	2.8	530	420	60 J-	430	2,300
59	LV-SE-05-RI	Rigaku, Inc.	31	271	120	216	308	1,216
59	LV-SE-20-RI	Rigaku, Inc.	33	263	123	221	270	1,196
59	LV-SE-43-RI	Rigaku, Inc.	33	269	127	222	276	1,211
60	LV-SE-15-XX	Reference Laboratory	500	230	92	300 J-	180	62
60	LV-SE-17-XX	Reference Laboratory	490	220	89	200 J-	170	58
60	LV-SE-51-XX	Reference Laboratory	470	200	76	250 J-	160	54
60	LV-SE-15-RI	Rigaku, Inc.	241	115	27	250	147	71
60	LV-SE-17-RI	Rigaku, Inc.	234	110	25	234	137	56
60	LV-SE-51-RI	Rigaku, Inc.	252	106	31	246	134	54

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
61	TL-SE-05-XX	Reference Laboratory	100 J+	34	0.34 J	40	4,900	24,000	1,200
61	TL-SE-09-XX	Reference Laboratory	100 J+	33	0.24 J	39	4,800	23,000	1,200
61	TL-SE-13-XX	Reference Laboratory	95 J+	31	0.45 J	36 J+	4,400 J+	22,000 J+	1,100 J+
61	TL-SE-05-RI	Rigaku, Inc.	248	-27	542	84	2,111	15,461	454
61	TL-SE-09-RI	Rigaku, Inc.	260	9	540	57	2,112	15,340	461
61	TL-SE-13-RI	Rigaku, Inc.	275	17	545	35	2,152	15,446	474
62	TL-SE-06-XX	Reference Laboratory	1.2 U	86	350	34	2000	22,000	1,700
62	TL-SE-17-XX	Reference Laboratory	1.2 U	85	340	33	2100	21,000	1,700
62	TL-SE-28-XX	Reference Laboratory	1.2 U	89	360	34	2100	22,000	1,700
62	TL-SE-06-RI	Rigaku, Inc.	241	55	675	31	1,119	15,139	783
62	TL-SE-17-RI	Rigaku, Inc.	268	51	687	52	1,129	15,114	809
62	TL-SE-28-RI	Rigaku, Inc.	301	39	693	19	1,180	15,217	824
63	TL-SE-07-XX	Reference Laboratory	30	11	48	66	2200	37,000	13
63	TL-SE-21-XX	Reference Laboratory	33	13	51	73	2300	44,000	15
63	TL-SE-30-XX	Reference Laboratory	31	11	47	64	2200	36,000	14
63	TL-SE-07-RI	Rigaku, Inc.	184	-32	514	71	1,084	27,719	-85
63	TL-SE-21-RI	Rigaku, Inc.	169	-43	490	88	1,076	28,311	-90
63	TL-SE-30-RI	Rigaku, Inc.	158	-36	467	65	1,051	27,607	-81
64	TL-SE-02-XX	Reference Laboratory	77	15	160	64	3,100	32,000	12
64	TL-SE-08-XX	Reference Laboratory	66	10	180	74	3,200	45,000	11
64	TL-SE-16-XX	Reference Laboratory	73	15	170	69	3,100	38,000	13
64	TL-SE-02-RI	Rigaku, Inc.	181	-33	516	113	1,422	27,920	-93
64	TL-SE-08-RI	Rigaku, Inc.	176	-15	510	89	1,466	28,667	-87
64	TL-SE-16-RI	Rigaku, Inc.	174	-16	518	55	1,463	28,379	-97

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
61	TL-SE-05-XX	Reference Laboratory	980	54	130	180 J-	66	100
61	TL-SE-09-XX	Reference Laboratory	820	53	130	170 J-	63	100
61	TL-SE-13-XX	Reference Laboratory	990	49	120	160 J	59 J+	96
61	TL-SE-05-RI	Rigaku, Inc.	325	39	34	195	117	58
61	TL-SE-09-RI	Rigaku, Inc.	308	38	29	193	115	58
61	TL-SE-13-RI	Rigaku, Inc.	304	38	32	197	113	64
62	TL-SE-06-XX	Reference Laboratory	2.2	44	45	56	78	83
62	TL-SE-17-XX	Reference Laboratory	2.6	43	44	56	78	81
62	TL-SE-28-XX	Reference Laboratory	2.8	44	45	57	81	83
62	TL-SE-06-RI	Rigaku, Inc.	13	38	18	198	110	63
62	TL-SE-17-RI	Rigaku, Inc.	14	39	15	193	116	57
62	TL-SE-28-RI	Rigaku, Inc.	20	34	17	196	111	57
63	TL-SE-07-XX	Reference Laboratory	40	94	120	63	110	160
63	TL-SE-21-XX	Reference Laboratory	120	100	140	67	120	170
63	TL-SE-30-XX	Reference Laboratory	100	93	120	62	100	160
63	TL-SE-07-RI	Rigaku, Inc.	5	46	32	175	193	78
63	TL-SE-21-RI	Rigaku, Inc.	16	48	33	169	192	78
63	TL-SE-30-RI	Rigaku, Inc.	4	48	28	158	178	74
64	TL-SE-02-XX	Reference Laboratory	400	99	44	120	110	160
64	TL-SE-08-XX	Reference Laboratory	350	100	39	130	120	170
64	TL-SE-16-XX	Reference Laboratory	420	100	44	120	110	160
64	TL-SE-02-RI	Rigaku, Inc.	44	48	8	165	174	81
64	TL-SE-08-RI	Rigaku, Inc.	42	47	10	162	178	83
64	TL-SE-16-RI	Rigaku, Inc.	51	53	11	166	163	74

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb	As	Cd	Cr	Cu	Fe	Pb
65	RF-SE-01-XX	Reference Laboratory	12	230	40	280	63	14,000	22
65	RF-SE-09-XX	Reference Laboratory	10	260	45	310	71	16,000	26
65	RF-SE-11-XX	Reference Laboratory	11	240	43	300	72	15,000	25
65	RF-SE-17-XX	Reference Laboratory	11	250	43	300	67	15,000	26
65	RF-SE-29-XX	Reference Laboratory	13	280	49	330	75	17,000	26
65	RF-SE-37-XX	Reference Laboratory	11	260	45	320	72	16,000	27
65	RF-SE-50-XX	Reference Laboratory	8.9	230	40	280	65	14,000	23
65	RF-SE-01-RI	Rigaku, Inc.	190	192	661	176	56	12,047	-18
65	RF-SE-09-RI	Rigaku, Inc.	182	171	711	163	61	11,379	-14
65	RF-SE-11-RI	Rigaku, Inc.	183	164	663	173	59	11,335	-16
65	RF-SE-17-RI	Rigaku, Inc.	230	209	685	195	55	11,264	-21
65	RF-SE-29-RI	Rigaku, Inc.	229	203	665	276	54	11,433	-28
65	RF-SE-37-RI	Rigaku, Inc.	176	155	678	183	55	11,488	-27
65	RF-SE-50-RI	Rigaku, Inc.	248	174	702	236	55	10,934	-30
66	RF-SE-08-XX	Reference Laboratory	14	460	67	510	1,800	18,000	580
66	RF-SE-10-XX	Reference Laboratory	12	400	58	440	1,500	16,000	510
66	RF-SE-33-XX	Reference Laboratory	13	440	64	490	1,700	18,000	570
66	RF-SE-08-RI	Rigaku, Inc.	241	269	662	308	1,327	12,503	295
66	RF-SE-10-RI	Rigaku, Inc.	225	273	647	258	1,318	12,340	299
66	RF-SE-33-RI	Rigaku, Inc.	242	257	658	272	1,258	12,280	284
67	RF-SE-16-XX	Reference Laboratory	85 J-	72 J-	310 J-	820 J-	73 J-	16,000 J-	24 J-
67	RF-SE-41-XX	Reference Laboratory	100	82	360	950	85	18,000	25
67	RF-SE-48-XX	Reference Laboratory	100	87	380	1,000	90	19,000	27
67	RF-SE-16-RI	Rigaku, Inc.	215	24	755	686	65	11,960	-21
67	RF-SE-41-RI	Rigaku, Inc.	178	49	787	475	66	12,153	-25
67	RF-SE-48-RI	Rigaku, Inc.	238	40	801	616	63	11,987	-27

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
65	RF-SE-01-XX	Reference Laboratory	47	200	21	37	29	1,700
65	RF-SE-09-XX	Reference Laboratory	45	220	23	42	32	1,900
65	RF-SE-11-XX	Reference Laboratory	52	210	20	40	29	1,800
65	RF-SE-17-XX	Reference Laboratory	20	210	22	40	30	1,800
65	RF-SE-29-XX	Reference Laboratory	20	240	26	44	35	2,100
65	RF-SE-37-XX	Reference Laboratory	22	220	23	44	32	1,900
65	RF-SE-50-XX	Reference Laboratory	19	200	20	38	29	1,700
65	RF-SE-01-RI	Rigaku, Inc.	53	149	16	229	56	1,239
65	RF-SE-09-RI	Rigaku, Inc.	54	132	16	241	54	1,127
65	RF-SE-11-RI	Rigaku, Inc.	54	131	13	231	53	1,113
65	RF-SE-17-RI	Rigaku, Inc.	64	131	18	214	50	1,112
65	RF-SE-29-RI	Rigaku, Inc.	71	131	18	215	50	1,117
65	RF-SE-37-RI	Rigaku, Inc.	54	139	15	228	54	1,123
65	RF-SE-50-RI	Rigaku, Inc.	59	125	17	223	41	1,041
66	RF-SE-08-XX	Reference Laboratory	29	250	42	0.39 U	120	120
66	RF-SE-10-XX	Reference Laboratory	27	220	39	0.34 U	100	110
66	RF-SE-33-XX	Reference Laboratory	28	240	41	0.33 U	120	130
66	RF-SE-08-RI	Rigaku, Inc.	65	147	20	216	98	83
66	RF-SE-10-RI	Rigaku, Inc.	60	141	20	221	90	84
66	RF-SE-33-RI	Rigaku, Inc.	64	129	19	222	92	86
67	RF-SE-16-XX	Reference Laboratory	260	1,700 J-	1.2 U	130 J-	32 J-	760 J-
67	RF-SE-41-XX	Reference Laboratory	230	1,900	1.2 U	140	39	830
67	RF-SE-48-XX	Reference Laboratory	250	2,000	2.2	150	40	880
67	RF-SE-16-RI	Rigaku, Inc.	183	941	13	214	56	441
67	RF-SE-41-RI	Rigaku, Inc.	170	956	7	228	48	455
67	RF-SE-48-RI	Rigaku, Inc.	185	922	14	218	54	442

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Sb		As	Cd	Cr	Cu	Fe	Pb
68	RF-SE-18-XX	Reference Laboratory	320		810	770	950	78	16,000	860
68	RF-SE-35-XX	Reference Laboratory	300		740	700	860	70	15,000	780
68	RF-SE-54-XX	Reference Laboratory	320		880	840	1,000	86	18,000	920
68	RF-SE-18-RI	Rigaku, Inc.	246		619	957	631	57	11,434	457
68	RF-SE-35-RI	Rigaku, Inc.	283		432	946	383	57	11,390	448
68	RF-SE-54-RI	Rigaku, Inc.	235		609	945	633	57	11,492	460
69	RF-SE-20-XX	Reference Laboratory	550		1300	540	94	93	20,000	28
69	RF-SE-46-XX	Reference Laboratory	270		590	240	44	40	8,900	13
69	RF-SE-51-XX	Reference Laboratory	480		1100	450	77	77	17,000	23
69	RF-SE-20-RI	Rigaku, Inc.	238		811	803	91	54	12,122	-16
69	RF-SE-46-RI	Rigaku, Inc.	238		804	814	48	57	12,343	-15
69	RF-SE-51-RI	Rigaku, Inc.	233		817	807	33	62	12,212	-8
70	RF-SE-21-XX	Reference Laboratory	1.3	U	62	1,700	76	1,000	16,000	2,100
70	RF-SE-40-XX	Reference Laboratory	1.3	U	70	1,900	85	1,100	18,000	2,400
70	RF-SE-47-XX	Reference Laboratory	1.3	U	72	1,900	90	1,200	19,000	2,400
70	RF-SE-21-RI	Rigaku, Inc.	201		158	1,368	41	734	11,906	1,311
70	RF-SE-40-RI	Rigaku, Inc.	442		58	1,407	89	759	11,948	1,356
70	RF-SE-47-RI	Rigaku, Inc.	196		154	1,326	71	713	12,192	1,268

Appendix D: Analytical Data Summary, Rigaku ZSX Mini II and Reference Laboratory (Continued)

Blend No.	Sample ID	Source of Data	Hg	Ni	Se	Ag	V	Zn
68	RF-SE-18-XX	Reference Laboratory	600	390	140	140	390	120
68	RF-SE-35-XX	Reference Laboratory	650	350	140	150	340	110
68	RF-SE-54-XX	Reference Laboratory	670	420	160	180	410	120
68	RF-SE-18-RI	Rigaku, Inc.	327	205	49	215	232	96
68	RF-SE-35-RI	Rigaku, Inc.	384	202	54	231	246	89
68	RF-SE-54-RI	Rigaku, Inc.	334	201	48	216	237	77
69	RF-SE-20-XX	Reference Laboratory	0.48	1,400	380	59	36	1,400
69	RF-SE-46-XX	Reference Laboratory	0.45	650	170	26	16	650
69	RF-SE-51-XX	Reference Laboratory	0.48	1,200	320	48	30	1,200
69	RF-SE-20-RI	Rigaku, Inc.	53	636	92	207	52	655
69	RF-SE-46-RI	Rigaku, Inc.	53	634	93	211	48	698
69	RF-SE-51-RI	Rigaku, Inc.	48	638	92	205	51	671
70	RF-SE-21-XX	Reference Laboratory	320	220	440	120	130	100
70	RF-SE-40-XX	Reference Laboratory	280	250	480	100	150	120
70	RF-SE-47-XX	Reference Laboratory	320	250	510	120	150	120
70	RF-SE-21-RI	Rigaku, Inc.	29	113	124	216	98	72
70	RF-SE-40-RI	Rigaku, Inc.	210	127	150	232	105	83
70	RF-SE-47-RI	Rigaku, Inc.	38	108	125	211	116	75

Notes:
All concentrations reported in milligrams per kilogram (mg/kg), or parts per million (ppm).
Sample results for which “0” or no value was reported were considered nondetections as reported by Xcalibur.
Reference laboratory data qualifiers were as follows:

J	Estimated concentration.
J+	Concentration is considered estimated and biased high.
J-	Concentration is considered estimated and biased low.
U	Analyte is not detected; the associated concentration value is the sample reporting limit.

