United States
Environmental Protection
Agency

Office of Research and
Development
Washington, D.C. 20460

EPA/600/R-97/145
March 1998

Environmental Technology Verification Report

Field Portable X-ray Fluorescence Analyzer

Spectrace TN 9000 and TN Pb Field Portable X-ray Fluorescence Analyzers

SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION

Environmental Technology Verification Program

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Notice

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**FIELD PORTABLE X-RAY FLUORESCENCE ANALYZER**
APPLICATION:	**MEASUREMENT OF METALS IN SOIL**
TECHNOLOGY NAME:	**TN 9000**
COMPANY:	**TN SPECTRACE**
ADDRESS:	**2555 N. INTERSTATE HWY 35** **P.O. BOX 800** **ROUND ROCK, TX 78680-0800**
PHONE:	**(512) 388-9100**

The U.S. Environmental Protection Agency (EPA) has created a program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the Environmental Technology Verification (ETV) Program is to further environmental protection by substantially accelerating the acceptance and use of improved and more cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. This document summarizes the results of a demonstration of the Spectrace TN 9000 Analyzer.

PROGRAM OPERATION

The EPA, in partnership with recognized testing organizations, objectively and systematically evaluates the performance of innovative technologies. Together, with the full participation of the technology developer, they develop plans, conduct tests, collect and analyze data, and report findings. The evaluations are conducted according to a rigorous demonstration plan and established protocols for quality assurance. The EPA's National Exposure Research Laboratory, which conducts demonstrations of field characterization and monitoring technologies, selected PRC Environmental Management, Inc., as the testing organization for the performance verification of field portable X-ray fluorescence (FPXRF) analyzers.

DEMONSTRATION DESCRIPTION

In April 1995, the performance of seven FPXRF analyzers was determined under field conditions. Each analyzer was independently evaluated by comparing field analysis results to those obtained using approved reference methods. Standard reference materials (SRM) and performance evaluation (PE) samples also were used to independently assess the accuracy and comparability of each instrument.

The demonstration was designed to detect and measure a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The demonstration sites were located in Iowa (the RV Hopkins site) and Washington (the ASARCO site). These sites were chosen because they exhibit a wide range of concentrations for most of the target metals and are located in different climatological regions of the United States; combined, they exhibit three distinct soil types: sand, clay, and loam. The conditions at these sites are representative of those environments under which the technology would be expected to operate. Details of the demonstration, including a data summary and

discussion of results, may be found in the report entitled "Environmental Technology Verification Report, Field Portable X-ray Fluorescence Analyzer, Spectrace TN 9000 and TN Pb Field Portable X-ray Fluorescence Analyzers." The EPA document number for this report is EPA/600/R-97/145.

The EPA Method 6200 was tested and validated using the data derived from this demonstration. This method may be used to support the general application of FPXRF for environmental analysis.

TECHNOLOGY DESCRIPTION

This analyzer operates on the principle of energy dispersive X-ray fluorescence spectroscopy where the characteristic components of the excited X-ray spectrum are analyzed directly by an energy proportional response in an X-ray detector. Energy dispersion affords a highly efficient, full-spectrum measurement which enables the use of low intensity excitation sources (such as radioisotopes) and compact battery-powered, field-portable electronics. FPXRF instruments are designed to provide rapid analysis of metals in soil. This information allows investigation and remediation decisions to be made on-site and reduces the number of samples that need to be submitted for laboratory analysis. In the operation of these instruments, the user must be aware that FPXRF analyzers do not respond well to chromium and that detection limits may be 5 to 10 times greater than conventional laboratory methods. As with all field analysis programs, a portion of the samples should be sent to a laboratory for confirmatory analyses.

The TN 9000 is a commercially available instrument that can use up to three radioactive sources and a mercuric iodide semiconductor detector for the analysis of metals in soil. It is field portable, weighing less than 20 pounds, and can be battery powered for up to 8 hours. For this demonstration, the TN 9000's Soils Application software was configured to report concentrations for chromium, iron, nickel, copper, zinc, arsenic, lead, cadmium, antimony, and barium. Contaminant concentrations are computed using a fundamental parameters (FP) calibrated algorithm included in the analyzer's operations software. The FP calibration does not require site-specific calibration standards. The TN 9000 can conduct *in situ* measurements or measure samples in cups. At the time of testing, the TN 9000 cost about $58,000, or it could be leased for $6,000 per month or $3,500 for 2 weeks.

VERIFICATION OF PERFORMANCE

The performance characteristics of the TN 9000 include the following:

- **Detection limits:** Precision-based detection limits were determined by collecting 10 replicate measurements on site-specific soil samples with metals concentrations 2 to 5 times the expected MDLs. The results were 100 milligrams per kilogram (mg/kg) or less for all of the reported analytes except chromium, which was determined to be 200 mg/kg using the Fe^{55} source and 500 mg/kg using the Cd^{109} source which was used for the other reported analytes. Values for iron and cadmium were not reported due to an insufficient number of samples in the required concentration range.
- **Throughput:** Average throughput was 8.5 to 10.5 analyses per hour using a source count time of 220 seconds. This rate only represents the analysis time, since different personnel were used to prepare the samples.
- **Drift:** This was evaluated using the results of a daily analysis of an SRM which contained quantifiable levels of arsenic, barium, copper, lead, and zinc. Over the 18 days of the demonstration, the RSD values for the mean recovery of barium, copper, lead, and zinc were all less than 8 percent. The corresponding value for arsenic was 18.2 percent.
- **Completeness:** The TN 9000 produced results for 1,259 of the 1,260 samples analyzed, resulting in a completeness of 99.9 percent. The remaining sample was lost due to operator error in transferring the data.
- **Blank results:** During the demonstration, 37 blank samples were analyzed. None of the reported primary analytes were detected above the method detection limits. However, iron frequently reported a value above the MDL after analyzing samples with an iron concentration of greater than 20,000 mg/kg.
- **Precision:** The goal of the demonstration was to achieve relative standard deviations (RSD) less than 20 percent at analyte concentrations of 5 to 10 times the method detection limit. The RSD values for antimony,

arsenic, barium, copper, lead, and zinc were less than 8 percent. The corresponding value for chromium was 22 percent. Values for cadmium, iron, and nickel were not reported because too few samples containing the required concentrations were measured.

- **Accuracy:** Intramethod accuracy was assessed using site-specific soil PE samples and soil SRMs. The data showed that 37 of 41 or 90.2 percent of the PE sample analytes had recoveries within the quantitative acceptance range of 80 - 120 percent. A corresponding 22 of 24 or 91.7 percent of the SRM analytes were within the 80 - 120 percent recovery range. The TN 9000 gave more accurate results when the reference sample closely matched the matrix used to set the fundamental parameters calibration for the analyzer.
- **Comparability:** This demonstration showed that the TN 9000 produced data that exhibited a $\log_{10}$-$\log_{10}$ linear correlation to the reference data. The coefficient of determination (r^2) which is a measure of the degree of correlation between the reference and field data was 0.95 for arsenic, 0.95 for copper, 0.96 for lead, 0.93 for zinc, 0.79 for barium, and 0.78 for chromium. Results for iron, nickel, cadmium, and antimony were not reported due to limited sample data.
- **Data quality levels:** Using the demonstration derived precision RSD results and the coefficient of determination as the primary qualifiers, the TN 9000 produced definitive level data for arsenic, copper, lead, and zinc; quantitative level data for barium; and data of qualitative screening level for chromium. Values for iron, nickel, cadmium, and antimony could not be assigned without adequate precision or comparability data.

The results of the demonstration show that the Spectrace TN 9000 can provide useful, cost-effective data for environmental problem-solving and decision-making. Undoubtedly, it will be employed in a variety of applications, ranging from serving as a complement to data generated in a fixed analytical laboratory to generating data that will stand alone in the decision-making process. As with any technology selection, the user must determine what is appropriate for the application and the project data quality objectives.

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

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DEMONSTRATION DESCRIPTION

In April 1995, the performance of seven FPXRF analyzers was determined under field conditions. Each analyzer was independently evaluated by comparing field analysis results to those obtained using approved reference methods. Standard reference materials (SRM) and performance evaluation (PE) samples also were used to independently assess the accuracy and comparability of each instrument.

The demonstration was designed to detect and measure a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The demonstration sites were located in Iowa (the RV Hopkins site) and Washington (the ASARCO site). These sites were chosen because they exhibit a wide range of concentrations for most of the target metals and are located in different climatological regions of the United States; combined, they exhibit three distinct soil types: sand, clay, and loam. The conditions at these sites are representative of those environments under which the technology would be expected to operate. Details of the demonstration, including a data summary and

discussion of results, may be found in the report entitled "Environmental Technology Verification Report, Field Portable X-ray Fluorescence Analyzer, Spectrace TN 9000 and TN Pb Field Portable X-ray Fluorescence Analyzers." The EPA document number for this report is EPA/600/R-97/145.

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TECHNOLOGY DESCRIPTION

This analyzer operates on the principle of energy dispersive X-ray fluorescence spectroscopy where the characteristic energy components of the excited X-ray spectrum are analyzed directly by an energy proportional response in the X-ray detector. Energy dispersion affords a highly efficient, full-spectrum measurement which enables the use of low intensity excitation sources (such as radioisotopes) and compact battery-powered, field-portable electronics. The FPXRF instruments are designed to provide rapid analysis of metals in soil. This information allows investigation and remediation decisions to be made on-site and reduces the number of samples that need to be submitted for laboratory analysis. In the operation of these instruments, the user must be aware that FPXRF analyzers do not respond well to chromium and that detection limits may be 5 to 10 times greater than conventional laboratory methods. As with all field collection programs, a portion of the samples should be sent to a laboratory for confirmatory analyses.

The TN Pb Analyzer was specifically designed to analyze for lead in a variety of matrices. It is field portable, weighing less than 20 pounds, and can be battery powered up to 8 hours. It uses a single radioactive source (cadmium-109) and a mercuric iodide semiconductor detector to analyze metals in soils using relatively short count times (60 seconds). The single radioactive source limits the number of analytes which can be detected. In this demonstration, the TN Pb Analyzer's Soils Application software was configured to report concentrations for arsenic, chromium, copper, lead, and zinc. Contaminant concentrations are computed using a fundamental parameters (FP) calibrated algorithm included in the analyzer's operations software. The FP method does not require site-specific calibration samples; however, such samples can be used to customize the calibration to a particular matrix. The TN Pb Analyzer can conduct *in situ* measurements or measure samples in cups. At the time of the demonstration, the cost of the TN Pb Analyzer was about $39,500, or it could be leased for $5,500 per month or $3,000 for 2 weeks.

VERIFICATION OF PERFORMANCE

The performance characteristics of the TN Pb Analyzer include the following:

- **Detection limits:** Precision-based detection limits were determined by collecting 10 replicate measurements on site-specific soil samples with metals concentrations 2 to 5 times the expected MDLs. The results were 115 milligrams per kilogram (mg/kg) or less for arsenic, copper, lead, and zinc. Chromium was determined to be 460 mg/kg.
- **Throughput:** Average throughput was between 20 and 25 analyses per hour using a count time of 60 seconds. This rate only represents the analysis time since different personnel were used to prepare the samples.
- **Drift:** Based on a daily analysis of an SRM, which contained quantifiable levels of arsenic, copper, lead, and zinc, the drift RSD values for the mean recovery of these analytes were less than 8 percent.
- **Completeness:** The TN Pb Analyzer produced results for all of the 1,260 samples for a completeness of 100 percent.
- **Blank results:** During the demonstration, a total of 20 SiO_2 blank samples was analyzed. None of the reported analytes were detected above the method detection limits.
- **Precision:** The goal of the demonstration was to achieve relative standard deviations (RSD) of less than 20 percent at analyte concentrations of 5 to 10 times the method detection limits. The RSD values for arsenic, copper, lead, and zinc were less than 10 percent. A value for chromium was not determined due to a lack of sufficient samples in the required concentration range.

- **Accuracy:** Intramethod accuracy was assessed using site-specific PE soil samples and soil SRMs. The data showed that 20 of 28 results (71.4 percent) of the PE sample analytes had recoveries within the 80 - 120 percent quantitative acceptance range and that 100 percent (16 of 16) of the SRM analytes were within this range. Results were more accurate when the sample closely matched the matrix used to set the fundamental parameters calibration.
- **Comparability:** This demonstration showed that the TN Pb Analyzer produced data that exhibited a $\log_{10}$-$\log_{10}$ linear correlation to the reference data. The coefficient of determination (r^2) which is a measure of the degree of correlation between the reference and field data was 0.95 for arsenic, 0.94 for copper, 0.95 for lead, and 0.92 for zinc. The value for chromium, 0.55, was derived primarily from clay soil at the RV Hopkins site.
- **Data quality levels:** Using the demonstration derived precision RSD results and the coefficient of determination as the primary qualifiers, the TN Pb Analyzer produced definitive level data for arsenic, copper, lead, and zinc. A value for chromium could not be assigned without adequate precision data.

The results of the demonstration show that the Spectrace TN Pb Analyzer can provide useful, cost-effective data for environmental problem-solving and decision-making. Undoubtedly, it will be employed in a variety of applications, ranging from serving as a complement to data generated in a fixed analytical laboratory to generating data that will stand alone in the decision-making process. As with any technology selection, the user must determine what is appropriate for the application and the project data quality objectives.

Gary J. Foley, Ph.D.
Director
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Office of Research and Development

Foreword

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

The National Exposure Research Laboratory (NERL) is the Agency's center for the 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 develop and evaluate technologies for the characterization and monitoring of air, soil, and water; support regulatory and policy decisions; and provide the science support needed to ensure effective implementation of environmental regulations and strategies.

The EPA's Superfund Innovative Technology Evaluation (SITE) Program evaluates technologies for the characterization and remediation of contaminated Superfund and Resource Conservation and Recovery Act (RCRA) corrective action sites. The SITE Program was created to provide reliable cost and performance data to speed the acceptance of innovative characterization and monitoring technologies.

Effective measurement and monitoring technologies are needed to assess the degree of contamination at a site, to provide data which can be used to determine the risk to public health or the environment, to supply the necessary cost and performance data to select the most appropriate technology, and to monitor the success or failure of a remediation process. One component of the SITE Program, the Monitoring and Measurement Technologies Program, demonstrates and evaluates innovative technologies to meet these needs.

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

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Abstract

In April 1995, the U.S. Environmental Protection Agency (EPA) conducted a demonstration of field portable X-ray fluorescence (FPXRF) analyzers. The primary objectives of this demonstration were (1) to determine how well FPXRF analyzers perform in comparison to a standard reference method, (2) to identify the effects of sample matrix variations on the performance of FPXRF, (3) to determine the logistical and economic resources needed to operate these analyzers, and (4) to test and validate an SW-846 draft method for FPXRF analysis. The demonstration design was subjected to extensive review and comment by the EPA's National Exposure Research Laboratory, EPA Regional and Headquarters Superfund technical staff, the EPA's Office of Solid Waste–Methods Section, and the technology developers.

Two sites were used for this demonstration: RV Hopkins and the ASARCO Tacoma Smelter. RV Hopkins is an active steel drum recycling facility and the location of a former battery recycling operation. It is located in Davenport, Iowa. The ASARCO site is a former copper and lead smelter and is located in Tacoma, Washington. The samples analyzed during this demonstration were represented by three distinct soil textures: sand, clay, and loam. The reference methods used to evaluate the comparability of data were EPA SW-846 Methods 3050A and 6010A, "Acid Digestion of Sediments, Sludges, and Soils" and "Inductively Coupled Plasma-Atomic Emission Spectroscopy," respectively.