APPENDIX E

STATISTICAL DATA SUMMARIES

Figure E-1: Linear Correlation Plot for Antimony

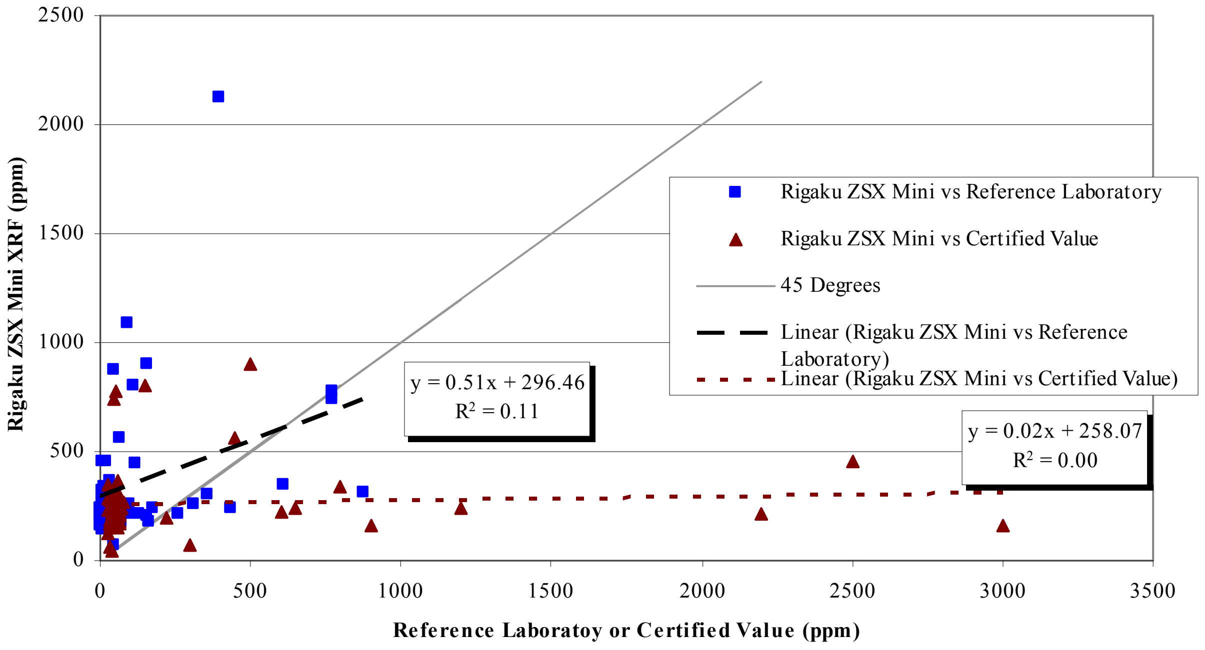


Figure E-2: Linear Correlation Plot for Arsenic

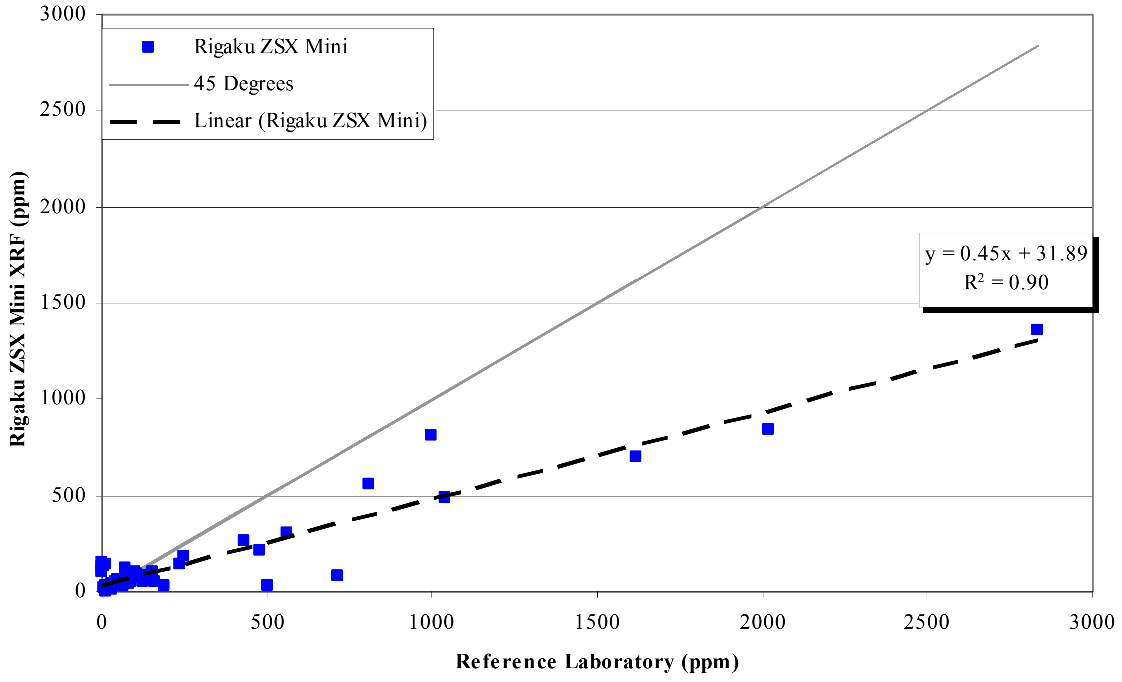


Figure E-3: Linear Correlation Plot for Cadmium

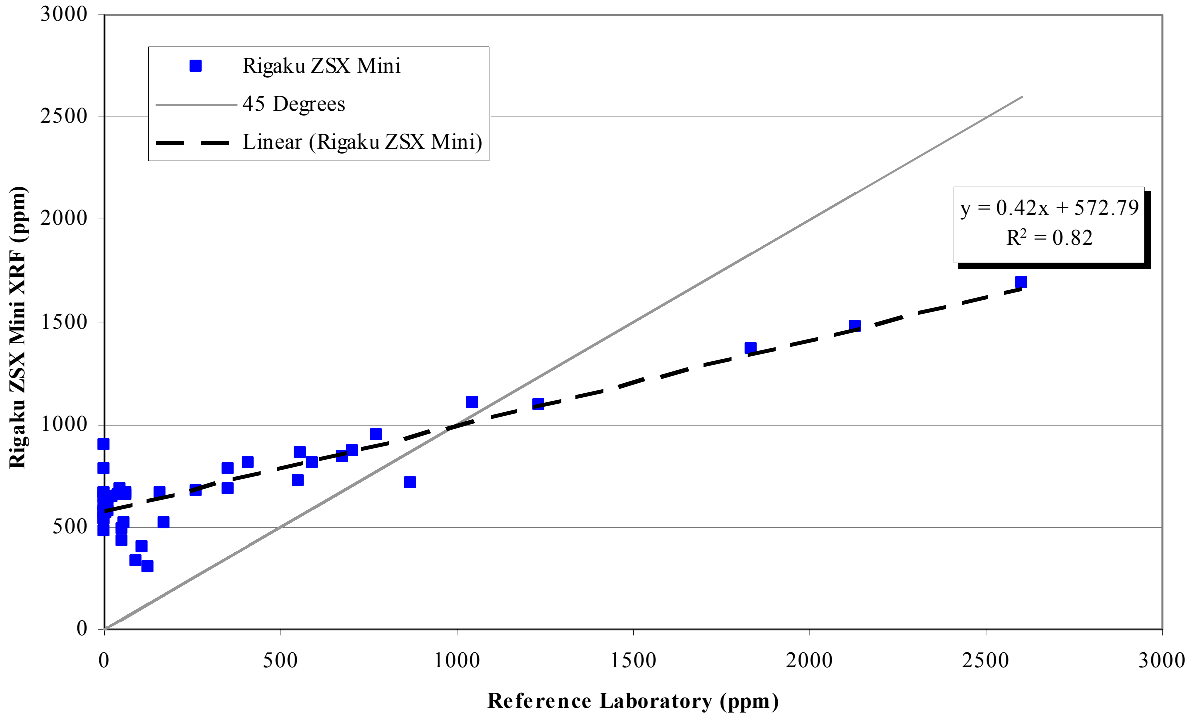


Figure E-4: Linear Correlation Plot for Chromium

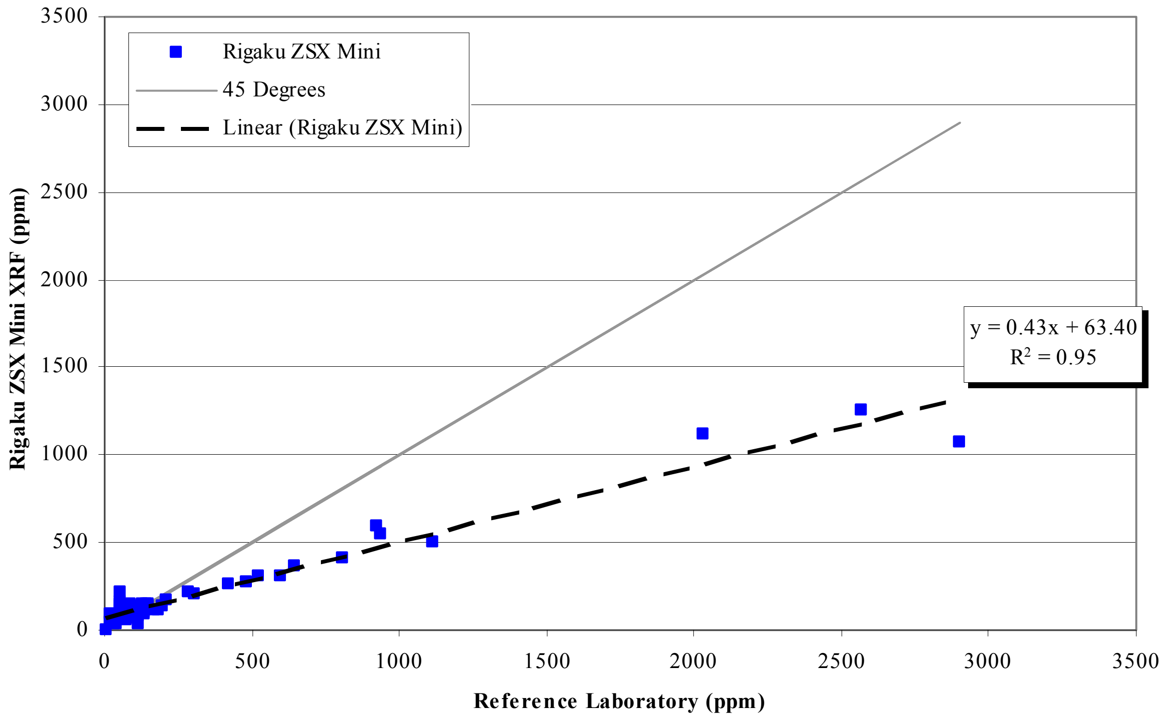


Figure E-5: Linear Correlation Plot for Copper

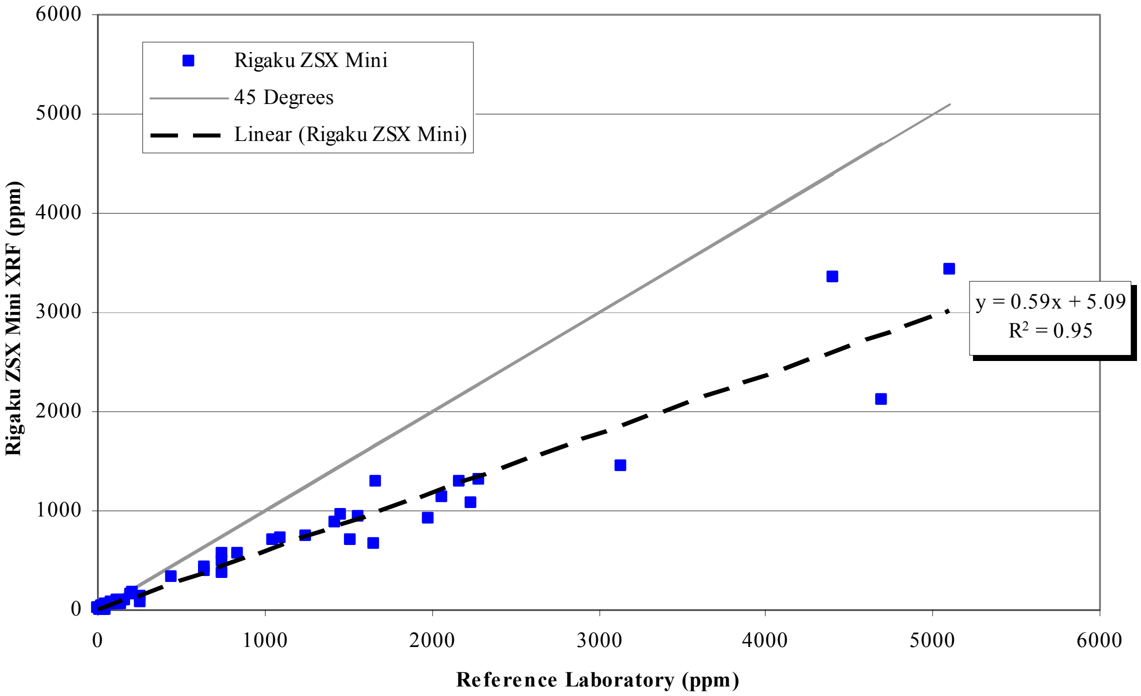


Figure E-6: Linear Correlation Plot for Iron

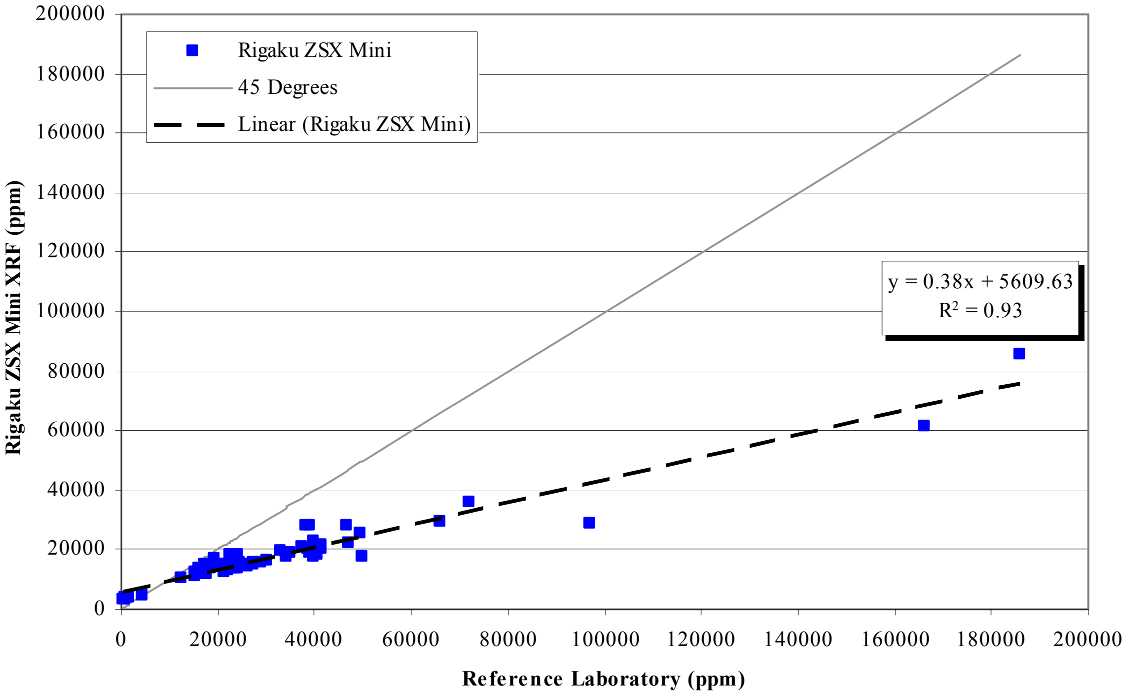


Figure E-7: Linear Correlation Plot for Lead