The FPXRF analyzers tested in this demonstration were designed to provide rapid, real-time analysis of metals concentrations in soil samples. This information will allow investigation and remediation decisions to be made on-site more efficiently and can reduce the number of samples that need to be submitted for confirmatory analysis. Of the seven commercially available analyzers tested, one is manufactured by Niton Corporation (the XL Spectrum Analyzer); two are manufactured by TN Spectrace (the TN 9000 and TN Pb Analyzer); two are manufactured by Metorex Inc. (the X-MET 920-P Analyzer and the X-MET 920-MP Analyzer); one is manufactured by HNU Systems, Inc. (the SEFA-P Analyzer); and one is manufactured by Scitec Corporation (the MAP Spectrum Analyzer). The X-MET 940, a prototype FPXRF analyzer developed by Metorex, was given special consideration and replaced the X-MET 920-P for part of the RV Hopkins sample analyses. This environmental technology verification report (ETVR) presents information regarding the TN 9000 and TN Pb Analyzers. Separate ETVRs have been published for the other analyzers demonstrated.

Quantitative data were provided by both of the Spectrace analyzers on a real-time basis. The TN Pb Analyzer reported fewer target analytes than the TN 9000 and used shorter count times. The shorter count times resulted in a nearly two- to threefold increase in sample throughput. Both the TN 9000 and the TN Pb analyzers provided definitive level (equivalent to reference data) quality data for arsenic, lead, zinc, and copper; the TN 9000 produced quantitative screening level (not equivalent to reference data, but correctable with confirmatory analysis) quality data for barium. TN 9000 data for chromium was classified as qualitative, based primarily on the results of the precision determination. Data quality levels

for the remaining analytes could not be assigned due to the lack of precision or correlation data. The TN Pb Analyzer did not report nickel, iron, barium, cadmium, or antimony and did not report a precision value for chromium in the concentration range specified to determine the data quality level. These results were obtained using a factory-set fundamental parameters calibration. Sample homogenization was the single most important factor influencing data comparability.

This study showed that the two analyzers produced data that exhibited a $\log_{10}$-$\log_{10}$ linear correlation. Through regression analysis of $\log_{10}$ transformed data, the analyzers' data can be corrected to be even more comparable to reference data. Correction of the in situ-prepared data resulted in up to an eightfold increase in average relative accuracy for both the TN Pb and TN 9000 analyzers. Unless a user has regulatory approval, confirmatory (reference) sampling and data correction is recommended when using these analyzers for site characterization or remediation monitoring.

This demonstration found that both TN Spectrace FPXRF analyzers were generally simple to operate in the field. The operators required no specialized experience or training. Ownership and operation of this analyzer may require specific licensing by state nuclear regulatory agencies. There are special radiation safety training requirements and costs associated with this type of license. Generally, either the developer's listed or field-based method detection limits were 5 times or more higher than the reference method detection limits. The TN 9000 and TN Pb Analyzer were both effective tools for field-based analysis of metals contamination in soil and may allow investigation or remediation decisions to be made more efficiently on-site which may reduce the number of samples that need to be submitted for confirmatory analysis.

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List of Abbreviations and Acronyms

α	alpha
β	beta
µg	microgram
µm	micrometer
AC	alternating current
Am^{241}	americium-241
CCB	continuing calibration blank
CCV	continuing calibration verification
Cd^{109}	cadmium-109
CI	confidence interval
CLP	Contract Laboratory Program
cm	centimeter
cm^2	square centimeter
cm^3	cubic centimeter
CRM	certified reference material
EPA	Environmental Protection Agency
ERA	Environmental Resource Associates
eV	electron volt
Fe^{55}	iron-55
FP	fundamental parameter
FPXRF	field portable X-ray fluorescence
HgI_2	mercuric iodide
ICAL	initial calibration
ICB	initial calibration blank
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICS	interference check standard
ICV	initial calibration verification
IDL	instrument detection limit
IDW	investigation-derived waste
ETVR	environmental technology verification report
keV	kiloelectron volt
LCS	laboratory control samples
log_{10}	base 10 logarithm
LRL	lower reporting limit
MCA	multichannel analyzer
mCi	millicurie
MDL	method detection limit
mg/kg	milligram per kilogram
mL	milliliter
mm	millimeter
mrem/hr	millirems per hour

MMTP	Monitoring and Measurement Technologies Program
MRI	Midwest Research Institute
NERL-ESD	National Exposure Research Laboratory—Environmental Sciences Division
NIST	National Institute of Standards and Technology
NRMRL	National Risk Management Research Laboratory
OSW	Office of Solid Waste
PAL	performance acceptance limit
PARCC	precision, accuracy, representativeness, completeness, and comparability
PC	personal computer
PE	performance evaluation
PI	prediction interval
ppm	part per million
PRC	PRC Environmental Management, Inc.
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
r	correlation coefficient
r^2	coefficient of determination
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
RSD	relative standard deviation
RTC	Resource Technology Corporation
SD	standard deviation
SiO_2	silicon dioxide
SITE	Superfund Innovative Technology Evaluation
SOP	standard operating procedure
SRM	standard reference material
TC	toxicity characteristic
USGS	United States Geological Survey
XRF	X-ray fluorescence

Acknowledgments

The U.S. Environmental Protection Agency (EPA) wishes to acknowledge the support of all those who helped plan and conduct this demonstration, interpret data, and prepare this report. In particular, for demonstration site access and relevant background information, Tom Aldridge (ASARCO) and Harold Abdo (RV Hopkins); for turnkey implementation of this demonstration, Eric Hess, Patrick Splichal, and Harry Ellis (PRC Environmental Management, Inc.); for editorial and publication support, Suzanne Ladish, Anne Witebsky, Karen Bollinger, and Ed Hubert (PRC Environmental Management, Inc.); for technical and peer review, Paula Hirtz, David Farnam, and Alan Byrnes (PRC Environmental Management, Inc.); for analyzer operation, Bryce Smith, TN 9000, and Robert Beilfuss, TN Pb Analyzer (PRC Environmental Management, Inc.); for sample preparation, Scott Schulte, Keith Brown, and Curt Enos (PRC Environmental Management, Inc.); for EPA project management, Stephen Billets, National Exposure Research Laboratory–Environmental Sciences Division; and for peer review, Sam Goforth (independent consultant), John Wallace (Wallace Technologies), Shirley Wasson (National Risk Management Research Laboratory), Brian Schumacher (National Exposure Research Laboratory), and Bill Engelmann (National Exposure Research Laboratory). In addition, we gratefully acknowledge the participation of Oliver Fordham, EPA Office of Solid Waste; Piper Peterson, EPA Region 10; Brian Mitchell, EPA Region 7; and Todd Rhea, Peter Berry, and Raj Natarajan, TN Spectrace.

Section 1
Executive Summary

In April 1995, the U.S. Environmental Protection Agency (EPA) sponsored a demonstration of field portable X-ray fluorescence (FPXRF) analyzers. The primary objectives of this demonstration were to evaluate these analyzers for: (1) their analytical performance relative to standard analytical methods, (2) the influence of sample matrix variations (texture, moisture, heterogeneity, and chemical composition) on performance, (3) the logistical and economic resources needed to operate these technologies in the field, and (4) to test and validate an SW-846 draft method for FPXRF analysis. Secondary objectives for this demonstration were to evaluate FPXRF analyzers for their reliability, ruggedness, cost, range of usefulness, data quality, and ease of operation.

This demonstration was intended to provide users a reference measure of performance and a guide for the application of this technology. In this demonstration, the reference methods for evaluating the comparability of data were SW-846 Methods 3050A and 6010A, "Acid Digestion of Sediments, Sludges, and Soils" and "Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)," respectively.

The EPA requested that PRC Environmental Management, Inc. (PRC) assist in the planning, execution, and reporting on a demonstration of FPXRF analyzers. This demonstration was conducted under the EPA's Superfund Innovative Technology Evaluation (SITE) Program and managed by the National Exposure Research Laboratory-Environmental Sciences Division (NERL-ESD) under the Monitoring and Measurement Technologies Program (MMTP), Las Vegas, Nevada.

The FPXRF analyzers, tested in this demonstration, were designed to provide rapid, real-time analysis of metals concentrations in soil samples. This information will allow investigation and remediation decisions to be made on-site more efficiently, and it should reduce the number of samples that need to be submitted for confirmatory analysis. Of the seven commercially available analyzers evaluated, one is manufactured by HNU Systems, Inc. (the SEFA-P Analyzer); two are manufactured by TN Spectrace (the TN 9000 and TN Pb Analyzer); one is manufactured by Niton Corporation (the Niton XL Spectrum Analyzer); one is manufactured by Scitec Corporation (the MAP Spectrum Analyzer); and two are manufactured by Metorex Inc. (the X-MET 920-P Analyzer and the X-MET 920-MP Analyzer). The X-MET 940, a prototype FPXRF analyzer developed by Metorex, was given special consideration and replaced the X-MET 920-P for part of the demonstration. This environmental technology evaluation report (ETVR) presents information relative to the TN Spectrace TN 9000 and TN Pb analyzers. Separate ETVRs will be published for the other analyzers that were demonstrated.

The target analytes for this demonstration were selected from the Resource Conservation and Recovery Act's (RCRA) Toxicity Characteristic (TC) list, analytes known to have a high aquatic toxicity, and

analytes likely to produce interferences for the FPXRF analyzers. The primary analytes for these comparisons were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. Because of design considerations, not all of these analytes were determined by each instrument.

To demonstrate the analyzers, hazardous waste sites in Iowa (the RV Hopkins site) and in Washington (the ASARCO site) were selected. The sites were chosen because they exhibit a wide range of concentrations for most of the target analytes, are located in different climatological regions of the United States, and combined they exhibit three distinct soil textures: sand, clay, and loam.

This demonstration found that the TN 9000 and TN Pb analyzers were simple to operate in the field. The developer provided a training course for the technology operators similar to that provided to a purchaser of the equipment. The training encompassed enough FPXRF theory and hands-on analyzer use to allow the operators to manipulate the data collection software, calibrate the analyzer, and adjust instrument parameters such as count times and target analytes. The training and subsequent technical support, required during the demonstration, provided additional guidance on calibration procedures and data usability. Based on this experience, more training would have helped in the successful application of this analyzer. The analyzers did not experience an operational failure resulting in project down time or data loss during the analysis of more than 1,260 soil samples. The analyzers were field portable, and could operate on battery power or on alternating current. The analyzers required an auxiliary computer to process and store data. Downloading data to both paper and electronic format was accomplished without difficulty.

The TN Pb Analyzer reports results for fewer analytes than the TN 9000. Of the target analytes for this demonstration, the TN Pb Analyzer reported lead, arsenic, copper, chromium, and zinc. Iron, nickel, cadmium and antimony were not reported by the TN Pb Analyzer. The TN 9000 reported all of the target analytes for this demonstration. The TN Pb Analyzer uses a single radioactive source and the TN 9000 can use up to three unique radioactive sources. The TN Pb Analyzer used only one source and a shorter count time resulted in a two- to threefold increase in sample throughput for the TN Pb Analyzer relative to the TN 9000.

The TN Pb Analyzer produced data meeting definitive level (equivalent to reference data) criteria for lead, zinc, arsenic, and copper. The TN 9000 provided definitive level quality data for arsenic, copper, lead, and zinc; and data of quantitative screening level quality for barium. This analyzer produced qualitative screening level data for chromium. Data quality levels could not be assigned for chromium with the TN Pb Analyzer and for nickel, iron, cadmium, and antimony for the TN 9000 due to a lack of adequate precision or correlation data.

Both analyzers exhibited precision similar to the reference methods at the 5 to 10 times the precision-based method detection limit (MDL) concentration level. As expected, the chromium data generally showed the poorest precision of the primary analytes. Of the four sample preparation steps evaluated, the initial sample homogenization had the greatest impact on data comparability. Site and soil texture did not appear to affect data comparability.

Based on the performance of both TN Spectrace analyzers, this demonstration found them to be effective tools for characterizing the concentration of metals in soil samples. As with all FPXRF analyzers, unless a user has regulatory approval, confirmatory (reference) sampling and data correction is recommended when using these analyzers for site characterization and remediation monitoring.

Section 2
Introduction

This environmental technology evaluation report (ETVR) presents information on the demonstration of both the Spectrace TN Pb and the TN 9000 analyzers. These analyzers were developed to perform elemental analyses (metals quantitation) in the petroleum and petrochemical industry, the mining and minerals industry, and the environmental field. These analyzers use a mercuric iodide (HgI_2) detector with radioactive sources to quantitate metals concentrations. Both analyzers can be operated in either an *in situ* or intrusive mode. The *in situ* mode is commonly called a "point-and-shoot" mode. In this mode of operation, the point of measurement on the soil surface is cleared of loose debris and organic matter, the analyzer's probe is then placed in direct contact with the soil surface, and a measurement is taken. In the intrusive mode of operation, a soil sample is physically collected, dried or sieved, and then placed into a sample cup. The cup is placed into an analysis chamber on the probe and a measurement is taken.

This section provides general information about the demonstration such as the purpose, objectives, and design. Section 3 presents and discusses the quality of the data produced by the reference methods against which both analyzers were evaluated. Section 4 discusses the TN Pb Analyzer, its capabilities, reliability, throughput, accuracy, precision, comparability to reference methods, and other performance factors. Section 5 provides the same information for the TN 9000. Section 6 discusses the potential applications of both analyzers, presents a method for data correction, and suggests a framework for a standard operating procedure (SOP). Section 7 lists references cited in this ETVR.

Demonstration Background, Purpose, and Objectives

The demonstration was conducted under the Monitoring and Measurement Technologies Program (MMTP), a component of the SITE Program. MMTP is managed by NERL-ESD, Las Vegas, Nevada. The goal of the MMTP is to identify and demonstrate new, innovative, and commercially available technologies that can sample, identify, quantify, or monitor changes in contaminants at hazardous waste sites. This includes those technologies that can be used to determine the physical characteristics of a site more economically, efficiently, and safely than conventional technologies. The SITE Program is administered by the National Risk Management Research Laboratory, Cincinnati, Ohio.

The purpose of this demonstration was to provide the information needed to fairly and thoroughly evaluate the performance of FPXRF analyzers to identify and quantify metals in soils. The primary objectives were to evaluate FPXRF analyzers in the following areas: (1) their accuracy and precision relative to conventional analytical methods; (2) the influence of sample matrix variations (texture, moisture, heterogeneity, and chemical composition) on their performances; (3) the logistical and economic resources needed to operate these analyzers; and (4) to test and validate an SW-846 draft method for FPXRF analysis.

Secondary objectives for this demonstration were to evaluate FPXRF analyzers for their reliability, ruggedness, cost, range of usefulness, data quality, and ease of operation. The performances of the FPXRF analyzers were not compared against each other. Instead, the performance of each analyzer was independently and individually compared to that of conventional analytical methods commonly used in regulatory enforcement or compliance activities. In addition, each analyzer's performance was assessed relative to measurements of standard reference materials (SRM), performance evaluation (PE) samples, and other quality control (QC) samples.

A special request was made by Mr. Oliver Fordham, the demonstration's technical advisor, EPA Office of Solid Waste (OSW), for Midwest Research Institute (MRI) to analyze some of the soil samples to validate the performance of draft Method 3052 "Microwave Assisted Acid Digestion of Ash and Other Siliceous Wastes." Thirty percent of the soil samples were extracted using draft Method 3052 and then analyzed by Method 6010A. The data generated from the draft Method 3052 and Method 6010A analysis were not used for comparative purposes to the FPXRF data obtained in this demonstration.

Reference Methods

To assess the performance of each analyzer, FPXRF data was compared to reference data. The reference methods used for this assessment were EPA SW-846 Methods 3050A/6010A, which are considered the standards for metals analysis in soil for environmental applications. For purposes of this demonstration, the term "reference" is substituted for "confirmatory" since the data was used as a baseline for comparison. MRI was awarded the subcontract to analyze soil samples using the reference methods in accordance with Federal Acquisition Regulations. The award was made based on MRI's costs, ability to meet the demonstration's quality assurance project plan (QAPP), requirements, and as the only commercial laboratory identified that could perform all the analyses in the required timeframe.

Method 3050A is the standard acid extraction method used for determining metals concentrations in soil samples. It is not a total digestion method, and potentially it does not extract all the metals in a soil sample. Method 6010A is the standard method used to analyze Method 3050A extracts. Both of these methods are described in Section 3.

High quality, well documented reference laboratory results were essential for meeting the objectives of the demonstration. For an accurate assessment, the reference methods had to provide a known level of data quality. For all measurement and monitoring activities conducted by the EPA, the Agency requires that data quality parameters be established based on the end uses of the data. Data quality parameters usually include five indicators of data quality referred to as the PARCC parameters: precision, accuracy, representativeness, completeness, and comparability. In addition, method detection limits (MDLs) are often used to assess data quality.

Reference methods were evaluated using the PARCC parameters to establish the quality of data generated and to ensure that the comparison of FPXRF analyzers to reference methods was acceptable. The following paragraphs provide definitions of each of the PARCC parameters.

Precision refers to the degree of mutual agreement between replicate measurements and provides an estimate of random error. Precision is often expressed in terms of relative standard deviation (RSD) between replicate samples. The term relative percent difference (RPD) is used to provide this estimate of random between duplicate samples.

Accuracy refers to the difference between a sample result and the reference or true value. Bias, a measure of the departure from perfect accuracy, can be calculated from the reference or true value. Accuracy and bias for the reference laboratory were assessed by evaluating calibration standard linearity, method blank results and the percent recoveries of matrix spike samples, laboratory control samples (LCS), standard reference materials (SRMs), and PE samples.

Representativeness refers to the degree to which data accurately and precisely measures the conditions and characteristics of the parameter of interest. Representativeness for the reference laboratory was ensured by executing consistent sample collection procedures including sample locations, sampling procedures, storage, packaging, shipping, equipment decontamination, and proper laboratory sample handling procedures. Representativeness was ensured by using the appropriate reference method at its optimum capability to provide results that represent the most accurate and precise measurement it is capable of achieving. The combination of the existing method requirements supplemented by the demonstration QAPP provided the guidance to assure optimum performance of the method. Representativeness was assessed by evaluating calibration standards, method blank samples, duplicate samples, and PE samples.

Completeness refers to the amount of data collected from a measurement process compared to the amount that was expected to be obtained. For the reference data, completeness referred to the proportion of valid, acceptable data generated.

Comparability refers to the confidence with which one data set can be compared to another. Data generated from the reference methods should provide comparable data to any other laboratory performing analysis of the same samples with the same analytical methods. Comparability for the reference methods was achieved through the use of standard operating procedures (SOPs), EPA-published guidance, and the demonstration QAPP. QC samples that were used to evaluate comparability include: calibration standards, method blank samples, matrix spike samples, replicate samples, LCSs, SRMs, and PE samples.

Site Selection

PRC conducted a search for suitable demonstration sites between September and November 1994. The following criteria were used to select appropriate sites:

- The site owner had to agree to allow access for the demonstration.
- The site had to have soil contaminated with some or all of the target heavy metals. (Slag, ash, and other deposits of mineralized metals would not be assessed during the demonstration.)
- The site had to be accessible to two-wheel drive vehicles.
- The site had to exhibit one or more of the following soil textures: sand, clay, or loam.
- The site had to exhibit surface soil contamination.
- The sites had to be situated in different climatological environments.

PRC contacted NERL-ESD, regional EPA offices, state environmental agencies, metals fabrication, and smelting contacts to create an initial list of potential demonstration sites. PRC received considerable assistance from the EPA RCRA and Superfund branches in Regions 4, 6, 7, 8, 9, and 10. PRC also contacted the Montana Department of Health and Environment, the Nevada Bureau of Mines and Geology,

the Oklahoma Department of Environmental Quality, the Arizona Department of Environmental Quality, the Missouri Department of Natural Resources, the Arizona Bureau of Geology, and the New Mexico Bureau of Mines and Mineral Resources. PRC surveyed its offices in Kansas City, Kansas; Atlanta, Georgia; Denver, Colorado; Dallas, Texas; Albuquerque, New Mexico; Helena, Montana; Chicago, Illinois; Seattle, Washington; and San Francisco, California, for information regarding potential sites. These PRC offices have existing RCRA, Superfund, or Navy environmental contracts that allow access to regional, state, and federal site information. PRC also used the Record of Decision Scan database (Morgan and others 1993) to search for appropriate sites.

PRC screened 46 potential sites based on the site-selection criteria with the assistance of the various contacts listed above. Based on this screening, PRC and EPA determined that the RV Hopkins and ASARCO sites met most of the site-selection criteria, and therefore, would be acceptable for the demonstration.

The ASARCO site consists of 67 acres of land adjacent to Commencement Bay. The site is marked by steep slopes leading into the bay, a slag fill that was used to extend the original shoreline, a cooling water pond, and various buildings associated with the smelting process. Partial facility demolition was conducted in 1987. Most of the buildings were demolished between 1993 and 1994. The only buildings remaining are the Fine Ore Building, the Administrative Building, and a Maintenance Garage.

Past soil sampling results targeted four general areas of the site as acceptable candidates for this demonstration: the plant administration area, the former cooling pond, the 1987 demolition area, and certain off-site residential areas adjacent to the smelter stack. Previous sampling has shown surficial soils to be more contaminated than subsurface soils. Arsenic, copper, and lead are the predominant contaminants in the local soils. The highest arsenic concentrations were found in the soils around the former arsenic kitchen, along with cadmium and mercury. The soils around the former cooling pond contained the highest copper concentrations and high levels of silver, selenium, barium, and chromium. Lead concentrations are highest northeast of the arsenic plant.

Much of the smelter site is covered with artificial fill material of varying thickness and composition. Two general types of fill are found on the site: granular and slag. The composition of the granular fill material ranges from sand to silt with demolition debris and slag debris mixed throughout. The slag fill is a solid, fractured media restricted to the plant site. The surface soil in the plant administration area has a layer of slag particles on top, ranging from 1 to 3 inches thick. Surficial material in the parking lot area and southwest of the stack is mostly of glacial origin and composed of various mixtures of sand, gravel, and cobbles. The soils around the former cooling pond are fine-grained lacustrine silts and clays. Alluvium upgradient of the former cooling pond has been almost entirely covered with granular fill material. Generally, soils in the arsenic kitchen and stack hill areas are sand mixed with gravel or sandy clay mixed with cobbles. No slag was analyzed as part of this demonstration.

The RV Hopkins site is located in the west end of Davenport, Iowa. The facility occupies approximately 6.7 acres in a heavy industrial/commercial zoned area. Industrial activities in the area of the RV Hopkins property included the manufacture of railroad locomotive engines during the mid-1800's. The RV Hopkins property was a rock quarry during the late 1800's. Aerial surveys beginning in 1929 show that the rock quarry occupied the majority of the site initially, gradually decreasing until it was completely filled by 1982. It was reported that the site was used to dispose of demolition debris, automotive, and scrap metal. The site also has been used by a company that recycled lead acid batteries.

RV Hopkins began operating as a drum reconditioner in 1951 across the street from its current location. In 1964, the site owner reportedly covered the former quarry area of the site with foundry sand. No foundry sand was analyzed as part of this demonstration. RV Hopkins receives between 400 and 600 drums per day for reconditioning, accepting only drums that meet the definition of "empty" according to 40 Code of Federal Regulations 261.7. Most of the drums received at the facility come from the paint, oil, and chemical industries. The surrounding area is reported to be underlain by Devonian-aged Wapsipinicon Limestone, and gray-green shale, lime mud, and sand stringers dating back to the Pennsylvanian age.

The RV Hopkins property is composed of five buildings: the office and warehouse, a warehouse used to store drums of hazardous waste and a waste pile, a manufacturing building, a drum reclamation furnace, and a cutting shed. The office and the warehouse are located on the southwest corner of the site. Areas investigated on each site include the furnace area, the old and new baghouses, the former drum storage area on the north end of the facility, the former landfill, and a drainage ditch. Major contaminants include barium, lead, chromium, and zinc, as well as lesser concentrations of other metals, such as copper and nickel, pesticides, and volatile organic compounds.

Based on historical data, the most concentrated contaminants in the furnace area are chromium, lead, and zinc. The highest concentrations of these elements are at the furnace entrance, as opposed to the furnace exit. The concentrations of lead are higher in the old baghouse than in the new, while the new baghouse exhibits a higher concentration of chromium, as well as high iron, lead, and barium concentrations. The former landfill has concentrations of barium, chromium, lead, nickel, and zinc greater than 1,000 mg/kg. Lead is the most prevalent contaminant in the former drum storage area with lesser concentrations of barium, chromium, and zinc.

Predemonstration Sampling

Predemonstration sampling was conducted at both sites between December 5 and 14, 1994. Those sampling events had the following objectives:

- To provide data on, or verify, the extent of surface contamination at each site and to locate optimum sampling areas for the demonstration.
- To allow the developers to analyze samples from the demonstration sites in advance of the demonstration, and if necessary, refine and recalibrate their technologies and revise their operating instructions.
- To evaluate samples for the presence of any unanticipated matrix effects or interferences that might occur during the demonstration.
- To check the quality assurance (QA) and QC procedures of the reference laboratory.

One hundred soil samples were analyzed on each site by the FPXRF analyzers during the predemonstration sampling activities. The samples represented a wide range in the concentration of metals and soil textures. Thirty-nine samples were submitted for reference method analysis using EPA SW-846 Methods 3050A/6010A. Twenty-nine of these samples were split and sent to the developers. Nine field duplicates were collected and submitted for reference method analysis to assess proposed sample homogenization procedures. One purchased PE sample also was submitted to the reference laboratory to provide an initial check of its accuracy.

Additionally, three samples representing low, medium, and high concentrations were collected at each site. These samples were dried, ground, and then analyzed by six independent laboratories before the demonstration began to create site-specific PE samples. These samples were analyzed with laboratory-grade X-ray fluorescence (XRF) analyzers.

Experimental Design

The experimental design of this demonstration was developed to meet the primary and secondary objectives stated above, and was approved by all participants prior to the start of the demonstration. The design is detailed in the demonstration plan and is summarized below.

Approximately 100 soil samples were collected from each of three target soil textures: clay, loam, and sand. This variety of soil textures allowed the examination of the effect of soil texture on data comparability. Splits of these samples were analyzed by all FPXRFs for all sample preparation steps and by the reference methods.

The two TN Spectrace analyzers demonstrated can be operated in either an *in situ* or intrusive mode. During the demonstration, these two modes of FPXRF analysis required different measurement and sampling procedures (Figure 2-1). Each procedure was designed to reflect common applications of FPXRF analyzers. For *in situ* analysis, an area 4 inches square was cleared of all vegetation, debris, and gravel larger than 2 mm in diameter. The FPXRF *in situ* analyzers took one measurement in each sample area. This data represented FPXRF *in situ* technology measurements for unprepared soils (*in situ*-unprepared). Replicate measurements were taken at 4 percent of these locations to assess analyzer precision.

After the *in situ*-unprepared analysis was complete at a given location, the soil within the 4-inch by 4-inch square was removed to a depth of 1 inch and homogenized in a plastic bag. This produced a soil sample of approximately 375 grams or 250 cubic centimeters (cm^3). Sample homogenization was monitored by adding 1 to 2 grams of sodium fluorescein salt (which fluoresces when exposed to ultraviolet light) to the sample homogenization bag. During the predemonstration, it was determined that sodium fluorescein did not affect the FPXRF or reference method analysis. Sample homogenization took place by kneading the sample and sodium fluorescein salt in a plastic bag for 2 minutes. After 2 minutes, the sample preparation technician examined the sample under ultraviolet light to assess the distribution of sodium fluorescein. If the sodium fluorescein salt was not evenly distributed throughout the sample, the homogenization and checking process were repeated until the sodium fluorescein was evenly distributed. This monitoring process assumed that thorough distribution of sodium fluorescein was indicative of good sample homogenization. The effectiveness of this homogenization is discussed later in this section.

The homogenized sample was then spread out inside a 1-inch-deep petri dish. Each FPXRF analyzer took one measurement from this homogenized material. This represented the homogenized sample analysis for the *in situ* analyzers (*in situ*-prepared). This approximated the common practice of sample homogenization in a plastic bag and subsequent sample measurement through the bag. Replicate measurements were also collected from 4 percent of these samples to assess analyzer precision. These replicate measurements were made on the same soils as the unprepared precision measurements.

Following the *in situ*-prepared analysis, the sample material was passed through a No. 10 mesh sieve (2-mm openings) and approximately 10 grams of this material was placed in a sample cup for analysis by the FPXRF analyzers in an intrusive mode. The same sample cup was used for each FPXRF analyzer. Replicate measurements were collected from 4 percent of these samples to assess analyzer precision.

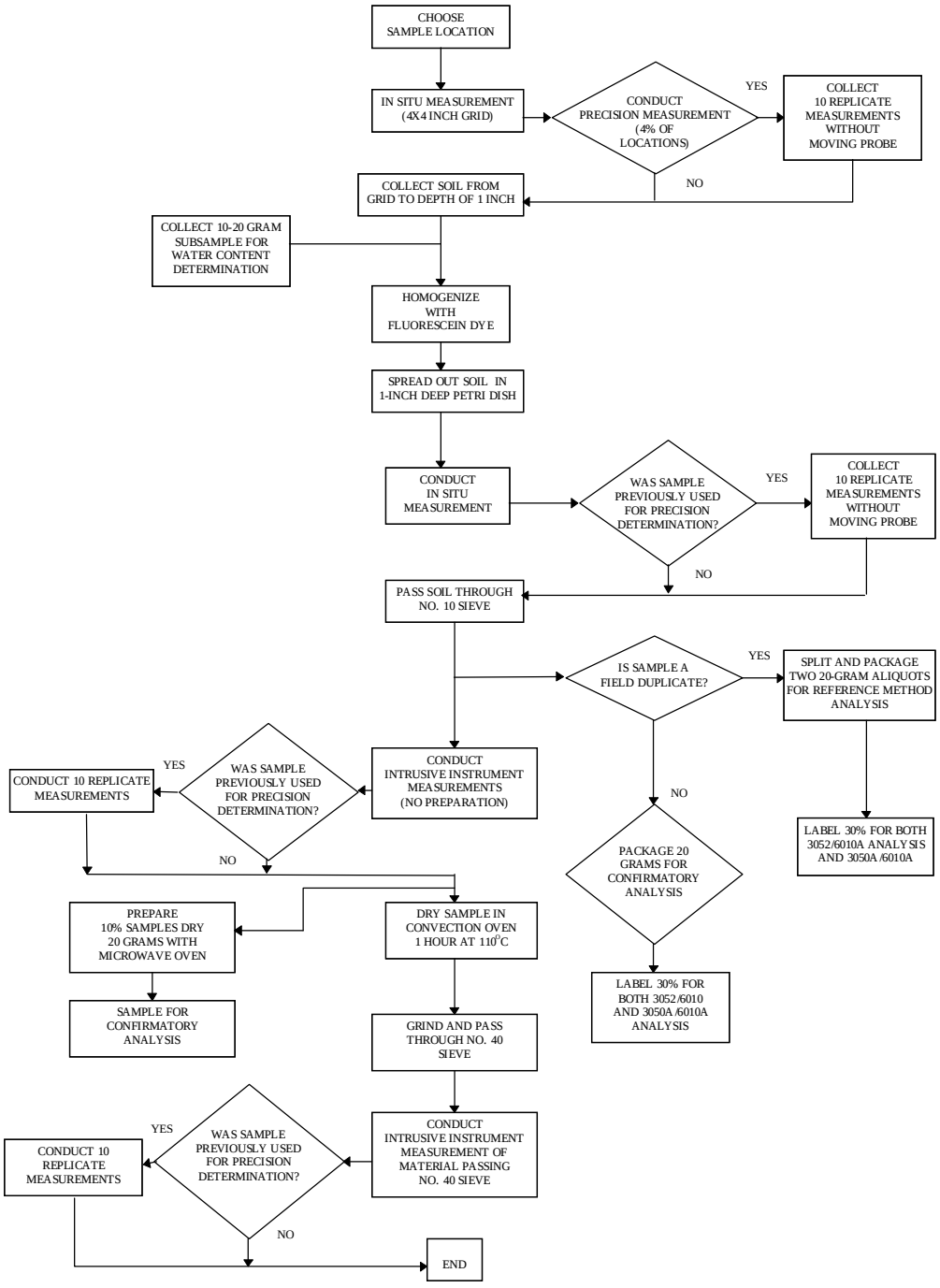


Figure 2-1. Sample Preparation and Analysis: This flowchart depicts the handling procedures for each sample taken during the demonstration.