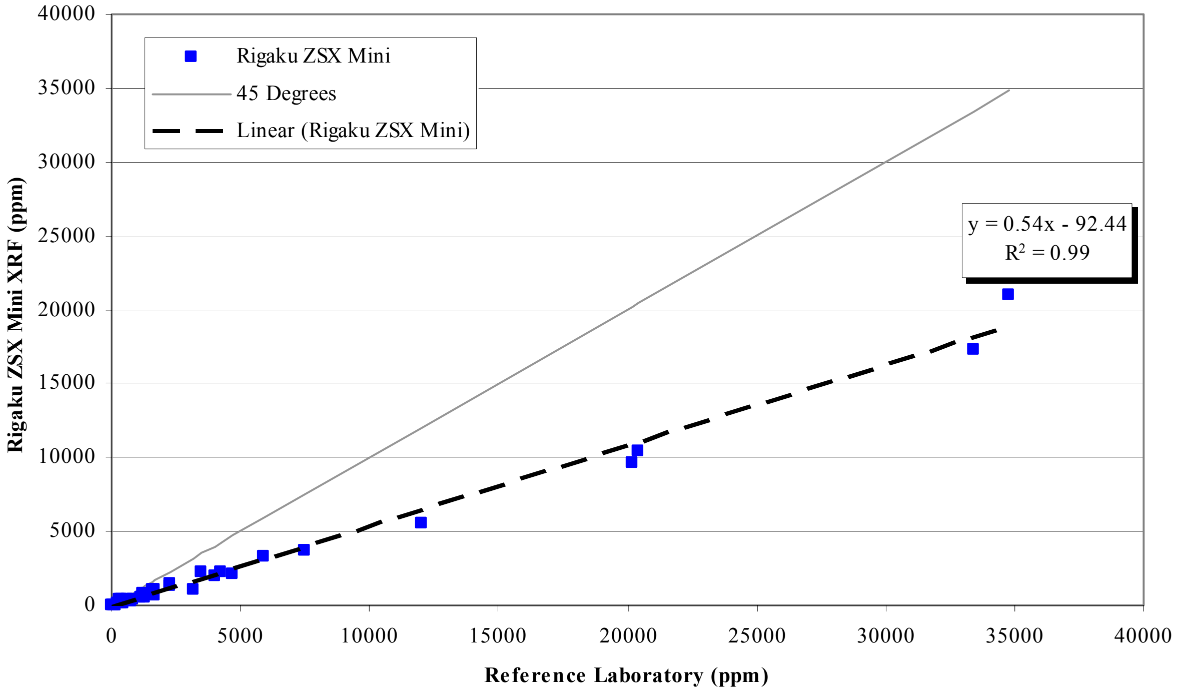


Figure E-8: Linear Correlation Plot for Mercury

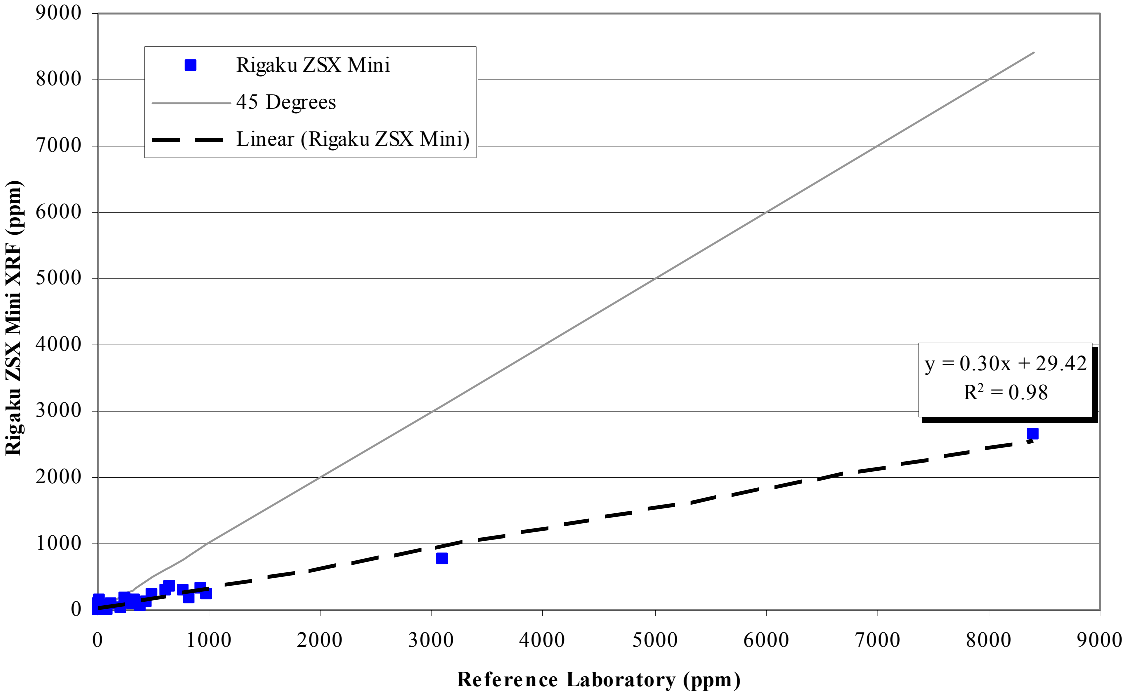


Figure E-9: Linear Correlation Plot for Nickel

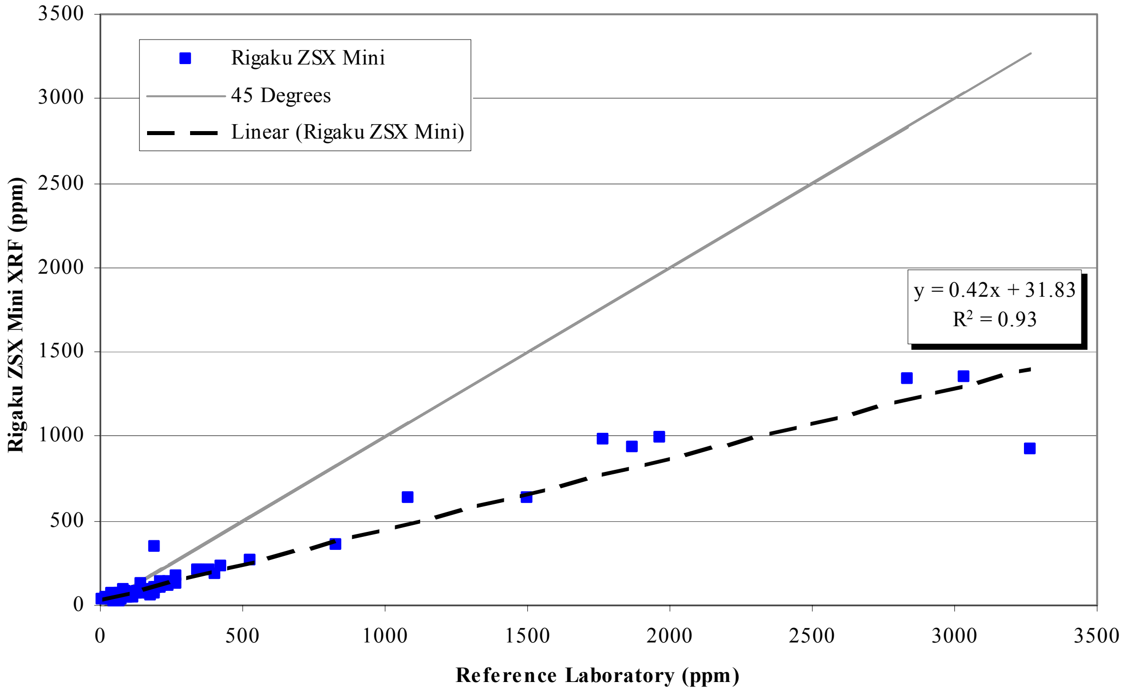


Figure E-10: Linear Correlation Plot for Selenium

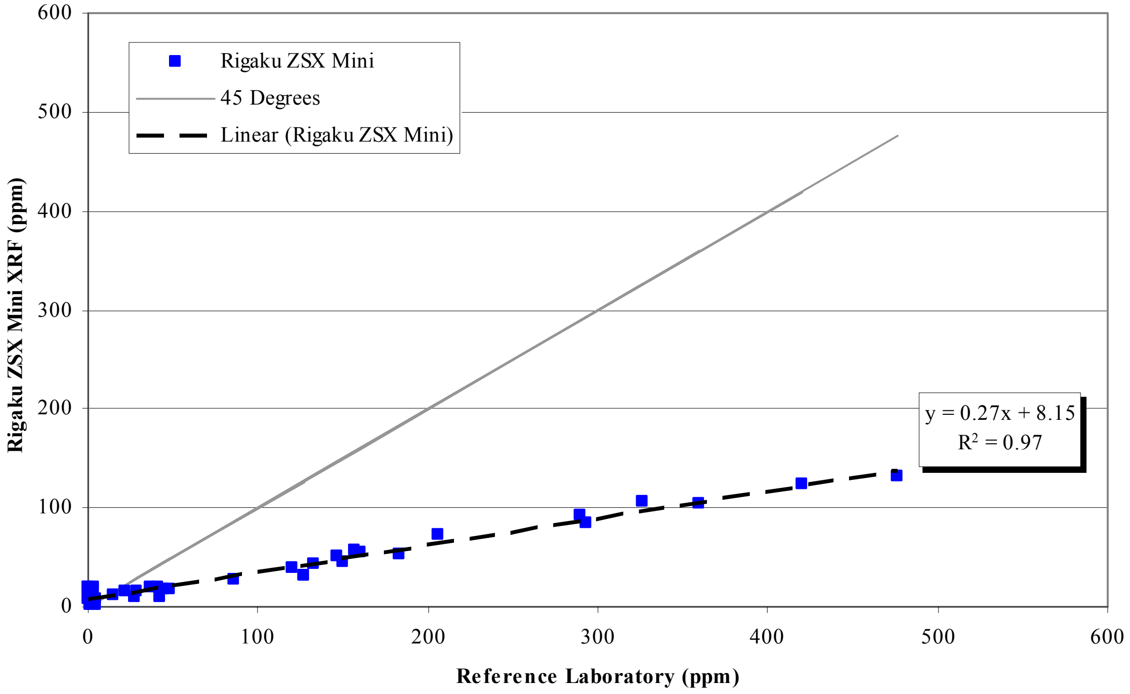


Figure E-11: Linear Correlation Plot for Silver

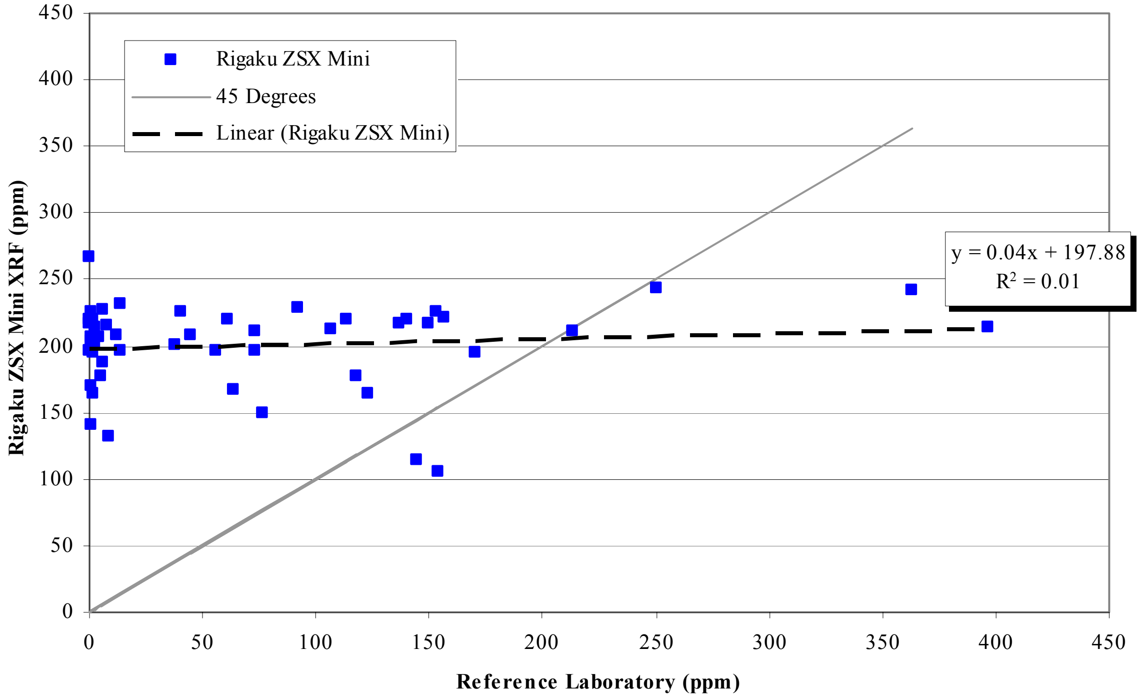


Figure E-12: Linear Correlation Plot for Vanadium

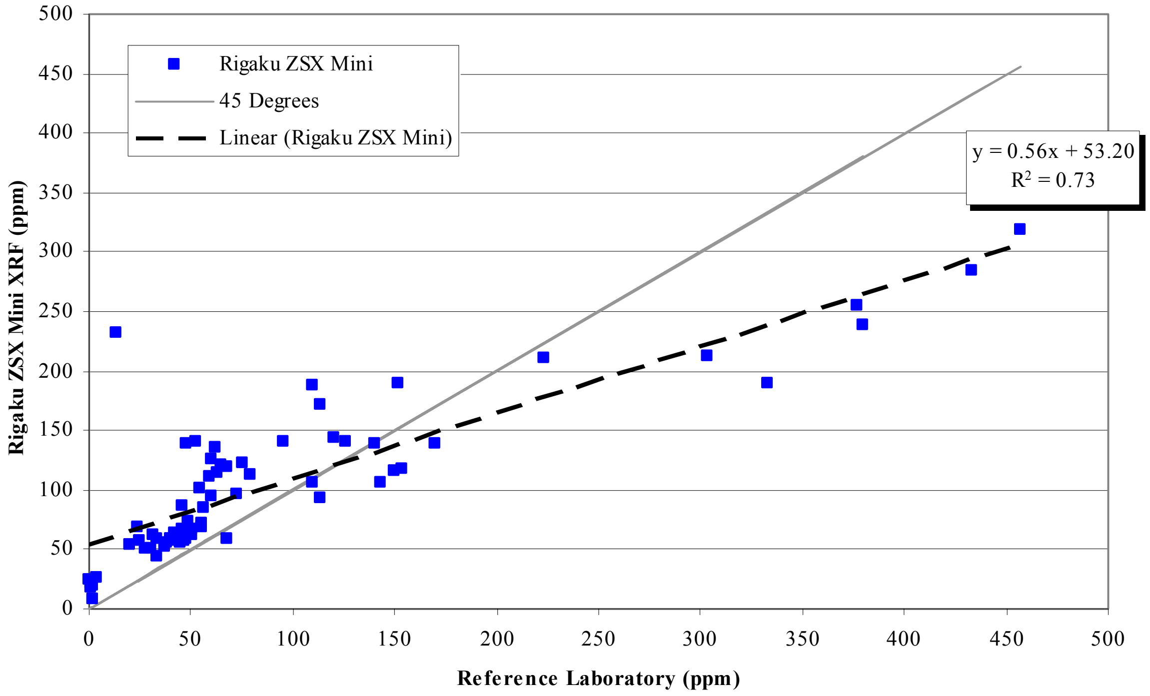
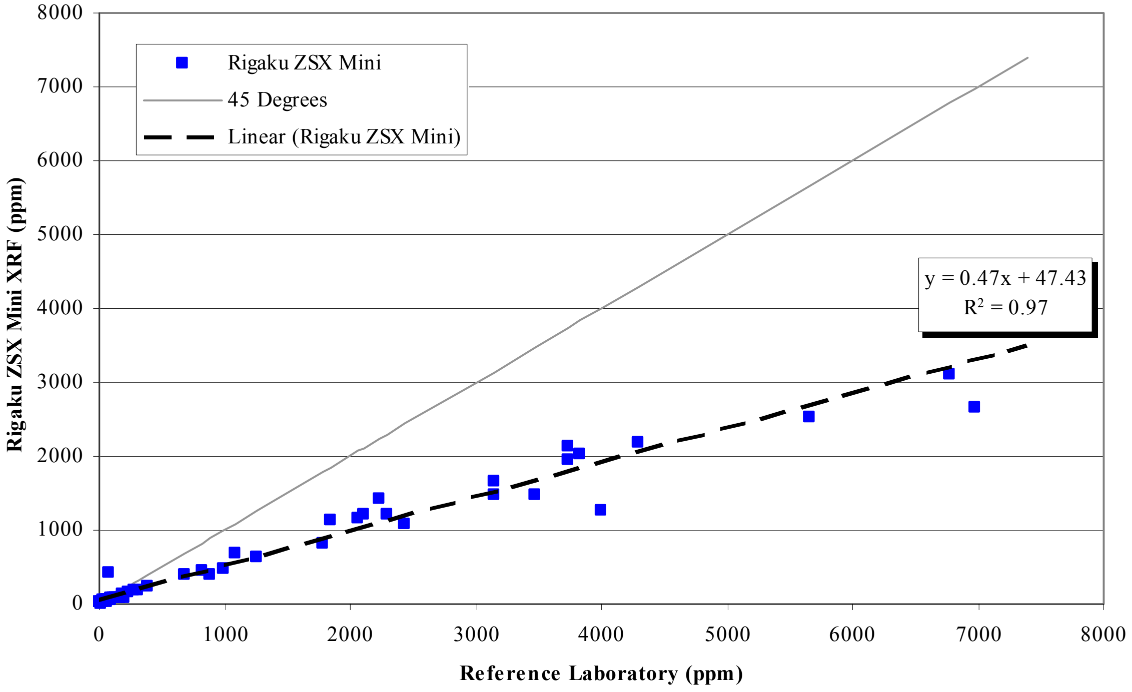
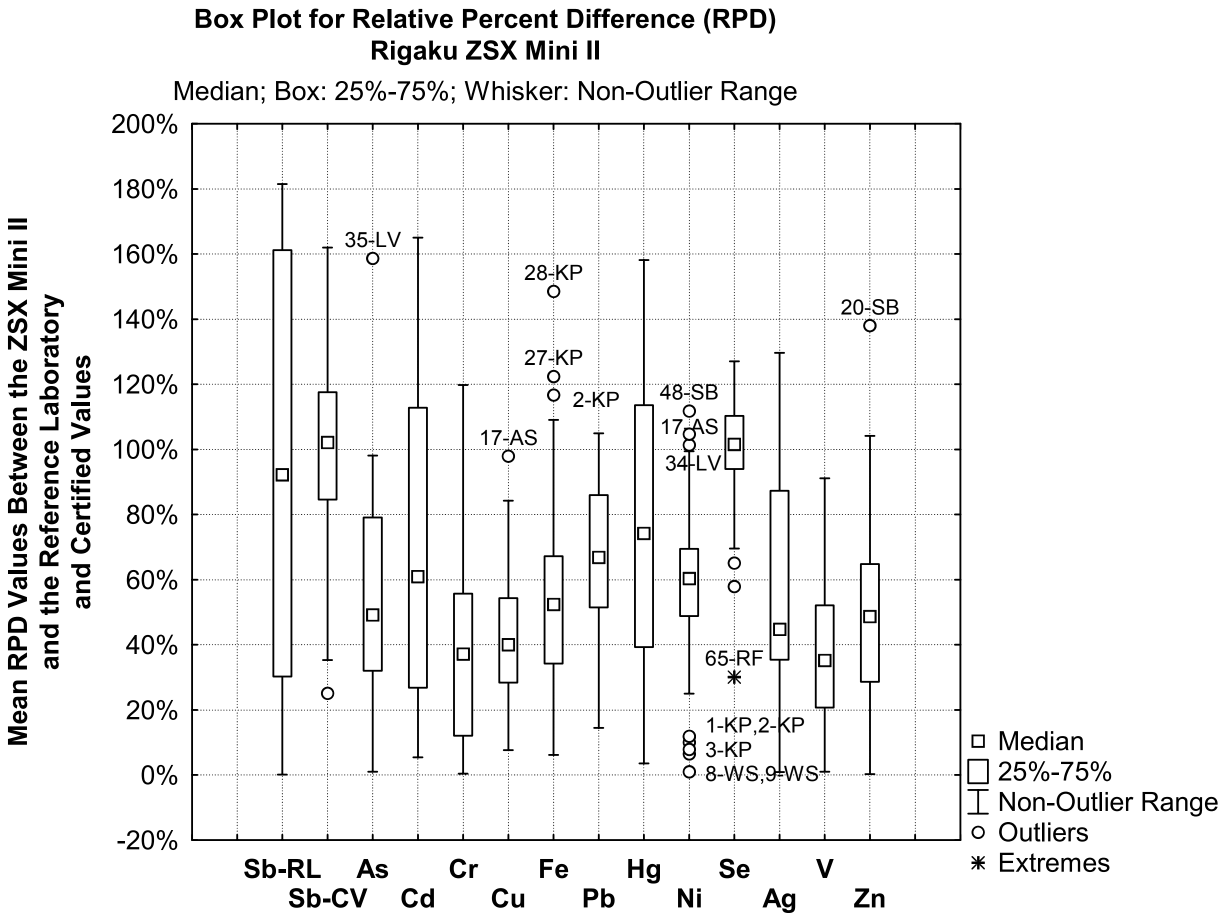


Figure E-13: Linear Correlation Plot for Zinc





Notes:

The "box" in each box plot presents the range of RPD values that lie between the 25th and 75th percentiles (that is, the "quartiles") of the full RPD population for each element. In essence, the box displays the "interquartile range" of RPD values. The square data point within each box represents the median RPD for the population. The "whiskers" emanating from the top and bottom of each box represent the largest and smallest data points, respectively, that are within 1.5 times the interquartile range. Values outside the whiskers are identified as outliers and extremes.