These replicate measurements were made on the same soils as the *in situ*-prepared precision measurements. These data represented FPXRF intrusive mode measurements on soils with no sample preparation (intrusive-unprepared). Sample material from this preparation step was collected and submitted to the reference laboratory for analysis.

Following the intrusive-unprepared step, a portion of the soil sample was dried in a convection oven at 110 °C for 1 hour and ground with a mortar and pestle until it passed through a No. 40 stainless-steel sieve (0.425-mm openings). The sample was then analyzed by the FPXRF in the intrusive mode. Four percent of these samples underwent replicate measurements to evaluate analyzer precision. These replicate measurements were performed on the same soils as in the intrusive-unprepared precision measurements. This data represented FPXRF intrusive measurements on prepared soils (intrusive-prepared).

Qualitative Factors

There are a number of factors important to data collection that are difficult to quantify and must be evaluated qualitatively. These are considered qualitative factors. One such factor was the level of training required to operate a given FPXRF analyzer. To assess this factor, PRC operators were trained by the developers on how to operate their respective FPXRF analyzers. All operators met or exceeded the developers' minimum requirements for education and previous experience. Demonstration procedures were designed to simulate routine field conditions as closely as possible. The developers trained the operators using their respective operator training manuals. Based on this training and field experience, the operators prepared a subjective evaluation assessing the training and technology operation during the demonstration (Sections 4 and 5).

Many analytical methods exhibit significant "operator effects," in which individual differences in sample preparation or operator technique result in a significant effect on the numerical results. To reduce the possible influence of operator effects, a single operator was used to operate each FPXRF analyzer. While this reduced some potential error from the evaluation, it did not allow the analyzers to be evaluated for their susceptibility to operator-induced error. A single operator was used to analyze all of the samples at both sites during this demonstration. Sample preparation variation effects were minimized in the field by using the same personnel to prepare samples. To eliminate the influence of operator effects on the reference method analysis, only one reference laboratory was used to analyze the samples. Based on this design, there can be no quantitative estimate of "operator effect."

Quantitative Factors

Many factors in this demonstration could be quantified by various means. Examples of quantitative factors evaluated during this demonstration include analyzer performance near regulatory action levels, the effects of sample preparation, effects of microwave sample drying, count times, health and safety considerations, costs, and interferences.

The data developed by the FPXRF analyzers were compared to reference data for the following primary analytes: arsenic, barium, chromium, copper, lead, and zinc; and for the following secondary analytes: nickel, iron, cadmium, and antimony. The TN 9000 Analyzer reported all 10 of these analytes. The TN Pb Analyzer reported arsenic, chromium, lead, zinc, and copper.

Evaluations of analyzer data comparability involved examining the effects of each site, soil texture, and sample preparation technique (Table 2-1). Two sites were sampled for this demonstration, and, therefore, two site variables were examined (RV Hopkins and ASARCO sites). These sites produced samples from three distinct soil textures, and therefore, three soil variables were examined (clay, sand, and loam). Four sample preparation steps were used: (1) *in situ*-unprepared, (2) *in situ*-prepared, (3) intrusive-unprepared, and (4) intrusive-prepared. These variables were nested as follows: each site was divided into RV Hopkins and ASARCO data sets; the RV Hopkins data represented the clay soil texture, and the ASARCO data was divided into sand and loam soil textures; then each soil texture was subdivided by the four soil preparations. This approach allowed the examination of particle size and homogenization effects on data comparability. These effects were seen to have the greatest impact on data comparability.

Table 2-1. Performance and Comparability Variables Evaluated

Variables		
Site Name (315)	**Soil Texture (315)**	**Preparation Step [1,260]**
ASARCO (215)	Sand (100)	in situ-unprepared [100] in situ-prepared [100] intrusive-unprepared [100] intrusive-prepared [100]
	Loam (115)	in situ-unprepared [115] in situ-prepared [115] intrusive-unprepared [115] intrusive-prepared [115]
RV Hopkins (100)	Clay (100)	in situ-unprepared [100] in situ-prepared [100] intrusive-unprepared [100] intrusive-prepared [100]

Notes: ( ) Total number of sample points.
[ ] Total number of measurements taken.

Of greatest interest to users is analyzer performance near action levels. For this reason, samples were approximately distributed as follows: 25 percent in the 0 - 100 mg/kg range, 50 percent in the 100 - 1,000 mg/kg range, and 25 percent in the greater than 1,000 mg/kg range. The lower range tested analyzer performance near MDLs; the middle range tested analyzer performance in the range of many action levels for inorganic contaminants; and the higher range tested analyzer performance on grossly contaminated soils. All samples collected for the demonstration were split between the FPXRF analyzers and reference laboratory for analysis. Metal concentrations measured using the reference methods were considered to represent the "true" concentrations in each sample. Where duplicate samples existed, concentrations for the duplicates were averaged and the average concentration was considered to represent the true value for the sample pair. This procedure was specified in the demonstration plan. If one or both samples in a duplicate pair exhibited a nondetect for a particular target analyte, that pair of data was not used in the statistical evaluation of that analyte. The reference methods reported measurable concentrations of target analytes in all of the samples analyzed.

In addition to the quantitative factors discussed above, the common FPXRF sample preparation technique of microwave drying of samples was evaluated. Sample temperatures during this procedure can be high enough to melt some mineral fractions in the sample or combust organic matter. Several metals that present environmental hazards can volatilize at elevated temperatures. Arsenic sublimes at 188 °C,

within the potential temperature range achieved during microwave drying of samples. To assess this effect, 10 percent of the homogenized, crushed, oven-dried, and sieved samples were split and heated in a microwave oven on high for 3 minutes. This time was chosen to approximate common microwave drying times used in the field. Splits of these samples were submitted for reference analysis. The reference data for these samples were compared to the corresponding reference data produced from the convection oven-dried samples. These data showed the effects of the microwave drying variable on analyte concentration. This was considered a minor variable and it was only evaluated for the reference laboratory in an attempt to identify any potential effect on data comparability.

Another quantitative variable evaluated was the count time used to acquire data. During the formal sample quantitation and precision measurement phase of the demonstration, the count times were set by the developers and remained constant throughout the demonstration. Count times can be tailored to produce the best results for specific target analytes. The developers, however, selected count times that produced the best compromise of results for the entire suite of target analytes. To allow a preliminary assessment of the effect of count times, select soil samples were analyzed in replicate using count times longer and shorter than those set by the developers. This allowed the evaluation of the effects of count times on analyzer performance. Since sample throughput can be affected by adjusting count times, operators used only the developer-specified count times throughout the demonstration.

An important health and safety issue during the demonstration was the effectiveness of radioactivity shielding of each FPXRF analyzer. Quantitative radiation readings were made with a gamma ray detector near each analyzer to assess the potential for exposure to radiation.

A compilation of the costs associated with the use of each FPXRF analyzer was another important evaluation factor. Cost includes analyzer purchase or rental, expendable supplies, such as liquid nitrogen and sample cups, and nonexpendable costs, such as labor, licensing agreements for the radioactive sources, operator training costs, and disposal of investigation-derived waste (IDW). This information is provided to assist the user in estimating the total cost associated with a field use of these instruments.

Factors that could have affected the quantitative evaluations included interference effects and matrix effects. Some of these effects and the procedures used to evaluate their influence during this demonstration are summarized below:

- Heterogeneity: For *in situ*-unprepared measurements, heterogeneity was partially controlled by restricting measurements within a 4-by-4-inch area. For measurements after the initial point-and-shoot preparation, heterogeneity was minimized by sample homogenization. This effect was evaluated through the sample preparation data.
- Particle Size: The effect of particle size was evaluated with the two intrusive sample preparations. Theoretically, precision and accuracy should increase as particle size decreases and becomes more uniform.
- Moisture Content: It has been suggested that major shifts in sample moisture content can affect a sample's relative fluorescence. This effect could not be evaluated as thoroughly as planned because of the small difference in sample moisture content observed at the two sites. This effect was partially examined in the comparison of analyzer performance between intrusive-unprepared and intrusive-prepared analyses. This step in sample preparation involved drying and grinding.

- Overlapping Spectra of Elements: Interferences result from overlapping spectra of metals that emit X-rays with similar energy levels. The reference method analysis provided data on the concentration of potential interferants in each sample.

Evaluation of Analyzer Performance

Metals concentrations measured by these analyzers were compared to the corresponding reference laboratory data, and to the QA/QC sample results. These comparisons were conducted independently for each target analyte. These measurements were used to determine an analyzer's accuracy, data quality level, method precision, and comparability to reference methods. PE and SRM samples were used to assess analyzer accuracy. Relative standard deviations (RSD) on replicate measurements were used to determine analyzer precision. These data were also used to help determine the data quality of each FPXRF analyzer's output. The data comparability and quality determination was primarily based on a comparison of the analyzer's data and the reference data. Linear regression and a matched pairs t-test were the statistical tools used to assess comparability and data quality.

A principal goal of this demonstration was the comparison of FPXRF data and the reference laboratory data. EPA SW-846 Methods 3050A/6010A were selected as the reference methods because they represent the regulatory standard against which FPXRF is generally compared. In comparing the FPXRF data and reference data, it is important to recognize that, while similar these methods are not identical. These differences allow the user to characterize the same sample in slightly different ways. Both have a role in site characterization and remediation. It is important to consider these differences and the measurement error intrinsic to each procedure when comparing the FPXRF method against a reference analytical method.

The reference method, chosen for this demonstration, employs a wet chemical analysis and partial digestion of approximately 1 to 2 grams of sample (approximately 0.25 cubic centimeters (cm^3) depending on sample bulk density). The digestion process extracts the most acid-soluble portion of the sample. Since the digestion is not complete, the less acid-soluble components are not digested and are not included in the analysis. These components may include the coarser-grained quartz, feldspar, lithic components, and certain metal complexes. In contrast, FPXRF analyzers generally produce X-ray excitation in an area of approximately 3 cm^2 to a depth of approximately 2.5 centimeters (cm). This equates to a sample volume of approximately 7.5 cm^3. X-rays returning to the detector are derived from all matrix material including the larger-grained quartz, feldspar, lithic minerals, metal complexes, and organics. Because the FPXRF method analyzes all material, it represents a total analysis in contrast to the reference methods, which may represent a select or partial analysis. This difference can result in FPXRF concentrations that are higher than corresponding reference data when metals are contained within nonacid soluble complexes or constituents. It is important to note that if metals are contained in nonacid soluble complexes, a difference between the FPXRF analyzers and the reference methods is not necessarily due to error in the FPXRF method but rather to the inherent differences in the nature of the analytical methods.

The comparison of FPXRF data and the reference data employs linear regression as the primary statistical tool. Linear regression analysis intrinsically contains assumptions and conditions that must be valid for each data set. The most important assumptions are: (1) the linearity of the relationship, (2) the confidence interval and constant error variance, and (3) an insignificant measurement error for the independent variable (reference data).

The first assumption requires that the independent variable (reference data) and the dependent variable (FPXRF data) are linearly related and are not related by some curvilinear or more complex relationship. This linearity condition applies to either the raw data or mathematical transformations of the raw data. Figure 2-2 illustrates that FPXRF data and reference data are, in fact, related linearly and that this assumption is correct.

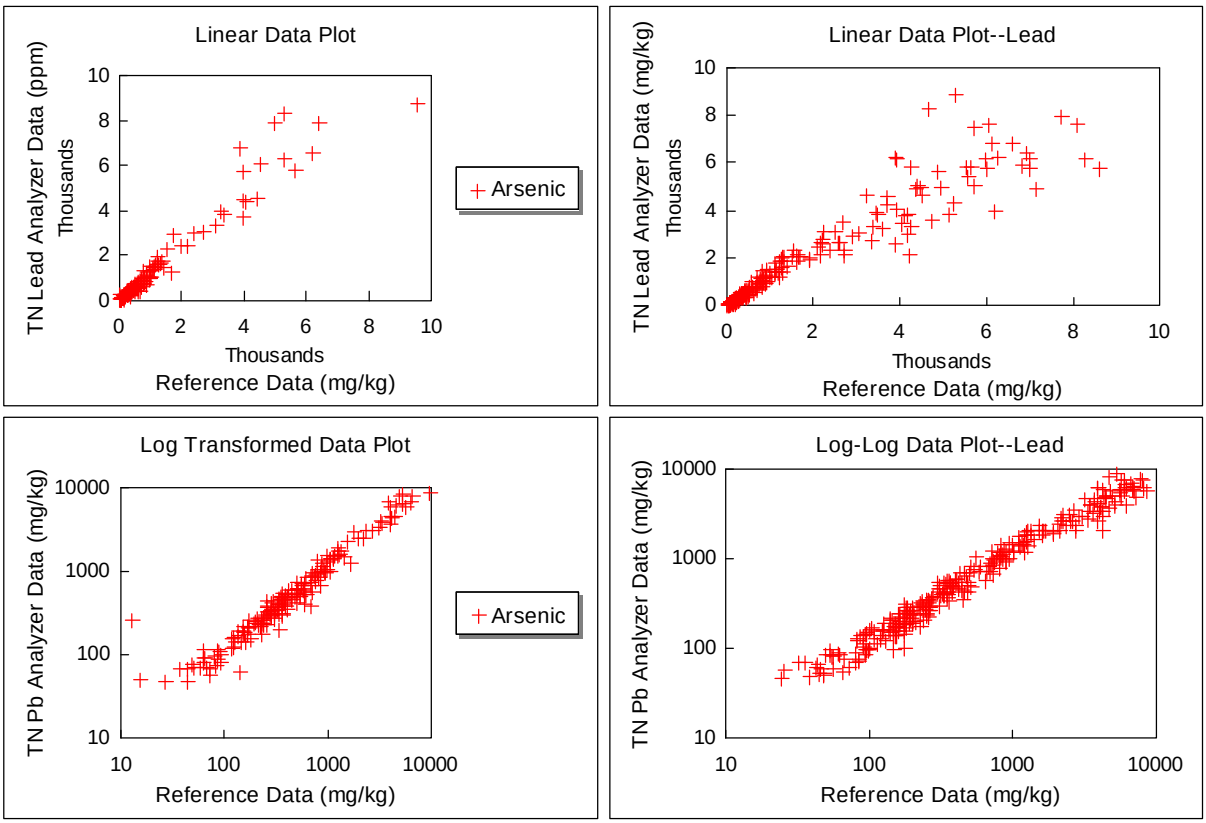


Figure 2-2. Linear and Log-log Data Plots: These graphs illustrate the linear relationship between the FPXRF data and the reference data. The linear data plots illustrate the concentration dependence of this relationship with increased scatter at higher concentrations. The log-log plots eliminate this concentration dependence effect. Scatter is relatively constant over the entire plot.

The second assumption requires that the error be normally distributed, the sum to equal zero, be independent, and exhibit a constant error variance for the data set. Figure 2-2 illustrates that for raw data, this assumption is not correct (at higher concentrations the scatter around the regression line increases), but that for the logarithmic transformation (shown as a log-log plot) of the data, this assumption is valid (the scatter around the regression line is relatively uniform over the entire concentration range). The change in error distribution (scatter) evident in the untransformed data results in the disproportionate influence of large data values compared with small data values on the regression analysis.

The use of least squares linear regression has certain limitations. Least squares regression provides a linear equation, which minimizes the squares of the differences between the dependent variable and the regression line. For data sets produced in this demonstration, the variance was proportional to the magnitude of the measurements. That is, a measurement of 100 parts per million (ppm) may exhibit a 10 percent variance of 10 ppm, while a 1,000 ppm measurement exhibits a 10 percent variance of 100 ppm.

For data sets with a large range in values, the largest measurements in a data set exert disproportionate influence on the regression analysis because the least squares regression must account for the variance associated with the higher valued measurements. This can result in an equation that has minimized error for high values, but almost neglects error for low values because their influence in minimizing dependent variable error is small or negligible. In some cases, the resulting equations, biased by high-value data, may lead to inappropriate conclusions concerning data quality. The range of the data examined for the analyzers spanned between 1 and 5 orders of magnitude (e.g., 10 - 100,000 ppm) for the target analytes. This wide range in values and the associated wide range in variance (influenced by concentration) created the potential for this problem to occur in the demonstration data set. To provide a correlation that was equally influenced by both high and low values, logarithms ($\log_{10}$) of the dependent and independent variables were used, thus, scaling the concentration measurements and providing equal weight in the least squares regression analysis to both small and large values (Figure 2-2). All statistical evaluations were carried out on $\log_{10}$ transformed data.

The third assumption, requiring an insignificant measurement error in the reference data, was not true for all analytes. The consequences of measurement error varied depending on whether the error is caused by the reference methods or the FPXRF method. If the error is random or if the error for the reference methods is small compared to the total regression error, then conventional regression analysis can be performed and the error becomes a part of the random error term of the regression model. This error (based on the $\log_{10}$ transformed data) is shown in the regression summary tables in Section 4 as the "standard error." In this case, deviations from perfect comparability can be tied to an analyzer's performance. If the error for the reference methods is large compared to the total error for the correlation of the FPXRF and the reference data, then deviations from perfect comparability might be due in part to measurement error in the reference methods.

It is a reasonable assumption that any measurement errors in either the reference or FPXRF methods are independent of each other. This assumption applies to either the raw data or the $\log_{10}$ transformed data. Given this assumption, the total regression error is approximately the sum of the measurement error associated with the reference methods and the measurement error associated with the FPXRF method. The reference methods' precision is a measure of independent variable error, and the mean square error expressed in the regression analysis is a relative measure of the total regression error that was determined during the regression analysis. Precision data for the reference methods, obtained from RPD analyses on the duplicate samples from each site, for each analyte, indicated the error for the reference methods was less than 10 percent of the total regression error for the target analytes. Subsequently, 90 percent of the total measurement error can be attributed to measurement error associated with the analyzers. Based on this interpretation, the reference data does allow unambiguous resolution of data quality.

The comparison of reference data to the FPXRF data is referred to as an intermethod comparison. All reference and QA/QC data were generated using an EPA-approved definitive level analytical method. If the data obtained by an analyzer were statistically similar to the reference methods, the analyzer was considered capable of producing definitive level data. As the statistical significance of the comparability decreased, an analyzer was considered to produce data of a correspondingly lower quality. Table 2-2 defines the criteria that determined the analyzer's level of data quality (EPA 1993).

Data from this demonstration were used to place analyzer data into one of three data quality levels as follows: (1) definitive, (2) quantitative screening, and (3) qualitative screening. The first two data quality levels are defined in EPA guidance (1993). The qualitative screening level criteria were defined in the demonstration plan (PRC 1995) to further differentiate the screening level data as defined by the EPA.

Table 2-2. Criteria for Characterizing Data Quality

Data Quality Level	Statistical Parameter[a,b]
Definitive Level	r^2 = 0.85 to 1.0. The precision (RSD) must be less than or equal to 10 percent and the inferential statistics indicate that the two data sets are statistically identical.
Quantitative Screening Level	r^2 = 0.70 to 1.0. The precision (RSD) must be less than 20 percent, and the inferential statistics indicate the data sets are statistically different.
Qualitative Screening	r^2 = less than 0.70. The precision (RSD) is greater than 20 percent. The data must have less than a 10 percent false negative rate.

Notes:
[a] The statistical tests and parameters are discussed later in the "Intermethod Comparison" subsection in Section 4.
[b] The regression parameters apply to either raw or $\log_{10}$ transformed data sets. The precision criteria apply to only the raw data.
r^2 Coefficient of determination.
RSD Relative standard deviation.

Definitive level data are considered the highest level of quality. These data are usually generated by using rigorous, well-defined, analytical methods, such as approved EPA or ASTM methods. The data is analyte-specific with full confirmation of analyte identity and concentration. In addition, either analytical or total measurement error must be determined. Definitive level data may be generated in the field, as long as the QA/QC requirements are satisfied.

Quantitative screening data provide unconfirmed analyte identification and quantification, although the quantification may be relatively imprecise. It is commonly recommended that at least 10 percent of the screening data be confirmed using analytical methods and QA/QC procedures and criteria associated with definitive data. The quality of unconfirmed screening data cannot be determined.

Qualitative screening level data indicates the presence or absence of contaminants in a sample matrix, but does not provide reliable concentration estimates. The data may be compound-specific or specific to classes of contaminants. Generally, confirmatory sampling is not required if an analyzer's operation is verified with one or more check samples.

At the time of this demonstration, approved EPA methods for FPXRF did not exist. As part of this project, PRC prepared draft Method 6200 "Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment." The draft method has been submitted for inclusion in Update 4 of SW-846 scheduled for approval in FY-97. For purposes of this demonstration, the absence of a current EPA-approved final method did not preclude the analyzers' data from being considered definitive. The main criterion for data quality level determination was based on the comparability of each analyzer's data to the data produced by the reference methods, as well as analyzer-specific criteria such as precision.

The comparability data set for each of these analyzers consisted of 1,260 matched pairs of FPXRF and reference method data. This data set was analyzed as a whole and then subdivided and analyzed with respect to each of the variables listed in Table 2-1. This nesting of variables allowed the independent assessment of the influence of each variable on comparability.

To obtain an adequate data set to evaluate the performance of these analyzers, a total of 315 soil samples was analyzed by the reference method. These samples were also analyzed by the FPXRF analyzers for each of the four sample preparation steps. This produced 1,260 data values for each analyzer. Seventy of the 315 samples submitted to the reference laboratory were split and submitted as field duplicates to assess the sample homogenization process. Thirty-three of the 315 samples were also split and microwave-dried, then submitted for reference method analysis to assess the effect of microwave drying. Of the 315 samples submitted for reference method analysis, 215 were collected from the ASARCO site and 100 were collected from the RV Hopkins site. Approximately twice as many samples were collected at the ASARCO site because two of the target soil textures (sands and loams) were found there. Only one target soil texture (clay) was found at the RV Hopkins site.

Evaluation of the influence of the site and soil variables was limited to the examination of the lead and zinc data. These were the only primary analytes that exhibited a wide distribution of concentrations across both sites and all soil textures. The effects of sample preparation variables were evaluated for all of the reported target analytes. If the evaluation of the influence of a given variable did not result in a better correlation, as exhibited by a higher coefficient of determination (r^2) and smaller standard error of the estimate (using $\log_{10}$ transformed data), then the influence was considered to be insignificant. However, if the correlation worsened, the cause was examined and an explanation proposed. If the correlation improved, resulting in an improved r^2 and reduced standard error of the estimate, then the impact of the variable was considered significant. For example, if the r^2 and standard error of the estimate for a given target analyte improved when the data set was divided into the four sample preparation steps, the sample preparation variable was determined to be significant. Once this was determined, the variables of site and soil texture were evaluated for each of the four sample preparations steps. If the site or soil texture variable improved the regression parameters for a given soil preparation, then that variable was also considered significant.

After the significant variables were identified, the impact of analyte concentration was examined. This was accomplished by dividing each variable's $\log_{10}$ transformed data into three concentration ranges: 0 - 100 mg/kg; 100 - 1,000 mg/kg; and greater than 1,000 mg/kg. Then, linear regression analysis was conducted on these data sets. If this did not result in improved r^2 values and reduced standard errors of the estimate, the relationship between the analyzer's $\log_{10}$ transformed data and the $\log_{10}$ transformed reference data was considered linear over the entire range of concentrations encountered during the demonstration. This would mean that there was no concentration effect.

Numerous statistical tests have been designed to evaluate the significance of differences between two populations. In comparing the performance of the FPXRF analyzers against the reference methods, the linear regression comparison and the paired t-test were considered the optimal statistical tests. The paired t-test provides a classic test for comparing two populations, but is limited to analysis of the average or mean difference between those populations. Linear regression analysis provides information not only about how the two populations compare on average, but also about how they compare over ranges of values. Therefore, this statistical analysis provides information about the structure of the relationship; that is, whether the methods differ at high or low concentrations or both. It also indicates whether the FPXRF data is biased or shifted relative to the reference data.

Linear regression provides an equation that represents a line (Equation 2-1). Five linear regression parameters were considered when assessing the level of data quality produced by the FPXRF analyzers. This assessment was made on the $\log_{10}$ transformed data sets. The five parameters were the y-intercept, the slope of the regression line, standard error of the estimate, the correlation coefficient (r), and r^2. In linear

regression analysis, the r provides a measure of the degree or strength of the correlation between the dependent variable (log_{10} transformed FPXRF data), and the independent variable (log_{10} transformed reference data). The r^2 provides a measure of the fraction of total variation which is accounted for by the regression relation (Havlick and Crain 1988). That is, it is a measure of the scatter about a regression line and, thus, is a measure of the strength of the linear association.

$$Y = mX + b \quad \textbf{(2-1)}$$

where

b is the y-intercept of the regression line, m is the slope of the regression line, and Y and X are the log_{10} transformed dependent and independent variables, respectively.

Values for r vary from a value of 1 to -1, with either extreme indicating a perfect positive or negative correlation between the independent and dependent variables. A positive correlation coefficient indicates that as the independent variable increases, the dependent variable also increases. A negative correlation coefficient indicates an inverse relationship, as the independent variable increases the dependent variable decreases. An r^2 of 1.0 indicates that the linear equation explains all the variation between the FPXRF and reference data. As the r^2 departs from 1.0 and approaches zero, there is more unexplained variation, due to such influences as lack of perfect association with the dependent variable (log_{10} transformed FPXRF data), or the influence of other independent variables.

If the regression correlation exhibited an r^2 between 0.85 and 1.0, the FPXRF data was considered to have met the first requirement for definitive level data classification (Table 2-2). The second criteria, precision RSD was then examined and required to be equal to or less than 10 percent RSD to return the definitive data quality level. If both these criteria are satisfied, then certain inferential statistical parameters are evaluated. For example, the regression line's y-intercept and slope may be examined. A slope of 1.0 and a y-intercept of 0.0 would mean that the results of the FPXRF analyzer matched those of the reference laboratory (log_{10} FPXRF=log_{10} reference). Theoretically, the more the slope and y-intercept differ from the values of 1.0 and 0.0, respectively, the less accurate the FPXRF analyzer. However, a slope or y-intercept can differ slightly from these values without that difference being statistically significant. To determine whether such differences were statistically significant, the Z test statistics for parallelism and for a common intercept was used at the 95 percent confidence level for the comparison (Equations 2-2 and 2-3) (Kleinbaum and Kupper 1978). If there is no significant difference between these values, then a final assignment to the definitive data quality level is made. These criteria were used in turn to assign a data quality level for each analyte.

Slope Test for Significant Differences **(2-2)**

$$Z = \frac{m - 1}{\sqrt{SE_m + 0}}$$

where

m is the slope of the regression line, SE is the standard error of the slope, and Z is the normal deviate test statistic.

Y-intercept Test for Significant Differences **(2-3)**

$$Z = \frac{b - 0}{\sqrt{SE_b - 0}}$$

where

b is the y-intercept of the regression line, SE is the standard error of the slope, and Z is the normal deviate test statistic.

The matched pairs t-test was also used to evaluate whether the two sets of $\log_{10}$ transformed data were significantly different. The paired t-test compares data sets, which are composed of matched pairs of data. The significance of the relationship between two matched-pairs sets of data can be determined by comparing the calculated t-statistic with the critical t-value determined from a standard t-distribution table at the desired level of significance and degrees of freedom. To meet definitive level data quality requirements, both the slope and y-intercept had to be statistically the same as their ideal values, as defined in the demonstration plan (PRC 1995), and the data had to be statistically similar as measured by the t-test. Log_{10} transformed data meeting these criteria were considered statistically equivalent to the $\log_{10}$ transformed reference data.

If the r^2 was between 0.70 and 1, the precision (RSD) less than 20 percent, and the slope or intercept were not statistically equivalent to their ideal values, the analyzer was considered to produce quantitative screening level data quality (Table 2-2). In this case, the linear regression is usually sufficiently significant so that bias could be identified and corrected. Therefore, quantitative screening data could be mathematically corrected if 10 - 20 percent of the samples are sent to a reference laboratory. Reference laboratory analysis results for a percentage of the samples would provide a basis for determining a correction factor.

Data placed in the qualitative screening level category exhibit r^2 values less than 0.70. These data either were not statistically similar to the reference data based on inferential statistics or they had a precision RSD of greater than 20 percent. An analyzer producing data at this level is considered capable of detecting the presence or lack of contamination, above its detection limit, with at least a 90 percent accuracy rate, but is not considered suitable for reporting of concentrations.

MDLs for the analyzers were determined in two ways. One approach followed standard SW-846 protocol. In this approach, standard deviations (SD) from precision measurements for samples exhibiting contamination 5 to 10 times the estimated detection levels of the analyzers were multiplied by 3. The result represents the lower MDL for the analyzers.

In a second approach, MDLs were determined by analysis of the low concentration outliers on the $\log_{10}$ transformed FPXRF and $\log_{10}$ transformed reference method data cross plots. These cross plots for all analytes characteristically exhibited a region below the MDL where the linearity of the relationship disintegrated. Above the MDL, the FPXRF concentrations increased linearly with increasing reference method values. Effectively, the linear correlation between the two methods abruptly changes to no correlation below the MDL. The value of the MDL was assigned by determining the concentration where the linear relationship disintegrates and is reported at two SDs above this concentration. This MDL represented a field- or performance-based value.