Some of the more significant extremes and outliers are labeled with the associated Blend numbers and sample site abbreviations (see the footnotes of Table E-5 for definitions). Also refer to Appendix D for the sampling site and analytical data associated with each Blend number.

Figure E-14. Box and Whiskers Plot for Mean RPD Values Showing Outliers and Extremes for Target Elements, Rigaku ZSX Mini II Data Set.

Table E-1. Evaluation of Accuracy - Relative Percent Differences Versus Reference Laboratory Data Calculated for the Rigaku ZSX Mini II

Matrix	Conc Range	Statistic	Antimony		Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury
			Ref Lab	ERA Spike							
Soil	Level 1	Number	8	1	8	7	23	16	5	4	7
		Minimum	28.3%	84.9%	1.0%	85.3%	2.0%	7.6%	6.1%	43.1%	3.6%
		Maximum	181.5%	84.9%	98.1%	165.0%	88.7%	97.9%	116.7%	104.1%	139.3%
		Mean	142.1%	84.9%	32.7%	126.8%	27.5%	38.9%	75.9%	78.9%	38.5%
		Median	161.2%	84.9%	14.0%	116.1%	21.0%	32.2%	93.3%	84.1%	24.3%
	Level 2	Number	5	1	4	7	4	8	13	4	6
		Minimum	12.7%	84.8%	58.5%	5.5%	55.7%	27.0%	12.8%	42.4%	65.4%
		Maximum	150.7%	84.8%	79.1%	36.4%	65.5%	65.0%	53.7%	90.7%	134.7%
		Mean	70.4%	84.8%	71.6%	23.2%	60.5%	47.1%	40.0%	67.7%	103.0%
		Median	32.1%	84.8%	74.4%	21.4%	60.4%	49.3%	48.6%	68.9%	106.6%
	Level 3	Number	4	3	4	2	2	2	13	8	2
		Minimum	0.1%	96.1%	70.2%	42.2%	68.7%	27.0%	49.8%	43.6%	104.3%
		Maximum	93.9%	162.0%	87.8%	57.1%	92.4%	39.0%	75.6%	104.9%	120.0%
		Mean	37.9%	122.1%	80.7%	49.7%	80.5%	33.0%	60.9%	65.2%	112.1%
		Median	28.8%	108.3%	82.4%	49.7%	80.5%	33.0%	60.3%	65.1%	112.1%
	Level 4	Number	--	--	--	--	--	--	7	5	--
		Minimum	--	--	--	--	--	--	49.6%	49.2%	--
		Maximum	--	--	--	--	--	--	109.1%	73.9%	--
		Mean	--	--	--	--	--	--	76.3%	64.4%	--
		Median	--	--	--	--	--	--	70.8%	64.5%	--
	All Soil	Number	17	5	16	16	29	26	38	21	15
		Minimum	0.1%	84.8%	1.0%	5.5%	2.0%	7.6%	6.1%	42.4%	3.6%
		Maximum	181.5%	162.0%	98.1%	165.0%	92.4%	97.9%	116.7%	104.9%	139.3%
		Mean	96.5%	107.2%	54.4%	71.9%	35.7%	41.0%	58.6%	68.1%	74.1%
		Median	116.8%	96.1%	71.3%	49.7%	29.3%	40.0%	58.5%	66.7%	78.3%

Table E-1. Evaluation of Accuracy - Relative Percent Differences Versus Reference Laboratory Data Calculated for the Rigaku ZSX Mini II (Continued)

Matrix	Conc Range	Statistic	Nickel	Selenium	Silver	Vanadium	Zinc
Soil	Level 1	Number	23	4	3	12	19
		Minimum	1.0%	57.9%	63.9%	13.7%	0.3%
		Maximum	101.3%	101.5%	96.7%	91.1%	138.0%
		Mean	45.1%	78.6%	84.2%	48.6%	35.6%
		Median	50.0%	77.6%	91.9%	57.8%	27.2%
	Level 2	Number	5	5	3	4	6
		Minimum	44.4%	97.5%	40.4%	1.0%	43.8%
		Maximum	74.7%	110.8%	85.3%	26.5%	81.4%
		Mean	60.3%	103.5%	56.9%	17.7%	61.4%
		Median	60.6%	102.3%	45.1%	21.7%	58.7%
	Level 3	Number	6	4	7	4	9
		Minimum	56.6%	95.8%	0.9%	6.0%	54.3%
		Maximum	111.8%	110.4%	59.6%	55.4%	104.2%
		Mean	77.2%	104.5%	33.7%	33.7%	72.0%
		Median	74.1%	105.9%	37.0%	36.8%	65.2%
	Level 4	Number	--	--	--	--	--
		Minimum	--	--	--	--	--
		Maximum	--	--	--	--	--
		Mean	--	--	--	--	--
		Median	--	--	--	--	--
	All Soil	Number	34	13	13	20	34
		Minimum	1.0%	57.9%	0.9%	1.0%	0.3%
		Maximum	111.8%	110.8%	96.7%	91.1%	138.0%
		Mean	53.0%	96.2%	50.7%	39.4%	49.8%
		Median	57.7%	101.5%	40.4%	31.4%	50.4%

Table E-1. Evaluation of Accuracy - Relative Percent Differences Versus Reference Laboratory Data Calculated for the Rigaku ZSX Mini II (Continued)

Matrix	Conc Range	Statistic	Antimony		Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury
			Ref Lab	ERA Spike							
Sediment	Level 1	Number	4	4	8	3	7	8	3	6	2
		Minimum	138.0%	25.1%	10.2%	100.7%	0.4%	19.9%	105.0%	14.5%	58.1%
		Maximum	179.7%	134.7%	82.3%	164.9%	119.8%	55.0%	148.5%	91.3%	77.0%
		Mean	166.6%	90.8%	47.5%	129.7%	32.5%	29.6%	125.3%	62.7%	67.5%
		Median	174.4%	101.7%	47.3%	123.3%	9.3%	26.7%	122.4%	82.0%	67.5%
	Level 2	Number	4	4	3	4	3	4	19	4	4
		Minimum	47.1%	35.3%	32.0%	42.5%	40.7%	38.4%	15.7%	60.9%	31.8%
		Maximum	90.6%	108.9%	158.7%	76.2%	52.9%	40.2%	44.7%	86.4%	158.1%
		Mean	74.4%	77.7%	79.5%	62.2%	48.8%	39.5%	32.5%	72.0%	91.0%
		Median	79.9%	83.3%	47.7%	65.0%	52.7%	39.7%	33.4%	70.3%	87.1%
	Level 3	Number	3	3	2	3	3	10	4	3	3
		Minimum	20.3%	111.7%	20.6%	12.3%	43.7%	24.7%	30.0%	43.6%	59.0%
		Maximum	58.7%	134.0%	37.7%	29.2%	75.7%	84.2%	57.1%	71.4%	99.4%
		Mean	33.2%	120.6%	29.1%	20.8%	57.2%	62.9%	43.1%	56.6%	76.6%
		Median	20.6%	116.2%	29.1%	20.9%	52.2%	71.4%	42.7%	54.7%	71.4%
	Level 4	Number	--	--	--	--	--	--	6	--	--
		Minimum	--	--	--	--	--	--	55.6%	--	--
		Maximum	--	--	--	--	--	--	92.1%	--	--
		Mean	--	--	--	--	--	--	71.5%	--	--
		Median	--	--	--	--	--	--	70.5%	--	--
	All Sediment	Number	11	11	13	10	13	22	32	13	9
		Minimum	20.3%	25.1%	10.2%	12.3%	0.4%	19.9%	15.7%	14.5%	31.8%
		Maximum	179.7%	134.7%	158.7%	164.9%	119.8%	84.2%	148.5%	91.3%	158.1%
		Mean	96.7%	94.2%	52.1%	70.0%	42.0%	46.6%	49.9%	64.1%	81.0%
		Median	84.3%	108.9%	45.5%	65.0%	43.7%	40.0%	38.0%	71.4%	71.4%

Table E-1. Evaluation of Accuracy - Relative Percent Differences Versus Reference Laboratory Data Calculated for the Rigaku ZSX Mini II (Continued)

Matrix	Conc Range	Statistic	Nickel	Selenium	Silver	Vanadium	Zinc
Sediment	Level 1	Number	18	5	5	6	18
		Minimum	31.3%	30.1%	89.3%	27.7%	4.1%
		Maximum	104.7%	127.1%	138.9%	59.0%	80.9%
		Mean	64.2%	83.8%	116.2%	41.1%	41.4%
		Median	62.0%	89.6%	112.6%	39.2%	39.6%
	Level 2	Number	6	4	4	8	5
		Minimum	45.9%	94.0%	13.7%	3.1%	46.5%
		Maximum	69.5%	121.3%	66.8%	52.1%	68.1%
		Mean	57.3%	108.0%	38.3%	24.7%	58.2%
		Median	57.1%	108.4%	36.3%	20.9%	59.4%
	Level 3	Number	4	3	3	3	4
		Minimum	52.0%	103.6%	2.6%	35.5%	48.4%
		Maximum	79.8%	112.9%	64.0%	45.8%	78.3%
		Mean	66.0%	108.5%	33.5%	40.9%	65.8%
		Median	66.0%	109.1%	34.0%	41.4%	68.3%
	Level 4	Number	--	--	--	--	--
		Minimum	--	--	--	--	--
		Maximum	--	--	--	--	--
		Mean	--	--	--	--	--
		Median	--	--	--	--	--
	All Sediment	Number	28	12	12	17	27
		Minimum	31.3%	30.1%	2.6%	3.1%	4.1%
		Maximum	104.7%	127.1%	138.9%	59.0%	80.9%
		Mean	63.0%	98.1%	69.6%	33.4%	48.1%
		Median	63.1%	103.2%	65.4%	35.5%	48.6%

Table E-1. Evaluation of Accuracy - Relative Percent Differences Versus Reference Laboratory Data Calculated for the Rigaku ZSX Mini II (Continued)

Matrix	Conc Range	Statistic	Antimony		Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury
			Ref Lab	ERA Spike							
All Samples	ZSX Mini II	Number	28	16	29	26	42	48	70	34	24
		Minimum	0.1%	25.1%	1.0%	5.5%	0.4%	7.6%	6.1%	14.5%	3.6%
		Maximum	181.5%	162.0%	158.7%	165.0%	119.8%	97.9%	148.5%	104.9%	158.1%
		Mean	96.6%	98.2%	53.4%	71.1%	37.7%	43.5%	54.6%	66.6%	76.7%
		Median	92.2%	102.2%	49.2%	60.9%	37.2%	40.0%	52.4%	66.8%	74.2%
All Samples	All Instruments	Number	206	110	320	209	338	363	558	392	192
		Minimum	0.1%	0.1%	0.2%	0.1%	0.1%	0.2%	0.0%	0.1%	0.0%
		Maximum	181.5%	162.0%	182.8%	168.1%	151.7%	111.1%	190.1%	135.2%	158.1%
		Mean	80.6%	62.7%	36.6%	29.6%	30.8%	24.6%	35.4%	30.9%	62.5%
		Median	84.3%	70.6%	26.2%	16.7%	26.0%	16.2%	26.0%	21.5%	58.6%

Table E-1. Evaluation of Accuracy - Relative Percent Differences Versus Reference Laboratory Data Calculated for the Rigaku ZSX Mini II (Continued)

Matrix	Conc Range	Statistic	Nickel	Selenium	Silver	Vanadium	Zinc
All Samples	ZSX Mini II	Number	62	25	25	37	61
		Minimum	1.0%	30.1%	0.9%	1.0%	0.3%
		Maximum	111.8%	127.1%	138.9%	91.1%	138.0%
		Mean	57.5%	97.1%	59.8%	36.7%	49.0%
		Median	60.4%	101.5%	45.1%	35.2%	48.6%
All Samples	All Instruments	Number	403	195	177	218	471
		Minimum	0.3%	0.0%	0.0%	0.1%	0.0%
		Maximum	146.5%	127.1%	129.7%	129.5%	138.0%
		Mean	31.0%	32.0%	36.0%	42.2%	26.3%
		Median	25.4%	16.7%	28.7%	38.3%	19.4%

Notes:

All RPDs presented in this table are absolute values.

--	No samples reported by the reference laboratory in this concentration range.
Conc	Concentration.
ERA	Environmental Resource Associates, Inc
Number	Number of demonstration samples evaluated.
Ref Lab	Reference laboratory (Shealy Environmental Services, Inc.).
.RPD	Relative percent difference.