Deviations from the Demonstration Plan

Seven deviations were made from the demonstration plan during the on-site activities. The first dealt with determining the moisture content of samples. The demonstration plan stated that a portion of the original sample would be used for determining moisture content. Instead, a small portion of soil was collected immediately adjacent to the original sample location and used for determining moisture content. This was done to conserve sample volume for the reference laboratory. The moisture content sample was not put through the homogenizing and sieving steps prior to drying.

The second deviation dealt with the sample drying procedures for moisture content determination. The demonstration plan required that the moisture content samples be dried in a convection oven at 150 °C for 2 hours. Through visual observation, it was found that the samples were completely dried in 1 hour with samples heated to only 110 °C. Therefore, to conserve time, and to reduce the potential volatilization of metals from the samples, the samples for moisture content determination and the intrusive-prepared samples were dried in a convection oven at 110 °C for 1 hour.

The third deviation involved an assessment of analyzer drift due to changes in temperature. The demonstration plan indicated that at each site, each analyzer would measure the same SRM or PE sample at 2-hour intervals during at least one day of field operation. However, since ambient air temperature did not fluctuate more than 20 °F on any day throughout the demonstration, potential analyzer drift due to changes in temperature was not assessed.

The fourth deviation involved the drying of samples with a microwave. Instead of microwaving the samples on high for 5 minutes, as described in the demonstration plan, the samples were microwaved on high for only 3 minutes. This modification was made because the plastic weigh boats, which contained the samples, were melting and burning when left in the microwave for 5 minutes. In addition, many of the samples were melting to form a slag. It was found (through visual observation) that the samples were completely dry after only 3 minutes. This interval is still within common microwave drying times used in the field.

An analysis of the microwaved samples showed that this drying process had a significant impact on the analytical results. The mean RPD for the microwaved and nonmicrowaved raw data were significantly different at a 95 percent confidence level. This suggests that the microwave drying process somehow increases error and sample concentration variability. This difference may be due to the extreme heat and drying altering the reference methods' extraction efficiency for target analytes. For the evaluation of the effects of microwave drying, there were 736 matched pairs of data where both element measurements were positive. Of these pairs, 471 exhibited RPDs less than 10 percent. This 10 percent level is within the acceptable precision limits for the reference laboratory as defined in the demonstration QAPP. Pairs exhibiting RPDs greater than 10 percent totaled 265. RPDs greater than 10 percent may have causes other than analysis-induced error. Of these 265, 96 pairs indicated an increase in metals concentration with microwaving, and 169 pairs indicated a reduction in metals concentration. The RPDs for the microwaved samples were 2 to 3 times worse than the RPDs from the field duplicates. This further supports the hypothesis that microwave drying increases variability.

The fifth deviation involved reducing the percentage of analyzer precision measuring points. The demonstration plan called for 10 percent of the samples to be used for assessment of analyzer precision. Due to the time required to complete analysis of an analyzer precision sample, only 4 percent of the samples were used to assess analyzer precision. This reduction in samples was approved by the EPA

technical advisor and the PRC field demonstration team leader. This eliminated 720 precision measurements and saved up to 3 days of analysis time. The final precision determinations for this demonstration were based on 48 sets of 10 replicate measurements for each analyzer.

The sixth deviation involved method blanks. Method blanks were to be analyzed each day and were to consist of a lithium carbonate that had been used in all sample preparation steps. Each analyzer had its own method blank samples, provided by the developer. Therefore, at the ASARCO site, each analyzer used its own method blank samples. However, at the RV Hopkins site, each analyzer used lithium carbonate method blanks that were prepared in the field, in addition to its own method blank samples. Both types of method blank analysis never identified method-induced contamination.

The seventh deviation involved assessing the accuracy of each analyzer. Accuracy was to be assessed through FPXRF analysis of 10 to 12 SRM or PE samples. Each analyzer measured a total of 28 SRM or PE samples. In addition, PE samples were used to evaluate the accuracy of the reference methods, and SRMs were used to evaluate the accuracy of the analyzers. This is because the PE concentrations are based on acid extractable concentrations while SRM concentrations represent total metals concentration. SRM data was used for comparative purposes for the reference methods as were PE data for the FPXRF data.

Sample Homogenization

A key quality issue in this demonstration was ensuring that environmental samples analyzed by the reference laboratory and by each of the FPXRF analyzers were splits from a homogenous sample. To address this issue, sample preparation technicians exercised particular care throughout the field work to ensure that samples were thoroughly homogenized before they were split for analysis. Homogenization was conducted by kneading the soil in a plastic bag for a minimum of 2 minutes. If after this time the samples did not appear to be well homogenized, they were kneaded for an additional 2 minutes. This continued until the samples appeared to be well homogenized.

Sodium fluorescein was used as an indicator of sample homogenization. Approximately one-quarter teaspoon of dry sodium fluorescein powder was added to each sample prior to homogenization. After the homogenization was completed, the sample was examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye was evenly dispersed in the sample, homogenization was considered complete. If the dye was not evenly distributed, the mixing was continued and checked until the dye was evenly distributed throughout the sample.

To evaluate the homogenization process used in this demonstration, 70 field duplicate sample pairs were analyzed by the reference laboratory. Sample homogenization was critical to this demonstration; it assured that the samples measured by the analyzers were as close as possible to samples analyzed by the reference laboratory. This evaluation was essential to the primary objectives of this demonstration, the evaluation of comparability between analyzer results and those of the reference methods.

The homogenization process was evaluated by determining the RPD between paired field duplicate samples. The RPDs for the field duplicate samples reflect the total error for the homogenization process and the analytical method combined (Equation 2-4). When total error for the reference laboratory was determined, the resultant mean RPD total (error) and 95 percent confidence interval was 9.7 ± 1.4, for all metals reported. When only the primary analytes were considered, the RPD total (error) and 95 percent

confidence interval was 7.6 ± 1.2. Including the secondary analytes in the RPD calculation produced a mean RPD total (error) and a 95 percent confidence interval of 9.3 ± 1.6.

$$Total\ Measurement\ Error = \sqrt{[(Sample\ Homogenization\ Error)^2 + (Laboratory\ Error)^2]} \quad \textbf{(2-4)}$$

Using internal QA/QC data from 27 analyses, it was possible to determine the reference laboratory's method error. The reference analytical method precision, as measured by the 95 percent confidence interval around the mean RPDs (laboratory error) of predigestion duplicate analyses, was 9.3 ± 2.9 for all of the target analytes.

To determine the error introduced by the sample homogenization alone, the error estimate for the reference methods was subtracted from the total error (Equation 2-5). Based on the data presented above, the laboratory-induced error was less than or approximately equal to the total error. This indicates that the sample homogenization (preparation) process contributed little or no error to the overall sample analysis process.

$$Sample\ Homogenization\ Error = \sqrt{[(Total\ Measurement\ Error)^2 - (Laboratory\ Error)^2]} \quad \textbf{(2-5)}$$

Although the possibility for poorly homogenized samples exists under any homogenization routine, at the scale of analysis used by this demonstration, the samples were considered to be completely homogenized.

Section 3
Reference Laboratory Results

All soil samples collected from the ASARCO and RV Hopkins sites were submitted to the reference laboratory for trace metals analysis. The results are discussed in this section.

Reference Laboratory Methods

Samples collected during this demonstration were homogenized and split for extraction using EPA SW-846 Method 3050A. This is an acid digestion procedure where 1 to 2 grams of soil are digested on a hot plate with nitric acid, followed by hydrogen peroxide, and then refluxed with hydrochloric acid. One gram of soil was used for extraction of the demonstration samples. The final digestion volume was 100 milliliters (mL). The soil sample extracts were analyzed by Method 6010A.

Method 6010A provides analysis of metals using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). This method requires that a plasma be produced by applying a radio-frequency field to a quartz tube wrapped by a coil or solenoid through which argon gas is flowing. The radio-frequency field creates a changing magnetic field in the flowing gas inside the coil, inducing a circulating eddy current on the argon gas that, in turn, heats it. Plasma is initiated by an ignition source and quickly stabilizes with a core temperature of 9,000 - 10,000 degrees Kelvin.

Soil sample extracts are nebulized, and the aerosol is injected into the plasma. Individual analytes introduced into the plasma absorb energy and are excited to higher energy states. These higher energy states have short lifetimes and the individual elements quickly fall back to their ground energy state by releasing a photon. The energy of the emitted photon is defined by the wavelength of electromagnetic radiation produced. Since many electronic transitions are possible for each individual element, several discrete emissions at different wavelengths are observed. Method 6010A provides one recommended wavelength to monitor for each analyte. Due to complex spectra with similar wavelengths from different elements in environmental samples, Method 6010A requires that interference corrections be applied for quantification of individual analytes.

Normal turnaround times for the analysis of soil samples by EPA SW-846 Methods 3050A/6010A range from 21 to 90 days depending on the complexity of the soil samples and the amount of QC documentation required. Faster turnaround times of 1 - 14 days can be obtained, but at additional cost.

Costs for the analysis of soil samples by EPA SW-846 Methods 3050A/6010A range from $150 to $350 per sample depending on turnaround times and the amount of QC documentation required. A sample turnaround of 28 days, a cost of $150 per sample, and a CLP documentation report for QC were chosen for this demonstration.

Reference Laboratory Quality Control

The reference laboratory, Midwest Research Institute (Kansas City, MO), holds certifications for performing target analyte list metals analysis with the U.S. Army Corps of Engineers-Missouri River Division, the State of California, and the State of Utah. These certifications include on-site laboratory audits, data package review audits, and the analysis of PE samples supplied by the certifying agency. PE samples are supplied at least once per year from each of the certifying agencies. The reference laboratory's results for the PE samples are compared to true value results and certifying agency acceptance limits for the PE samples. Continuation of these certifications hinges upon acceptable results for the audits and the PE samples.

The analysis of soil samples by the reference laboratory was governed by the QC criteria in its SOPs, Method 6010A, and the demonstration QAPP. Table 3-1 provides QAPP QC requirements that were monitored and evaluated for the target analytes. Method 6010A QC guidelines also are included in Table 3-1. Due to the complex spectra derived from the analysis of the demonstration samples, the QAPP QC requirements were applied only to the primary analytes. The QAPP QC requirements also were monitored and evaluated for the secondary analytes and other analytes reported by the reference laboratory. However, corrective actions were not required for the secondary analytes.

Table 3-1. Reference Laboratory Quality Control Parameters[a]

Parameter	Frequency	Reference Method Requirement	QAPP Requirement
Initial Calibration Verification (ICV) Standard	With each initial calibration	±10 percent of true value	±10 percent of true value
Continuing Calibration Verification (CCV) Standard	After analysis of every 10 samples and at the end of analytical run	±10 percent of true value	±10 percent of true value
Initial and Continuing Calibration Blanks (ICB) and (CCB)	With each continuing calibration, after analysis of every 10 samples, and at the end of analytical run	±3 standard deviations of the analyzer background mean	No target analytes at concentrations greater than 2 times the lower reporting limit (LRL)
Interference Check Standard (ICS)	With every initial calibration and after analysis of 20 samples	±20 percent of true value	±20 percent of true value
High Level Calibration Check Standard	With every initial calibration	±5 percent of true value	±10 percent of true value
Method Blanks	With each batch of samples of a similar matrix	No QC requirement specified	No target analytes at concentrations greater than 2 times the LRL
Laboratory Control Samples	With each batch of samples of a similar matrix	No QC requirement specified	80 - 120 percent recovery
Predigestion Matrix Spike Samples	With each batch of samples of a similar matrix	80 - 120 percent recovery	80 - 120 percent recovery
Postdigestion Matrix Spike Samples	With each batch of samples of a similar matrix	75 - 125 percent recovery	80 - 120 percent recovery

Table 3-1. ***Continued***

Parameter	Frequency	Reference Method Requirement	QAPP Requirement
Performance Evaluation Samples	As submitted during demonstration	No QC requirement specified	80 - 120 percent recovery within performance acceptance limits (PAL)
Predigestion Laboratory Duplicate Samples	With each batch of samples of a similar matrix	20 percent relative percent difference (RPD)[b]	20 percent RPD[c]
Postdigestion Laboratory Duplicate Samples	With each batch of samples of a similar matrix	No QC requirement specified	10 percent RPD[c]

Notes: [a] Quality control parameters were evaluated on the raw reference data.

[b] RPD control limits only pertain to original and laboratory duplicate sample results that were greater than 10 times the instrument detection limit (IDL).

[c] RPD control limits only pertain to original and laboratory duplicate sample results that were greater than or equal to 10 times the LRL.

PRC performed three on-site audits of the reference laboratory during the analysis of predemonstration and demonstration samples. These audits were conducted to observe and evaluate the procedures used by the reference laboratory and to ensure that these procedures adhered to the QAPP QC requirements. Audit findings revealed that the reference laboratory followed the QAPP QC requirements. It was determined that the reference laboratory had problems meeting two of the QAPP QC requirements: method blank results and the high level calibration check standard's percent recovery. Due to these problems, these two QAPP QC requirements were widened. The QC requirement for method blank sample results was changed from no target analytes at concentrations greater than the lower reporting limit (LRL) to two times the LRL. The QC requirement for the high level calibration standard percent recovery was changed from ±5 to ±10 percent of the true value. These changes were approved by the EPA and did not affect the results of the demonstration.

The reference laboratory internally reviewed its data before releasing it. PRC conducted a QC review on the data based on the QAPP QC requirements and corrective actions listed in the demonstration plan.

Quality Control Review of Reference Laboratory Data

The QC data review focused upon the compliance of the data with the QC requirements specified in the demonstration QAPP. The following sections discuss results from the QC review of the reference laboratory data. All QC data evaluations were based on raw data.

Reference Laboratory Sample Receipt, Handling, and Storage Procedures

Demonstration samples were divided into batches of no more than 20 samples per batch prior to delivery to the reference laboratory. A total of 23 batches containing 315 samples and 70 field duplicate samples was submitted to the reference laboratory. The samples were shipped in sealed coolers at ambient temperature under a chain of custody.

Upon receipt of the demonstration samples, the reference laboratory assigned each sample a unique number and logged each into its laboratory tracking system. The samples were then transferred to the reference laboratory's sample storage refrigerators to await sample extraction.

Samples were transferred to the extraction section of laboratory under an internal chain of custody. Upon completion of extraction, the remaining samples were returned to the sample storage refrigerators. Soil sample extracts were refrigerated in the extraction laboratory while awaiting sample analysis.

Sample Holding Times

The maximum allowable holding time from the date of sample collection to the date of extraction and analysis using EPA SW-846 Methods 3050A/6010A is 180 days. Maximum holding times were not exceeded for any samples during this demonstration.

Initial and Continuing Calibrations

Prior to sample analysis, initial calibrations (ICAL) were performed. ICALs for Method 6010A consist of the analysis of three concentrations of each target analyte and a calibration blank. The low concentration standard is the concentration used to verify the LRL of the method. The remaining standards are used to define the linear range of the ICP-AES. The ICAL is used to establish calibration curves for each target analyte. Method 6010A requires an initial calibration verification (ICV) standard to be analyzed with each ICAL. The method control limit for the ICV is ±10 percent. An interference check sample (ICS) and a high level calibration check standard is required to be analyzed with every ICAL to assess the accuracy of the ICAL. The control limits for the ICS and high level calibration check standard were ±20 percent recovery and ±10 percent of the true value, respectively. All ICALs, ICVs, and ICSs met the respective QC requirements for all target analytes.

Continuing calibration verification (CCV) standards and continuing calibration blanks (CCB) were analyzed following the analysis of every 10 samples and at the end of an analytical run. Analysis of the ICS was also required after every group of 20 sample analyses. These QC samples were analyzed to check the validity of the ICAL. The control limits for the CCVs were ±10 percent of the true value. The control limits for CCBs were no target analyte detected at concentrations greater than 2 times the LRL. All CCVs, CCBs, and ICSs met the QAPP requirements for the target analytes with the exception of one CCV where the barium recovery was outside the control limit. Since barium was a primary analyte, the sample batch associated with this CCV was reanalyzed and the resultant barium recovery met the QC criteria.

Detection Limits

The reference laboratory LRLs for the target analytes are listed in Table 3-2. These LRLs were generated through the use of an MDL study of a clean soil matrix. This clean soil matrix was also used for method blank samples and LCSs during the analysis of demonstration samples. The MDL study involved seven analyses of the clean soil matrix spiked with low concentrations of the target analytes. The mean and standard deviation of the response for each target analyte was calculated. The LRL was defined as the mean plus three times the standard deviation of the response for each target analyte included in the method detection limit study. All LRLs listed in Table 3-2 were met and maintained throughout the analysis of the demonstration samples.

The reference laboratory reported soil sample results in units of milligram per kilogram wet weight. All reference laboratory results referred to in this report are wet-weight sample results.

Table 3-2. SW-846 Method 6010A LRLs for Target Analytes

Analyte	LRL (mg/kg)	Analyte	LRL (mg/kg)
Antimony	6.4	Copper*	1.2
Arsenic*	10.6	Iron	600[a]
Barium*	5.0	Lead*	8.4
Cadmium	0.80	Nickel	3.0
Chromium*	2.0	Zinc*	2.0

Notes:
[a] LRL elevated due to background interference.
* Primary analyte.
mg/kg Milligrams per kilogram.

Method Blank Samples

Method blanks were prepared using a clean soil matrix and acid digestion reagents used in the extraction procedure. A minimum of one method blank sample was analyzed for each of the 23 batches of demonstration samples submitted for reference laboratory analysis. All method blanks provided results for target analytes at concentrations less than 2 times the levels shown in Table 3-2.

Laboratory Control Samples

All LCSs met the QAPP QC requirements for all primary and secondary analytes except those discussed below.

The primary analytes copper and lead were observed outside the QC limits in one of the 23 batches of samples analyzed. Reanalysis of the affected batches was not performed by the reference laboratory. These data were qualified by the reference laboratory. Copper and lead data for all samples included in the affected batches were rejected and not used for demonstration statistical comparisons.

Concentrations of secondary analytes antimony, nickel, and cadmium were observed outside the QC limits in the LCSs. Antimony LCS recoveries were continually outside the control limits, while nickel and cadmium LCS recoveries were only occasionally outside QC limits. Antimony was a problem analyte and appeared to be affected by acid digestion, which can cause recoveries to fall outside control limits. Antimony recoveries ranged from 70 to 80 percent. Since secondary analytes were not subject to the corrective actions listed in the demonstration QAPP, no reanalysis was performed based on the LCS results of the secondary target analytes. These values were qualified by the reference laboratory. All other secondary analyte LCS recoveries fell within the QAPP control limits.

Predigestion Matrix Spike Samples

One predigestion matrix spike sample and duplicate were prepared by the reference laboratory for each batch of demonstration samples submitted for analysis. The predigestion matrix spike duplicate sample was not required by the QAPP, but it is a routine sample prepared by the reference laboratory. This duplicate sample can provide data that indicates if out-of-control recoveries are due to matrix interferences or laboratory errors.

Predigestion spike recovery results for the primary analytes arsenic, barium, chromium, copper, lead, and zinc were outside control limits for at least 1 of the 23 sample batches analyzed by the reference

method. These control limit problems were due to either matrix effects or initial spiking concentrations below native analyte concentrations.

Barium, copper, and lead predigestion matrix spike recovery results were outside control limits in sample batches 2, 3, and 5. In all of these cases, the unacceptable recoveries were caused by spiking concentrations that were much lower than native concentrations of the analytes. These samples were re-prepared, spiked with higher concentrations of analytes, reextracted, and reanalyzed. Following this procedure, the spike recoveries fell within control limits upon reanalysis.

One predigestion matrix spike recovery was outside control limits for arsenic. The predigestion matrix spike duplicate sample also was outside of control limits. This sample exhibited an acceptable RPD for the recovery of arsenic in the predigestion matrix spike and duplicate. A matrix interference may have been responsible for the low recovery. This sample was not reanalyzed.

Chromium predigestion matrix spike recoveries were outside control limits in 7 of the 23 batches of samples analyzed. Five of these seven failures exhibited recoveries ranging from 67 to 78 percent, close to the low end of the control limits. These recoveries were similar in the predigestion matrix spike duplicate samples prepared and analyzed in the same batch. This indicates that these five failures were due to matrix interferences. The predigestion matrix spike duplicate samples prepared and analyzed along with the remaining two failures did not agree with the recoveries of the postdigestion matrix spike samples, indicating that these two failures may be due to laboratory error, possibly inaccuracies in sample spiking. These seven predigestion matrix spike samples were not reanalyzed.

The zinc predigestion matrix spike recovery data were outside control limits for four batches of samples analyzed. In three of the spike recovery pairs, recoveries ranged from 70 to 76 percent, close to the lower end of the control limits. The fourth recovery was much less than the lower end of the control limits. All of the predigestion matrix spike duplicate samples provided recoveries that agreed with the recoveries for the predigestion matrix spike sample recoveries indicating that the low recoveries were due to matrix effects. These predigestion matrix spikes and associated samples were not reanalyzed.

The secondary analytes, cadmium, iron, and nickel, had predigestion spike recoveries outside control limits. Cadmium spike recoveries were outside control limits six times. These recoveries ranged from 71 to 85 percent. Iron spike recoveries were outside of control limits once. Nickel spike recoveries were outside control limits four times. These recoveries ranged from 74 to 83 percent. Antimony spike recoveries were always outside control limits. No corrective action was taken for these secondary target analytes.

Demonstration sample results for all target analytes that did not meet the control limits for predigestion matrix spike recovery were qualified by the reference laboratory.

Postdigestion Matrix Spike Samples

All postdigestion matrix spike results were within the control limit of 80 - 120 percent recovery for the primary analytes.

Secondary analytes, antimony, and iron were observed outside the control limits. However, no corrective action was taken for secondary analytes as stated in the demonstration QAPP. All postdigestion spike recoveries for target analytes met the QA/QC requirements of the QAPP and were considered acceptable.

Predigestion Laboratory Duplicate Samples

Predigestion laboratory duplicate RPD results were within the control limit of 20 percent for analyte concentrations greater than 10 times the LRL except for the following instances. RPDs for primary analytes barium, arsenic, lead, chromium, and copper were observed above the control limit in five predigestion laboratory duplicate samples. These samples were reanalyzed according to the corrective actions listed in the QAPP. The reanalysis produced acceptable RPD results for these primary analytes.

RPD results for the secondary analytes antimony, nickel, and cadmium were observed outside the control limit for a number of sample batches. No corrective action was taken for secondary analytes that exceeded the RPD control limit.

Postdigestion Laboratory Duplicate Samples

All primary analyte postdigestion laboratory duplicate RPD results were less than the 10 percent control limit for analyte concentrations greater than 10 times the LRL.

The RPDs for secondary analytes antimony and iron were observed above the 10 percent control limit in two sample batches. No corrective action was taken for secondary target analytes that exceeded the RPD control limit.

Performance Evaluation Samples

PE samples were purchased from Environmental Resource Associates (ERA). The PE samples are Priority PollutnT™/Contract Laboratory Program (CLP) QC standards for inorganics in soil. This type of sample is used by the EPA to verify accuracy and laboratory performance. Trace metal values are certified by interlaboratory round robin analyses. ERA lists performance acceptance limits (PAL) for each analyte that represent a 95 percent confidence interval (CI) around the certified value. PALs are generated by peer laboratories in ERA's InterLaB™ program using the same samples that the reference laboratory analyzed and the same analytical methods. The reported value for each analyte in the PE sample must fall within the PAL range for the accuracy to be acceptable. Four PE samples were submitted "double blind" (the reference laboratory was not notified that the samples were QC samples or of the certified values for each element) to the reference laboratory for analysis by EPA SW-846 Methods 3050A/6010A. Reference laboratory results for all target analytes are discussed later in this section.

Four certified reference materials (CRM) purchased from Resource Technology Corporation (RTC) also were used as PE samples to verify the accuracy and performance of the reference laboratory. These four CRMs were actual samples from contaminated sites. They consisted of two soils, one sludge, and one ash CRM. Metal values in the CRMs are certified by round robin analyses of at least 20 laboratories according to the requirements specified by the EPA Cooperative Research and Development Agreement. The certified reference values were determined by EPA SW-846 Methods 3050A/6010A. RTC provides a 95 percent PAL around each reference value in which measurements should fall 19 of 20 times. The reported value from the reference laboratory for each analyte must fall within this PAL for the accuracy to be considered acceptable. As with the four PE samples, the four CRMs were submitted "double blind" to the reference laboratory for analysis by EPA SW-846 Methods 3050A/6010A. The reference laboratory results for the target analytes are discussed later in the Accuracy subsection.

Standard Reference Material Samples

As stated in the demonstration plan (PRC 1995), PE samples also consisted of SRMs. The SRMs consisted of solid matrices such as soil, ash, and sludge. Certified analyte concentrations for SRMs are determined on an analyte by analyte basis by multiple analytical methods including but not limited to ICP-AES, flame atomic absorption spectroscopy, ICP-mass spectrometry, XRF, instrumental neutron activation analysis, hydride generation atomic absorption spectroscopy, and polarography. These certified values represent total analyte concentrations and complete extraction. This is different from the PE samples, CRM samples, and the reference methods, which use acid extraction that allows quantitation of only acid extractable analyte concentrations.

The reference laboratory analyzed 14 SRMs supplied by the National Institute of Standards and Technology (NIST), U.S. Geological Survey (USGS), National Research Council Canada, South African Bureau of Standards, and Commission of the European Communities. The percentage of analyses of SRMs that were within the QAPP-defined control limits of 80 - 120 percent recovery was calculated for each primary and secondary analyte.

Analyses of SRMs were not intended to assess the accuracy of EPA SW-846 Methods 3050A/6010A as were the ERA PE or RTC CRM samples. Comparison of EPA SW-846 Methods 3050A/6010A acid leach data to SRM data cannot be used to establish method validity (Kane and others 1993). This is because SRM values are acquired by analyzing the samples by methods other than the ICP-AES method. In addition, these other methods use sample preparation techniques different from those for EPA SW-846 Methods 3050A/6010A. This is one reason no PALs are published with the SRM certified values. Therefore, the SRMs were not considered an absolute test of the reference laboratory's accuracy for EPA SW-846 Methods 3050A/6010A.

The SRM sample results were not used to assess method accuracy or to validate the reference methods. This was due to the fact that the reported analyte concentrations for SRMs represent total analyte concentrations. The reference methods are not an analysis of total metals; rather they target the leachable concentrations of metals. This is consistent with the NIST guidance against using SRMs to assess performance on leaching based analytical methods (Kane and others 1993).

Data Review, Validation, and Reporting

Demonstration data were internally reviewed and validated by the reference laboratory. Validation involved the identification and qualification of data affected by QC procedures or samples that did not meet the QC requirements of the QAPP. Validated sample results were reported using both hard copy and electronic disk deliverable formats. QC summary reports were supplied with the hard copy results. This qualified data was identified and discussed in the QC summary reports provided by the reference laboratory.

Demonstration data reported by the reference laboratory contained three types of data qualifiers: C, Q, and M. Type C qualifiers included the following:

- U - the analyte was analyzed for but not detected.
- B - the reported value was obtained from a reading that was less than the LRL but greater than or equal to the IDL.

Type Q qualifiers included the following:

- N - spiked sample recovery was not within control limits.
- * - duplicate analysis was not within control limits.

Type M qualifiers include the following:

- P - analysis performed by ICP-AES (Method 6010).

Quality Assessment of Reference Laboratory Data

An assessment of the reference laboratory data was performed using the PARCC parameters discussed in Section 2. PARCC parameters are used as indicators of data quality and were evaluated using the review of reference laboratory data discussed above. The following sections discuss the data quality for each PARCC parameter. This quality assessment was based on raw reference data and the raw PE sample data.

The quality assessment was limited to an evaluation of the primary analytes. Secondary and other analytes reported by the reference laboratory were not required to meet the QC requirements specified in the QAPP. Discussion of the secondary analytes is presented in the precision, accuracy, and comparability sections for informational purposes only.

Precision

Precision for the reference laboratory data was assessed through an evaluation of the RPD produced from the analysis of predigestion laboratory duplicate samples and postdigestion laboratory duplicate samples. Predigestion laboratory duplicate samples provide an indication of the method precision, while postdigestion laboratory duplicate samples provide an indication of instrument performance. Figure 3-1 provides a graphical summary of the reference method precision data.

The predigestion duplicate RPDs for the primary and secondary analytes fell within the 20 percent control limit, specified in the QAPP, for 17 out of 23 batches of demonstration samples. The six results that exceeded the control limit involved only 11 of the 230 samples evaluated for predigestion duplicate precision (Figure 3-1). This equates to 95 percent of the predigestion duplicate data meeting the QAPP control limits. Six of the analytes exceeding control limits had RPDs less than 30 percent. Three of the analytes exceeding control limits had RPDs between 30 and 40 percent. Two of the analytes exceeding control limits had RPDs greater than 60 percent. These data points are not shown in Figure 3-1. Those instances where the control limits were exceeded are possibly due to nonhomogeneity of the sample or simply to chance, as would be expected with a normal distribution of precision analyses.

The postdigestion duplicate RPDs for the primary and secondary analytes fell within the 10 percent control limit, specified in the QAPP, for 21 out of 23 batches of demonstration samples. The two results that exceeded the control limit involved only 3 of the 230 samples evaluated for postdigestion duplicate precision in the 23 sample batches (Figure 3-1). This equates to 99 percent of the postdigestion duplicate data meeting the QAPP control limits. The RPDs for the three results that exceeded the control limit ranged from 11 to 14 percent.