Table E-2. Evaluation of Precision - Relative Standard Deviations Calculated for the Rigaku ZSX Mimi

Matrix	Conc Range	Statistic	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel
Soil	Level 1	Number	8	8	7	23	16	5	4	7	23
		Minimum	3.4%	3.4%	0.9%	6.2%	1.6%	0.5%	3.6%	1.4%	1.4%
		Maximum	41.4%	20.1%	4.1%	29.5%	50.5%	2.5%	26.3%	136.8%	164.2%
		Mean	12.9%	13.2%	2.2%	15.7%	7.7%	1.2%	11.2%	26.2%	11.6%
		Median	6.2%	13.0%	1.8%	14.8%	4.5%	1.0%	7.5%	9.6%	4.7%
	Level 2	Number	5	4	7	4	8	13	4	6	5
		Minimum	6.3%	1.6%	0.4%	1.6%	0.8%	0.2%	1.7%	2.2%	1.1%
		Maximum	7.3%	11.4%	3.6%	8.1%	4.3%	2.5%	2.6%	49.8%	2.7%
		Mean	6.9%	4.9%	2.0%	4.6%	2.1%	0.6%	2.1%	12.8%	2.1%
		Median	6.9%	3.2%	2.2%	4.3%	1.9%	0.5%	2.1%	5.2%	2.3%
	Level 3	Number	4	4	2	2	2	13	8	2	6
		Minimum	3.7%	0.7%	0.9%	2.6%	0.4%	0.2%	0.4%	2.3%	0.5%
		Maximum	6.5%	3.7%	1.2%	2.7%	0.8%	43.2%	2.2%	2.6%	77.8%
		Mean	5.0%	1.9%	1.1%	2.7%	0.6%	4.3%	1.6%	2.4%	13.9%
		Median	4.9%	1.7%	1.1%	2.7%	0.6%	0.6%	1.8%	2.4%	1.3%
	Level 4	Number	--	--	--	--	--	7	5	--	--
		Minimum	--	--	--	--	--	0.4%	0.5%	--	--
		Maximum	--	--	--	--	--	1.3%	1.4%	--	--
		Mean	--	--	--	--	--	0.8%	0.9%	--	--
		Median	--	--	--	--	--	0.7%	0.8%	--	--
	All Soil	Number	17	16	16	29	26	38	21	15	34
		Minimum	3.4%	0.7%	0.4%	1.6%	0.4%	0.2%	0.4%	1.4%	0.5%
		Maximum	41.4%	20.1%	4.1%	29.5%	50.5%	43.2%	26.3%	136.8%	164.2%
		Mean	9.3%	8.3%	2.0%	13.2%	5.5%	2.0%	3.3%	17.7%	10.6%
		Median	6.3%	6.1%	1.8%	13.0%	3.4%	0.6%	1.8%	5.3%	3.9%

Table E-2. Evaluation of Precision - Relative Standard Deviations Calculated for the Rigaku ZSX Mimi

Matrix	Conc Range	Statistic	Nickel	Selenium	Silver	Vanadium	Zinc
Soil	Level 1	Number	23	4	3	12	19
		Minimum	1.4%	3.9%	2.4%	9.7%	0.9%
		Maximum	164.2%	49.2%	3.4%	22.4%	192.9%
		Mean	11.6%	17.2%	2.8%	13.6%	14.3%
		Median	4.7%	7.9%	2.5%	12.3%	4.2%
	Level 2	Number	5	5	3	4	6
		Minimum	1.1%	0.1%	0.9%	1.1%	0.8%
		Maximum	2.7%	4.6%	3.5%	11.1%	2.4%
		Mean	2.1%	2.8%	2.1%	5.8%	1.5%
		Median	2.3%	3.2%	2.0%	5.5%	1.4%
	Level 3	Number	6	4	7	4	9
		Minimum	0.5%	1.2%	1.2%	0.4%	0.6%
		Maximum	77.8%	2.3%	2.8%	5.8%	82.5%
		Mean	13.9%	1.8%	2.3%	4.1%	10.2%
		Median	1.3%	1.9%	2.4%	5.2%	1.0%
	Level 4	Number	--	--	--	--	--
		Minimum	--	--	--	--	--
		Maximum	--	--	--	--	--
		Mean	--	--	--	--	--
		Median	--	--	--	--	--
	All Soil	Number	34	13	13	20	34
		Minimum	0.5%	0.1%	0.9%	0.4%	0.6%
		Maximum	164.2%	49.2%	3.5%	22.4%	192.9%
		Mean	10.6%	6.9%	2.3%	10.2%	10.9%
		Median	3.9%	3.2%	2.4%	11.1%	2.1%

Table E-2. Evaluation of Precision - Relative Standard Deviations Calculated for the Rigaku ZSX Mini (Continued)

Matrix	Conc Range	Statistic	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury
Sediment	Level 1	Number	4	8	3	7	8	3	6	2
		Minimum	3.9%	8.8%	0.8%	6.1%	0.6%	0.4%	1.6%	3.8%
		Maximum	16.3%	46.2%	1.2%	22.0%	7.1%	1.4%	6.2%	11.4%
		Mean	10.5%	19.4%	1.1%	17.1%	3.8%	0.7%	3.8%	7.6%
		Median	11.0%	15.8%	1.2%	17.8%	3.4%	0.4%	4.0%	7.6%
	Level 2	Number	4	3	4	3	4	19	4	4
		Minimum	2.0%	3.2%	0.7%	1.8%	1.3%	0.2%	1.4%	3.6%
		Maximum	14.4%	15.8%	3.0%	20.5%	3.1%	2.9%	2.6%	110.0%
		Mean	6.8%	10.0%	1.9%	10.5%	2.2%	0.9%	2.2%	32.1%
		Median	5.5%	11.2%	1.9%	9.1%	2.1%	0.7%	2.3%	7.3%
	Level 3	Number	3	2	3	3	10	4	3	3
		Minimum	1.2%	0.8%	0.7%	9.7%	0.8%	0.5%	0.9%	2.7%
		Maximum	10.0%	19.0%	3.7%	26.2%	2.9%	1.4%	3.3%	9.0%
		Mean	6.1%	9.9%	2.5%	18.0%	1.7%	1.0%	2.3%	5.1%
		Median	7.2%	9.9%	3.0%	18.2%	1.7%	1.1%	2.6%	3.6%
	Level 4	Number	--	--	--	--	--	6	--	--
		Minimum	--	--	--	--	--	0.3%	--	--
		Maximum	--	--	--	--	--	17.8%	--	--
		Mean	--	--	--	--	--	3.5%	--	--
		Median	--	--	--	--	--	0.7%	--	--
	All Sediment	Number	11	13	10	13	22	32	13	9
		Minimum	1.2%	0.8%	0.7%	1.8%	0.6%	0.2%	0.9%	2.7%
		Maximum	16.3%	46.2%	3.7%	26.2%	7.1%	17.8%	6.2%	110.0%
		Mean	8.0%	15.8%	1.8%	15.8%	2.6%	1.4%	3.0%	17.6%
		Median	7.2%	14.4%	1.3%	17.8%	2.1%	0.7%	2.6%	4.5%

Table E-2. Evaluation of Precision - Relative Standard Deviations Calculated for the Rigaku ZSX Mini (Continued)

Matrix	Conc Range	Statistic	Nickel	Selenium	Silver	Vanadium	Zinc
Sediment	Level 1	Number	18	5	4	6	18
		Minimum	1.8%	2.5%	1.2%	1.7%	1.8%
		Maximum	25.5%	12.6%	5.2%	7.4%	18.4%
		Mean	5.7%	9.4%	2.3%	4.3%	6.1%
		Median	4.0%	10.8%	1.4%	4.4%	4.8%
	Level 2	Number	6	4	4	8	18
		Minimum	0.7%	2.0%	0.9%	3.1%	1.8%
		Maximum	8.4%	7.6%	3.3%	19.2%	3.6%
		Mean	4.5%	6.0%	1.7%	6.8%	2.7%
		Median	5.2%	7.2%	1.3%	4.7%	2.8%
	Level 3	Number	4	3	3	3	4
		Minimum	0.3%	0.9%	3.6%	2.8%	0.8%
		Maximum	1.8%	11.2%	5.0%	7.1%	5.2%
		Mean	1.3%	5.0%	4.2%	4.9%	2.6%
		Median	1.6%	3.1%	4.1%	4.7%	2.2%
	Level 4	Number	--	--	--	--	--
		Minimum	--	--	--	--	--
		Maximum	--	--	--	--	--
		Mean	--	--	--	--	--
		Median	--	--	--	--	--
	All Sediment	Number	28	12	11	17	27
		Minimum	0.3%	0.9%	0.9%	1.7%	0.8%
		Maximum	25.5%	12.6%	5.2%	19.2%	18.4%
		Mean	4.8%	7.2%	2.6%	5.6%	5.0%
		Median	3.7%	7.6%	1.5%	4.7%	3.6%

Table E-2. Evaluation of Precision - Relative Standard Deviations Calculated for the Rigaku ZSX Mini (Continued)

Matrix	Conc Range	Statistic	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury
All Samples	ZSX Mini II	Number	28	29	26	42	48	70	34	24
		Minimum	1.2%	0.7%	0.4%	1.6%	0.4%	0.2%	0.4%	1.4%
		Maximum	41.4%	46.2%	4.1%	29.5%	50.5%	43.2%	26.3%	136.8%
		Mean	8.8%	11.6%	1.9%	14.0%	4.1%	1.7%	3.2%	17.7%
		Median	6.4%	10.1%	1.6%	14.7%	2.3%	0.6%	2.0%	4.9%
All Samples	All Instruments	Number	206	320	209	338	363	558	392	192
		Minimum	0.5%	0.2%	0.4%	0.6%	0.1%	0.1%	0.2%	1.0%
		Maximum	97.7%	71.7%	92.8%	116.3%	58.3%	101.8%	115.6%	137.1%
		Mean	8.9%	11.2%	8.2%	15.9%	7.5%	5.2%	9.3%	14.3%
		Median	6.1%	8.2%	3.6%	12.1%	5.1%	2.2%	4.9%	6.8%

Table E-2. Evaluation of Precision - Relative Standard Deviations Calculated for the Rigaku ZSX Mini (Continued)

Matrix	Conc Range	Statistic	Nickel	Selenium	Silver	Vanadium	Zinc
All Samples	ZSX Mini II	Number	62	25	24	37	61
		Minimum	0.3%	0.1%	0.9%	0.4%	0.6%
		Maximum	164.2%	49.2%	5.2%	22.4%	192.9%
		Mean	8.0%	7.0%	2.5%	8.1%	8.3%
		Median	3.7%	3.9%	2.4%	5.9%	2.5%
All Samples	All Instruments	Number	403	195	177	218	471
		Minimum	0.3%	0.1%	0.6%	0.4%	0.1%
		Maximum	164.2%	98.8%	125.3%	86.1%	192.9%
		Mean	10.8%	7.2%	10.3%	12.5%	8.0%
		Median	7.0%	4.5%	5.2%	8.5%	5.3%

Notes:

--	No samples reported by the reference laboratory in this concentration range.
Number	Number of demonstration samples evaluated.
RSD	Relative standard deviation

Table E-3. Evaluation of Precision - Relative Standard Deviations Calculated for the Reference Laboratory

Matrix	Statistic	Antimony	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Selenium	Silver
All Soil	Number	17	23	15	34	26	38	33	16	35	13	13
	Minimum	3.6%	1.4%	0.9%	1.4%	0.0%	1.6%	0.0%	0.0%	0.0%	0.0%	2.3%
	Maximum	38.0%	45.8%	21.4%	137.0%	21.0%	46.2%	150.0%	50.7%	44.9%	22.7%	37.1%
	Mean	14.3%	11.7%	11.1%	14.3%	10.1%	10.2%	17.6%	13.8%	11.4%	8.9%	12.4%
	Median	9.8%	12.4%	9.0%	10.6%	9.1%	8.7%	13.2%	6.6%	10.0%	7.1%	7.5%
All Sediment	Number	7	24	10	26	21	31	22	10	27	12	10
	Minimum	2.9%	2.4%	2.9%	4.6%	1.8%	2.7%	0.0%	2.8%	0.6%	1.3%	1.0%
	Maximum	33.6%	36.7%	37.5%	35.5%	38.8%	37.5%	41.1%	48.0%	35.8%	37.3%	21.3%
	Mean	14.4%	10.7%	11.4%	9.8%	9.7%	9.9%	11.6%	14.3%	9.4%	10.0%	9.4%
	Median	9.1%	9.2%	8.2%	7.5%	8.9%	8.1%	7.4%	6.9%	7.3%	7.6%	6.6%
All	Number	24	47	25	60	47	69	55	26	62	25	23
	Minimum	2.9%	1.4%	0.9%	1.4%	0.0%	1.6%	0.0%	0.0%	0.0%	0.0%	1.0%
	Maximum	38.0%	45.8%	37.5%	137.0%	38.8%	46.2%	150.0%	50.7%	44.9%	37.3%	37.1%
	Mean	14.3%	11.2%	11.2%	12.4%	9.9%	10.1%	15.2%	14.0%	10.6%	9.4%	11.1%
	Median	9.5%	9.5%	9.0%	8.4%	8.9%	8.5%	8.6%	6.6%	8.2%	7.4%	7.1%

Table E-3. Evaluation of Precision - Relative Standard Deviations Calculated for the Reference Laboratory (Continued)

Matrix	Statistic	Vanadium	Zinc
All Soil	Number	21	35
	Minimum	0.0%	1.0%
	Maximum	18.1%	46.5%
	Mean	8.4%	10.4%
	Median	6.6%	9.1%
All Sediment	Number	17	27
	Minimum	2.2%	1.4%
	Maximum	21.9%	35.8%
	Mean	8.4%	8.9%
	Median	8.1%	6.9%
All	Number	38	62
	Minimum	0.0%	1.0%
	Maximum	21.9%	46.5%
	Mean	8.4%	9.8%
	Median	7.2%	7.4%

Notes:

Number	Number of demonstration samples evaluated.
RSD	Relative standard deviation

Table E-4. Evaluation of the Effects of Interferent Elements on RPDs (Accuracy) of Other Target Elements[1]

Parameter	**Statistic**	**Lead Effects on Arsenic**			**Copper Effects on Nickel**			**Nickel Effects on Copper**		
Interferent/Element Ratio		<5	5 - 10	>10	<5	5 - 10	>10	<5	5 - 10	>10
Number of Samples		15	7	7	43	5	14	39	1	8
RPD of Target Element[2]	Minimum	-3.3%	40.7%	-57.9%	-56.5%	44.6%	1.0%	7.6%	31.1%	11.9%
	Maximum	158.7%	87.8%	82.1%	111.8%	66.4%	78.8%	97.9%	31.1%	70.2%
	Mean	54.2%	71.1%	15.1%	57.7%	56.4%	47.8%	46.3%	31.1%	31.4%
	Median	45.5%	76.5%	11.7%	62.7%	55.3%	53.3%	46.1%	31.1%	30.1%
RPD of Target Element (Absolute Value)[2]	Minimum	3.3%	40.7%	1.0%	7.9%	44.6%	1.0%	7.6%	31.1%	11.9%
	Maximum	158.7%	87.8%	82.1%	111.8%	66.4%	78.8%	97.9%	31.1%	70.2%
	Mean	54.7%	71.1%	32.9%	60.8%	56.4%	47.8%	46.3%	31.1%	31.4%
	Median	45.5%	76.5%	16.3%	62.7%	55.3%	53.3%	46.1%	31.1%	30.1%
Interferent Concentration Range	Minimum	47	317	805	1	494	385	33	203	635
	Maximum	455	21053	9647	735	1301	3436	355	203	1357
	Mean	206	7435	2654	98	754	1398	94	203	976
	Median	173	3716	1390	62	700	1017	80	203	963
Target Element Concentration Range	Minimum	49	77	48	18	58	38	30	57	57
	Maximum	1361	2016	844	1357	139	226	3436	57	94
	Mean	264	762	192	273	92	81	724	57	73
	Median	92	487	93	99	88	60	565	57	70

Table E-4. Evaluation of the Effects of Interferent Elements on RPDs (Accuracy) of Other Target Elements[1] (Continued)

Parameter	Statistic	Zinc Effects on Copper			Copper Effects on Zinc		
Interferent/Element Ratio		<5	5 - 10	>10	<5	5 - 10	>10
Number of Samples		35	2	11	48	3	10
RPD of Target Element	Minimum	7.6%	40.9%	12.0%	-138.0%	11.2%	-4.1%
	Maximum	84.2%	47.4%	97.9%	104.2%	80.9%	72.3%
	Mean	44.1%	44.1%	41.7%	42.3%	43.5%	44.4%
	Median	40.2%	44.1%	31.0%	50.2%	38.4%	46.2%
RPD of Target Element (Absolute Value)	Minimum	7.6%	40.9%	12.0%	0.3%	11.2%	4.1%
	Maximum	84.2%	47.4%	97.9%	138.0%	80.9%	72.3%
	Mean	44.1%	44.1%	41.7%	50.2%	43.5%	45.2%
	Median	40.2%	44.1%	31.0%	53.0%	38.4%	46.2%
Interferent Concentration Range	Minimum	51	401	446	16	565	708
	Maximum	3102	3980	2670	1316	735	3436
	Mean	509	2190	1487	218	659	1682
	Median	92	2190	1430	73	676	1301
Target Element Concentration Range	Minimum	30	99	56	37	77	59
	Maximum	3436	965	107	3980	92	184
	Mean	771	532	76	827	86	90
	Median	567	532	77	410	88	78

Notes:

1. Concentrations are reported in units of milligrams per kilogram (mg/kg), or parts per million (ppm).
2. Table presents statistics for raw (unmodified) RPDs as well as absolute value RPDs.

< Less than.

> Greater than.

RPD Relative percent difference

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements

				Antimony				Arsenic		Cadmium	
				Reference Laboratory		Certified Value		Reference Laboratory		Reference Laboratory	
Matrix	Site	Matrix Description	Statistic	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val
Soil	AS	Fine to medium sand (steel processing)	Number	--	--	--	--	--	--	3	3
			Minimum	--	--	--	--	--	--	-162.5%	5.5%
			Maximum	--	--	--	--	--	--	-5.5%	162.5%
			Mean	--	--	--	--	--	--	-94.7%	94.7%
			Median	--	--	--	--	--	--	-116.1%	116.1%
Soil	BN	Sandy loam, low organic (ore residuals)	Number	4	4	1	1	6	6	5	5
			Minimum	-160.3%	3.5%	108.3%	108.3%	16.3%	16.3%	-87.4%	19.6%
			Maximum	3.5%	160.3%	108.3%	108.3%	79.1%	79.1%	57.1%	87.4%
			Mean	-112.2%	114.0%	108.3%	108.3%	56.2%	56.2%	-11.8%	42.4%
			Median	-146.1%	146.1%	108.3%	108.3%	64.4%	64.4%	-21.4%	26.8%
Soil	CN	Sandy loam (burn pit residue)	Number	2	2	2	2	1	1	2	2
			Minimum	-162.1%	12.7%	-84.9%	84.8%	-3.3%	3.3%	-165.0%	21.2%
			Maximum	-12.7%	162.1%	84.8%	84.9%	-3.3%	3.3%	-21.2%	165.0%
			Mean	-87.4%	87.4%	0.0%	84.9%	-3.3%	3.3%	-93.1%	93.1%
			Median	-87.4%	87.4%	0.0%	84.9%	-3.3%	3.3%	-93.1%	93.1%
Soil & Sediment	KP	Soil: Fine to medium quartz sand. Sed.: Sandy loam, high organic. (Gun and skeet ranges)	Number	2	2	--	--	--	--	--	--
			Minimum	-169.5%	137.3%	--	--	--	--	--	--
			Maximum	-137.3%	169.5%	--	--	--	--	--	--
			Mean	-153.4%	153.4%	--	--	--	--	--	--
			Median	-153.4%	153.4%	--	--	--	--	--	--
Sediment	LV	Clay/clay loam, salt crust (iron and other precipitate)	Number	4	4	4	4	3	3	5	5
			Minimum	-169.6%	0.1%	-84.4%	81.3%	11.7%	11.7%	-123.3%	12.3%
			Maximum	20.3%	169.6%	116.2%	116.2%	158.7%	158.7%	36.4%	123.3%
			Mean	-49.1%	59.3%	52.3%	94.5%	84.2%	84.2%	-29.8%	49.3%
			Median	-23.5%	33.7%	88.7%	90.2%	82.3%	82.3%	-31.9%	36.4%
Sediment	RF	Silty fine sand (tailings)	Number	5	5	5	5	10	10	5	5
			Minimum	-179.7%	20.6%	-134.7%	35.3%	-57.9%	10.2%	-164.9%	20.9%
			Maximum	58.7%	179.7%	134.0%	134.7%	49.2%	57.9%	29.2%	164.9%
			Mean	-71.0%	102.7%	5.5%	106.9%	26.3%	37.9%	-59.6%	71.3%
			Median	-75.6%	75.6%	35.3%	118.9%	36.6%	40.2%	-65.4%	65.4%

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements (Continued)

				Antimony				Arsenic		Cadmium	
				Reference Laboratory		Certified Value		Reference Laboratory		Reference Laboratory	
Matrix	Site	Matrix Description	Statistic	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val
Soil	SB	Coarse sand and gravel (ore and waste rock)	Number	5	5	1	1	2	2	1	1
			Minimum	-181.5%	14.8%	162.0%	162.0%	86.1%	86.1%	42.2%	42.2%
			Maximum	93.9%	181.5%	162.0%	162.0%	98.1%	98.1%	42.2%	42.2%
			Mean	-10.2%	75.3%	162.0%	162.0%	92.1%	92.1%	42.2%	42.2%
			Median	14.8%	54.1%	162.0%	162.0%	92.1%	92.1%	42.2%	42.2%
Sediment	TL	Silt and clay (slag-enriched)	Number	3	3	3	3	1	1	2	2
			Minimum	-138.0%	84.3%	25.1%	25.1%	56.8%	56.8%	-100.7%	64.7%
			Maximum	-84.3%	138.0%	108.9%	108.9%	56.8%	56.8%	-64.7%	100.7%
			Mean	-104.3%	104.3%	73.1%	73.1%	56.8%	56.8%	-82.7%	82.7%
			Median	-90.6%	90.6%	85.4%	85.4%	56.8%	56.8%	-82.7%	82.7%
Soil	WS	Coarse sand and gravel (roaster slag)	Number	3	3	--	--	6	6	3	3
			Minimum	-180.9%	28.3%	--	--	-4.5%	1.0%	-158.6%	85.3%
			Maximum	-28.3%	180.9%	--	--	87.8%	87.8%	-85.3%	158.6%
			Mean	-108.7%	108.7%	--	--	54.3%	55.8%	-118.9%	118.9%
			Median	-116.8%	116.8%	--	--	79.3%	79.3%	-112.8%	112.8%
	All		Number	28	28	16	16	29	29	26	26
			Minimum	-181.5%	0.1%	-134.7%	25.1%	-57.9%	1.0%	-165.0%	5.5%
			Maximum	93.9%	181.5%	162.0%	162.0%	158.7%	158.7%	57.1%	165.0%
			Mean	-77.6%	96.6%	45.4%	98.2%	48.8%	53.4%	-56.0%	71.1%
			Median	-87.4%	92.2%	85.1%	102.2%	47.7%	49.2%	-53.6%	60.9%

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements (Continued)

Matrix	Site	Matrix Description	Statistic	Chromium		Copper		Iron	
				Reference Laboratory		Reference Laboratory		Reference Laboratory	
				RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val
Soil	AS	Fine to medium sand (steel processing)	Number	2	2	3	3	3	3
			Minimum	38.3%	38.3%	39.0%	39.0%	19.2%	19.2%
			Maximum	48.5%	48.5%	97.9%	97.9%	109.1%	109.1%
			Mean	43.4%	43.4%	70.4%	70.4%	74.1%	74.1%
			Median	43.4%	43.4%	74.3%	74.3%	94.0%	94.0%
Soil	BN	Sandy loam, low organic (ore residuals)	Number	4	4	6	6	7	7
			Minimum	-14.2%	14.2%	29.7%	29.7%	48.6%	48.6%
			Maximum	92.4%	92.4%	53.6%	53.6%	58.9%	58.9%
			Mean	45.2%	52.3%	40.7%	40.7%	52.5%	52.5%
			Median	51.4%	51.4%	40.0%	40.0%	52.7%	52.7%
Soil	CN	Sandy loam (burn pit residue)	Number	1	1	3	3	3	3
			Minimum	16.5%	16.5%	7.6%	7.6%	25.7%	25.7%
			Maximum	16.5%	16.5%	65.0%	65.0%	76.3%	76.3%
			Mean	16.5%	16.5%	34.5%	34.5%	51.1%	51.1%
			Median	16.5%	16.5%	31.0%	31.0%	51.3%	51.3%
Soil & Sediment	KP	Soil: Fine to medium quartz sand. Sed.: Sandy loam, high organic. (Gun and skeet ranges)	Number	3	3	2	2	6	6
			Minimum	27.1%	27.1%	12.5%	12.5%	-148.5%	70.3%
			Maximum	43.0%	43.0%	27.0%	27.0%	-70.3%	148.5%
			Mean	35.7%	35.7%	19.8%	19.8%	-107.4%	107.4%
			Median	37.0%	37.0%	19.8%	19.8%	-105.0%	105.0%
Sediment	LV	Clay/clay loam, salt crust (iron and other precipitate)	Number	7	7	4	4	12	12
			Minimum	-119.8%	0.4%	11.9%	11.9%	-105.0%	12.8%
			Maximum	75.7%	119.8%	55.0%	55.0%	92.1%	105.0%
			Mean	8.7%	62.6%	37.2%	37.2%	31.3%	48.8%
			Median	52.7%	62.9%	40.9%	40.9%	33.7%	39.4%
Sediment	RF	Silty fine sand (tailings)	Number	6	6	13	13	13	13
			Minimum	-9.3%	0.9%	19.9%	19.9%	22.3%	22.3%
			Maximum	52.9%	52.9%	48.9%	48.9%	57.1%	57.1%
			Mean	29.9%	33.3%	31.8%	31.8%	37.0%	37.0%
			Median	42.2%	42.2%	31.1%	31.1%	35.2%	35.2%

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements (Continued)

Matrix	Site	Matrix Description	Statistic	Chromium Reference Laboratory RPD	 RPD ABS Val	Copper Reference Laboratory RPD	 RPD ABS Val	Iron Reference Laboratory RPD	 RPD ABS Val
Soil	SB	Coarse sand and gravel (ore and waste rock)	Number	10	10	4	4	12	12
			Minimum	-46.3%	2.0%	30.6%	30.6%	-6.1%	6.1%
			Maximum	68.7%	68.7%	70.2%	70.2%	75.6%	75.6%
			Mean	-1.1%	17.5%	48.6%	48.6%	55.9%	56.9%
			Median	-3.8%	7.8%	46.9%	46.9%	59.7%	59.7%
Sediment	TL	Silt and clay (slag-enriched)	Number	2	2	7	7	7	7
			Minimum	-5.0%	5.0%	57.6%	57.6%	20.7%	20.7%
			Maximum	23.3%	23.3%	84.2%	84.2%	76.5%	76.5%
			Mean	9.1%	14.1%	72.3%	72.3%	42.7%	42.7%
			Median	9.1%	14.1%	72.5%	72.5%	35.4%	35.4%
Soil	WS	Coarse sand and gravel (roaster slag)	Number	7	7	6	6	7	7
			Minimum	-88.7%	16.8%	12.0%	12.0%	34.8%	34.8%
			Maximum	55.7%	88.7%	50.8%	50.8%	69.5%	69.5%
			Mean	-19.0%	45.7%	38.1%	38.1%	55.1%	55.1%
			Median	-22.0%	29.3%	44.1%	44.1%	60.3%	60.3%
	All		Number	42	42	48	48	70	70
			Minimum	-119.8%	0.4%	7.6%	7.6%	-148.5%	6.1%
			Maximum	92.4%	119.8%	97.9%	97.9%	109.1%	148.5%
			Mean	12.0%	37.7%	43.5%	43.5%	33.0%	54.6%
			Median	16.7%	37.2%	40.0%	40.0%	46.6%	52.4%

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements (Continued)

Matrix	Site	Matrix Description	Statistic	Lead Reference Laboratory		Mercury Reference Laboratory		Nickel Reference Laboratory	
				RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val
Soil	AS	Fine to medium sand (steel processing)	Number	3	3	--	--	3	3
			Minimum	90.7%	90.7%	--	--	60.6%	60.6%
			Maximum	104.9%	104.9%	--	--	101.3%	101.3%
			Mean	99.9%	99.9%	--	--	77.7%	77.7%
			Median	104.1%	104.1%	--	--	71.3%	71.3%
Soil	BN	Sandy loam, low organic (ore residuals)	Number	5	5	1	1	6	6
			Minimum	63.6%	63.6%	-39.9%	39.9%	31.7%	31.7%
			Maximum	74.7%	74.7%	-39.9%	39.9%	81.0%	81.0%
			Mean	70.5%	70.5%	-39.9%	39.9%	58.9%	58.9%
			Median	73.5%	73.5%	-39.9%	39.9%	62.0%	62.0%
Soil	CN	Sandy loam (burn pit residue)	Number	2	2	2	2	3	3
			Minimum	86.3%	86.3%	-18.8%	18.8%	7.9%	7.9%
			Maximum	93.6%	93.6%	65.4%	65.4%	74.7%	74.7%
			Mean	90.0%	90.0%	23.3%	42.1%	51.4%	51.4%
			Median	90.0%	90.0%	23.3%	42.1%	71.5%	71.5%
Soil & Sediment	KP	Soil: Fine to medium quartz sand. Sed.: Sandy loam, high organic. (Gun and skeet ranges)	Number	6	6	--	--	3	3
			Minimum	-14.5%	14.5%	--	--	-10.0%	10.0%
			Maximum	64.5%	64.5%	--	--	11.9%	11.9%
			Mean	34.4%	39.3%	--	--	4.6%	11.2%
			Median	42.8%	42.8%	--	--	11.8%	11.8%
Sediment	LV	Clay/clay loam, salt crust (iron and other precipitate)	Number	2	2	4	4	11	11
			Minimum	43.6%	43.6%	-3.6%	3.6%	48.8%	48.8%
			Maximum	43.6%	43.6%	71.4%	71.4%	104.7%	104.7%
			Mean	43.6%	43.6%	43.4%	45.1%	70.4%	70.4%
			Median	43.6%	43.6%	52.8%	52.8%	65.5%	65.5%
Sediment	RF	Silty fine sand (tailings)	Number	8	8	5	5	13	13
			Minimum	54.7%	54.7%	-77.0%	31.8%	45.9%	45.9%
			Maximum	91.3%	91.3%	107.2%	107.2%	69.5%	69.5%
			Mean	75.3%	75.3%	12.6%	66.6%	57.8%	57.8%
			Median	78.5%	78.5%	31.8%	59.0%	55.9%	55.9%

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements (Continued)

				Lead		Mercury		Nickel	
				Reference Laboratory		Reference Laboratory		Reference Laboratory	
Matrix	Site	Matrix Description	Statistic	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val
Soil	SB	Coarse sand and gravel (ore and waste rock)	Number	--	--	10	10	10	10
			Minimum	--	--	-139.3%	5.3%	-56.5%	50.0%
			Maximum	--	--	134.7%	139.3%	111.8%	111.8%
			Mean	--	--	65.7%	94.6%	58.4%	69.7%
			Median	--	--	97.8%	112.1%	65.3%	65.3%
Sediment	TL	Silt and clay (slag-enriched)	Number	2	2	2	2	6	6
			Minimum	71.4%	71.4%	99.4%	99.4%	31.3%	31.3%
			Maximum	86.4%	86.4%	158.1%	158.1%	78.8%	78.8%
			Mean	78.9%	78.9%	128.8%	128.8%	60.0%	60.0%
			Median	78.9%	78.9%	128.8%	128.8%	66.8%	66.8%
Soil	WS	Coarse sand and gravel (roaster slag)	Number	6	6	--	--	7	7
			Minimum	46.5%	46.5%	--	--	1.0%	1.0%
			Maximum	70.7%	70.7%	--	--	50.4%	50.4%
			Mean	58.1%	58.1%	--	--	29.8%	29.8%
			Median	57.6%	57.6%	--	--	37.6%	37.6%
	All		Number	34	34	24	24	62	62
			Minimum	-14.5%	14.5%	-139.3%	3.6%	-56.5%	1.0%
			Maximum	104.9%	104.9%	158.1%	158.1%	111.8%	111.8%
			Mean	65.7%	66.6%	48.2%	76.7%	55.4%	57.5%
			Median	66.8%	66.8%	66.2%	74.2%	60.4%	60.4%

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements (Continued)

				Selenium		Silver		Vanadium		Zinc	
				Reference Laboratory		Reference Laboratory		Reference Laboratory		Reference Laboratory	
Matrix	Site	Matrix Description	Statistic	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val
Soil	AS	Fine to medium sand (steel processing)	Number	1	1	1	1	1	1	3	3
			Minimum	97.5%	97.5%	40.4%	40.4%	13.7%	13.7%	43.7%	43.7%
			Maximum	97.5%	97.5%	40.4%	40.4%	13.7%	13.7%	89.3%	89.3%
			Mean	97.5%	97.5%	40.4%	40.4%	13.7%	13.7%	71.5%	71.5%
			Median	97.5%	97.5%	40.4%	40.4%	13.7%	13.7%	81.4%	81.4%
Soil	BN	Sandy loam, low organic (ore residuals)	Number	4	4	4	4	4	4	7	7
			Minimum	57.9%	57.9%	-91.9%	36.8%	-27.6%	19.6%	21.2%	21.2%
			Maximum	110.4%	110.4%	-36.8%	91.9%	55.4%	55.4%	74.4%	74.4%
			Mean	90.2%	90.2%	-53.6%	53.6%	8.4%	32.1%	51.1%	51.1%
			Median	96.2%	96.2%	-42.8%	42.8%	3.0%	26.6%	54.6%	54.6%
Soil	CN	Sandy loam (burn pit residue)	Number	2	2	2	2	1	1	3	3
			Minimum	65.0%	65.0%	-96.7%	85.3%	26.5%	26.5%	0.3%	0.3%
			Maximum	110.8%	110.8%	-85.3%	96.7%	26.5%	26.5%	61.3%	61.3%
			Mean	87.9%	87.9%	-91.0%	91.0%	26.5%	26.5%	39.2%	39.2%
			Median	87.9%	87.9%	-91.0%	91.0%	26.5%	26.5%	56.1%	56.1%
Soil & Sediment	KP	Soil: Fine to medium quartz sand. Sed.: Sandy loam, high organic. (Gun and skeet ranges)	Number	--	--	--	--	--	--	2	2
			Minimum	--	--	--	--	--	--	-23.3%	11.2%
			Maximum	--	--	--	--	--	--	11.2%	23.3%
			Mean	--	--	--	--	--	--	-6.0%	17.2%
			Median	--	--	--	--	--	--	-6.0%	17.2%
Sediment	LV	Clay/clay loam, salt crust (iron and other precipitate)	Number	5	5	4	4	9	9	9	9
			Minimum	94.0%	94.0%	-112.6%	0.9%	-40.3%	3.1%	-9.9%	4.1%
			Maximum	109.1%	109.1%	2.6%	112.6%	41.4%	41.4%	62.3%	62.3%
			Mean	100.4%	100.4%	-44.0%	45.7%	1.0%	22.5%	24.2%	28.8%
			Median	100.3%	100.3%	-33.0%	34.7%	3.1%	19.8%	17.4%	17.4%
Sediment	RF	Silty fine sand (tailings)	Number	5	5	5	5	3	3	13	13
			Minimum	30.1%	30.1%	-138.9%	34.0%	19.2%	19.2%	28.4%	28.4%
			Maximum	112.9%	112.9%	-34.0%	138.9%	45.8%	45.8%	78.3%	78.3%
			Mean	82.7%	82.7%	-82.2%	82.2%	31.6%	31.6%	52.5%	52.5%
			Median	97.6%	97.6%	-64.0%	64.0%	29.7%	29.7%	48.4%	48.4%

Table E-5. Evaluation of the Effects of Soil Type on RPDs (Accuracy) of Target Elements (Continued)

				Selenium		Silver		Vanadium		Zinc	
				Reference Laboratory		Reference Laboratory		Reference Laboratory		Reference Laboratory	
Matrix	Site	Matrix Description	Statistic	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val	RPD	RPD ABS Val
Soil	SB	Coarse sand and gravel (ore and waste rock)	Number	3	3	1	1	9	9	10	10
			Minimum	101.5%	101.5%	-38.3%	38.3%	-91.1%	1.0%	-138.0%	10.8%
			Maximum	110.3%	110.3%	-38.3%	38.3%	38.3%	91.1%	104.2%	138.0%
			Mean	106.1%	106.1%	-38.3%	38.3%	-48.3%	57.0%	20.6%	50.3%
			Median	106.6%	106.6%	-38.3%	38.3%	-60.9%	60.9%	30.9%	36.2%
Sediment	TL	Silt and clay (slag-enriched)	Number	4	4	4	4	7	7	7	7
			Minimum	89.6%	89.6%	-110.6%	13.7%	-59.0%	22.0%	33.0%	33.0%
			Maximum	127.1%	127.1%	-13.7%	110.6%	-22.0%	59.0%	80.9%	80.9%
			Mean	114.3%	114.3%	-60.5%	60.5%	-42.0%	42.0%	60.2%	60.2%
			Median	120.3%	120.3%	-58.8%	58.8%	-41.0%	41.0%	63.9%	63.9%
Soil	WS	Coarse sand and gravel (roaster slag)	Number	1	1	4	4	3	3	7	7
			Minimum	101.5%	101.5%	-63.9%	22.8%	-27.6%	20.7%	28.6%	28.6%
			Maximum	101.5%	101.5%	59.6%	63.9%	35.2%	35.2%	76.1%	76.1%
			Mean	101.5%	101.5%	13.9%	45.8%	-4.4%	27.8%	57.1%	57.1%
			Median	101.5%	101.5%	29.9%	48.3%	-20.7%	27.6%	60.1%	60.1%
	All		Number	25	25	25	25	37	37	61	61
			Minimum	30.1%	30.1%	-138.9%	0.9%	-91.1%	1.0%	-138.0%	0.3%
			Maximum	127.1%	127.1%	59.6%	138.9%	55.4%	91.1%	104.2%	138.0%
			Mean	97.1%	97.1%	-46.7%	59.8%	-15.2%	36.7%	42.7%	49.0%
			Median	101.5%	101.5%	-44.3%	45.1%	-20.7%	35.2%	48.4%	48.6%

Notes:
Difference is the mean of all RPDs minus the mean site RPD (absolute values).

AS	Alton Steel Mill
BN	Burlington Northern Railroad/ASARCO East
CN	Naval Surface Warfare Center, Crane Division
KP	KARS Park – Kennedy Space Center
LV	Leviathan Mine/Aspen Creek
RF	Ramsey Flats – Silver Bow Creek
SB	Sulfur Bank Mercury Mine
TL	Torch Lake Superfund Site
WS	Wickes Smelter Site

Other Notes:

--	No samples reported by the reference laboratory in this concentration range.
Number	Number of demonstration samples evaluated.
RPD	Relative Percent Difference (raw value).
RPD ABS Val	Relative Percent Difference (absolute value).