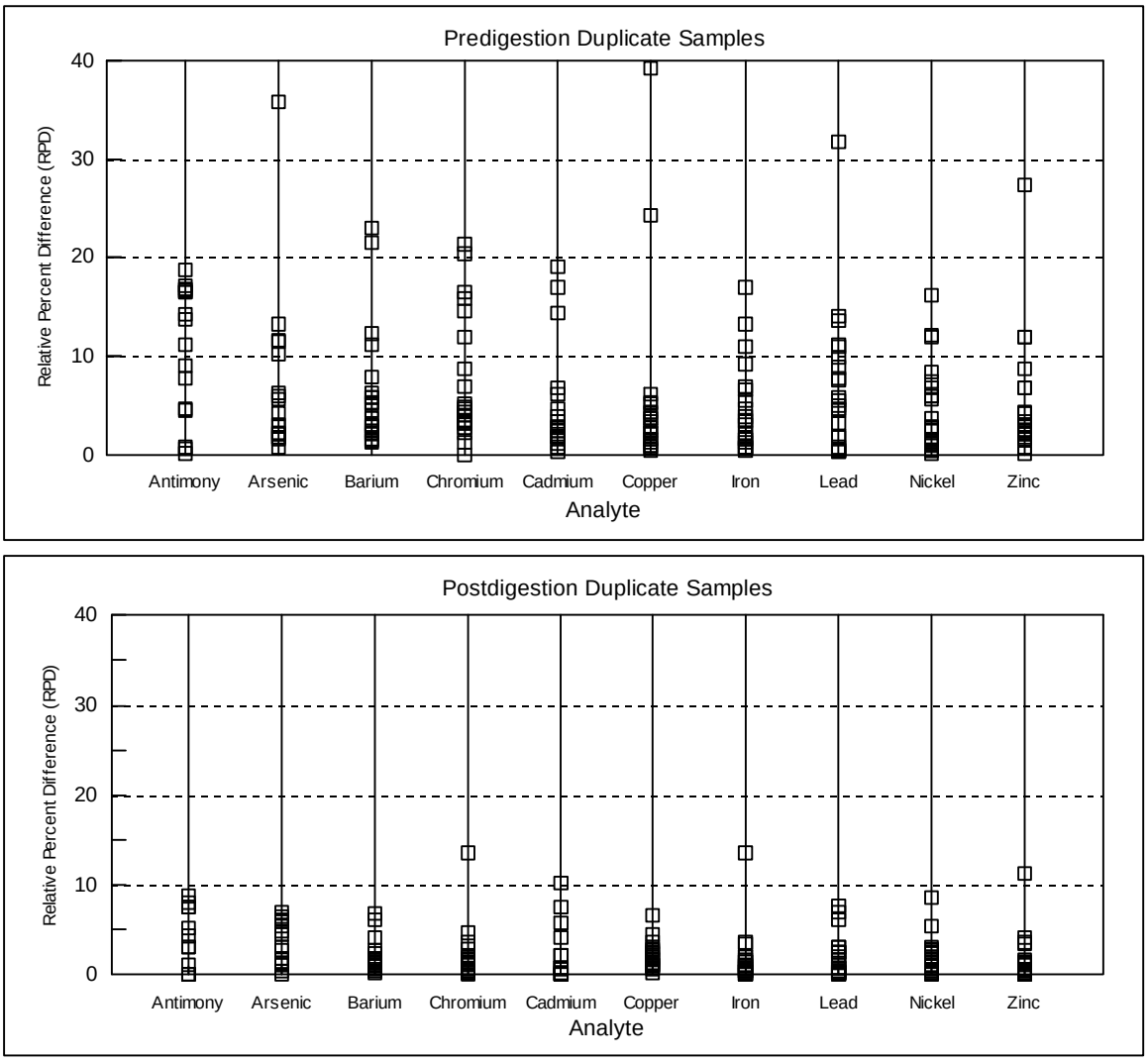


Figure 3-1. Pre- and Postdigestion Duplicate Samples: The top graph illustrates the reference laboratory's performance on analyzing predigestion duplicate samples. Twenty percent RPD represents the predigestion duplicate control limits defined in the demonstration QAPP. Two points were deleted from this top graph: barium at 65 percent RPD and copper at 138 percent RPD. The bottom graph illustrates the reference laboratory's performance on analyzing postdigestion duplicate samples. Ten percent RPD represents the postdigestion duplicate control limits defined in the demonstration QAPP.

Accuracy

Accuracy for the reference laboratory data was assessed through evaluations of the PE samples (including the CRMs), LCSs, method blank sample results, and pre- and postdigestion matrix spike samples. PE samples were used to assess the absolute accuracy of the reference laboratory method as a whole, while LCSs, method blanks, and pre- and postdigestion matrix spike samples were used to assess the accuracy of each batch of demonstration samples.

A total of eight PE and CRM samples was analyzed by the reference laboratory. These included four ERA PE samples and four RTC CRM samples. One of the ERA PE samples was submitted to the reference laboratory in duplicate, thereby producing nine results to validate accuracy. The accuracy data for all primary and secondary analytes are presented in Table 3-3 and displayed in Figure 3-2. Accuracy was assessed over a wide-concentration range for all 10 analytes with concentrations for most analytes spanning one or more orders of magnitude.

Reference laboratory results for all target analytes in the ERA PE samples fell within the PALs. In the case of the RTC CRM PE samples, reference laboratory results for copper in one CRM and zinc in two CRMs fell outside the published acceptance limits. One of the two out-of-range zinc results was only slightly above the upper acceptance limit (811 versus 774 mg/kg). The other out-of-range zinc result and the out-of-range copper result were about three times higher than the certified value and occurred in the same CRM. These two high results skewed the mean percent recovery for copper and zinc shown in Table 3-3. Figure 3-2 shows that the remaining percent recoveries for copper and zinc were all near 100 percent.

Table 3-3 shows that a total of 83 results was obtained for the 10 target analytes. Eighty of the 83 results or 96.4 percent fell within the PALs. Only 3 out of 83 times did the reference method results fall outside PALs. This occurred once for copper and twice for zinc. Based on this high percentage of acceptable results for the ERA and CRM PE samples, the accuracy of the reference methods was considered acceptable.

Table 3-3. Reference Laboratory Accuracy Data for Target Analytes

Analyte	n	Percent Within Acceptance Range	Mean Percent Recovery	Range of Percent Recovery	SD of Percent Recovery	Concentration Range (mg/kg)
Antimony	6	100	104	83 - 125	15	50 - 4,955
Arsenic	8	100	106	90 - 160	22	25 - 397
Barium	9	100	105	83 - 139	21	19 - 586
Cadmium	9	100	84	63 - 93	10	1.2 - 432
Chromium	9	100	91	77 - 101	8	11 - 187
Copper	9	89	123	90 - 332	79	144 - 4,792
Iron	7	100	98	79 - 113	12	6,481 - 28,664
Lead	8	87.5	86	35 - 108	22	52 - 5,194
Nickel	9	100	95	79 - 107	10	13 - 13,279
Zinc	9	78	120	79 - 309	72	76 - 3,021

Notes: n Number of samples with detectable analyte concentrations.
SD Standard deviation.
mg/kg Milligrams per kilogram.

LCS percent recoveries for all the primary analytes were acceptable in 21 of the 23 sample batches. Lead recovery was unacceptable in one sample batch and lead results for each sample in that batch were rejected.

Copper recovery was unacceptable in another sample batch, and copper results for each sample in this batch also were rejected. Percent recoveries of the remaining primary analytes in each of these two batches were acceptable. In all, 136 of 138 LCS results or 98.5 percent fell within the control limits.

Method blank samples for all 23 batches of demonstration samples provided results of less than 2 times the LRL for all primary analytes. This method blank control limit was a deviation from the QAPP, which had originally set the control limit at no target analytes at concentrations greater than the LRL. This control limit was widened at the request of the reference laboratory. A number of batches were providing method blank results for target analytes at concentrations greater than the LRL, but less than 2 times the LRL. This alteration was allowed because even at 2 times the LRL, positive results for the method blank samples were still significantly lower than the MDLs for each of the FPXRF analyzers. The results from the method blank samples did not affect the accuracy of the reference data as it was to be used in the demonstration statistical evaluation of FPXRF analyzers.

The percent recovery for the predigestion matrix spike samples fell outside of the 80 - 120 percent control limit specified in the QAPP in several of the 23 batches of demonstration samples. The predigestion matrix spike sample results indicate that the accuracy of specific target analytes in samples from the affected batches may be suspect. These results were qualified by the reference laboratory. These data were not excluded from use for the demonstration statistical comparison. A discussion of the use of this qualified data is included in the "Use of Qualified Data for Statistical Analysis" subsection.

The RPD for the postdigestion matrix spike samples fell within the 80 - 120 percent control limit specified in the QAPP for all 23 batches of demonstration samples.

The QA review of the reference laboratory data indicated that the absolute accuracy of the method was acceptable. Based on professional judgement, it was determined that the small percentage of outliers did not justify rejection of any demonstration sample results from the reference laboratory. The accuracy assessment also indicated that most of the batch summary data were acceptable. Two batches were affected by LCS outliers, and some data were qualified due to predigestion matrix spike recovery outliers. This data was rejected or qualified. Rejected data was not used. Qualified data were used as discussed below.

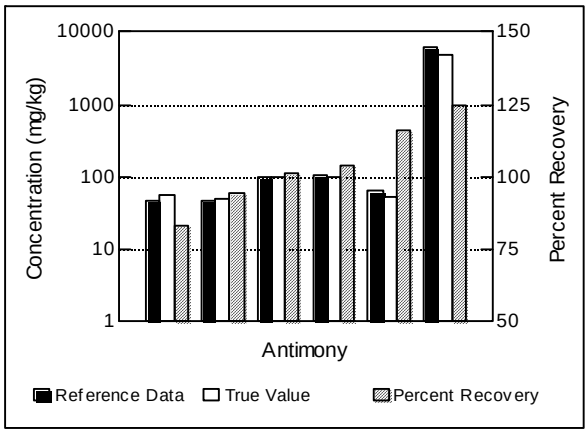
Representativeness

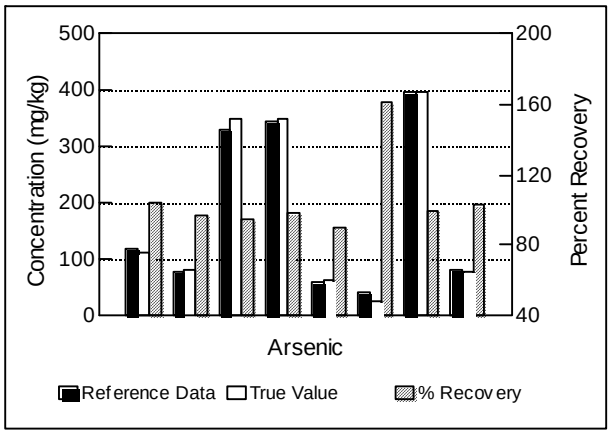
Representativeness of the analytical data was evaluated through laboratory audits performed during the course of sample analysis and by QC sample analyses, including method blank samples, laboratory duplicate samples, and CRM and PE samples. These QC samples were determined to provide acceptable results. From these evaluations, it was determined that representativeness of the reference data was acceptable.

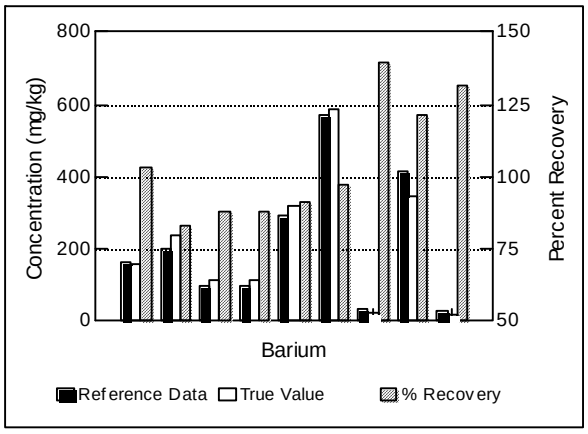
Completeness

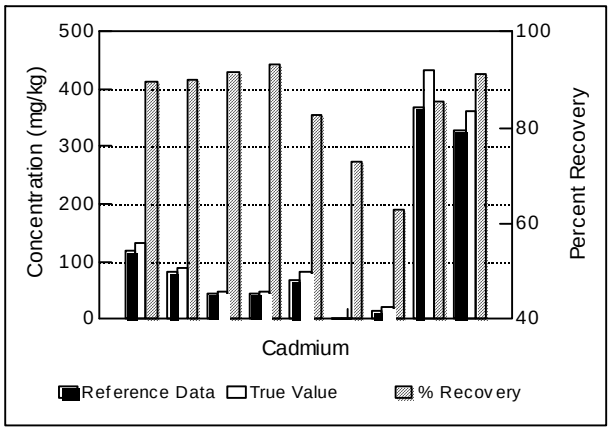
Results were obtained for all soil samples extracted and analyzed by EPA SW-846 Methods 3050A/6010A. Some results were rejected or qualified. Rejected results were deemed incomplete. Qualified results were usable for certain purposes and were deemed as complete.

To calculate completeness, the number of nonrejected results was determined. This number was divided by the total number of results expected, and then multiplied by 100 to express completeness as a percentage. A total of 385 samples was submitted for analysis. Six primary analytes were reported, resulting in an expected 2,310 results. Forty of these were rejected, resulting in 2,270 complete results. Reference laboratory completeness was determined to be 98.3 percent, which exceeded the objective for this demonstration of 95 percent. The reference laboratory's completeness was, therefore, considered acceptable.









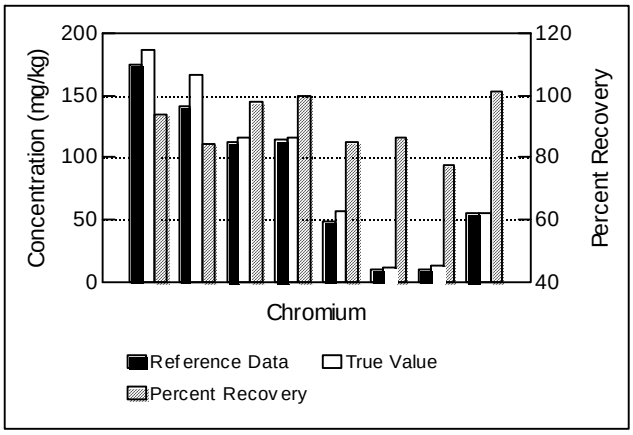
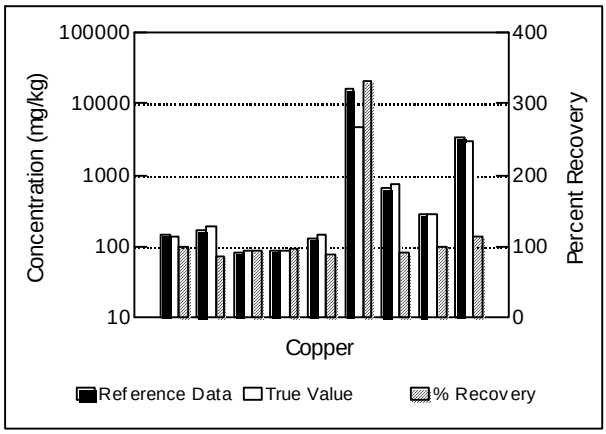
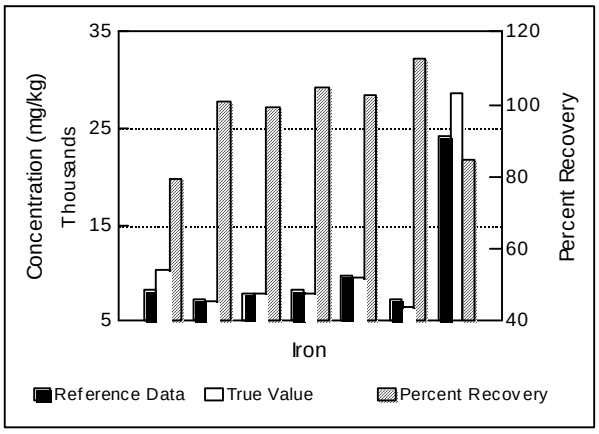
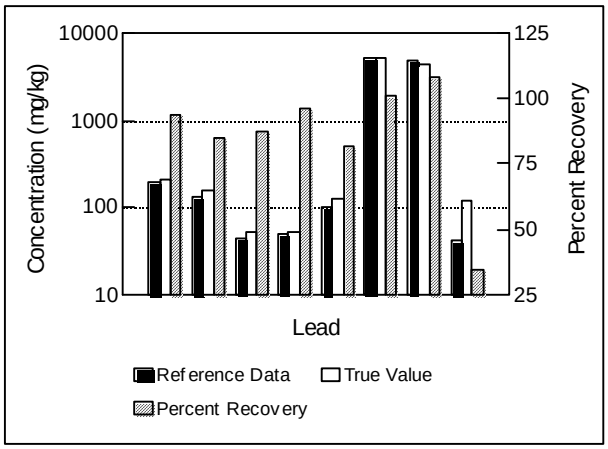
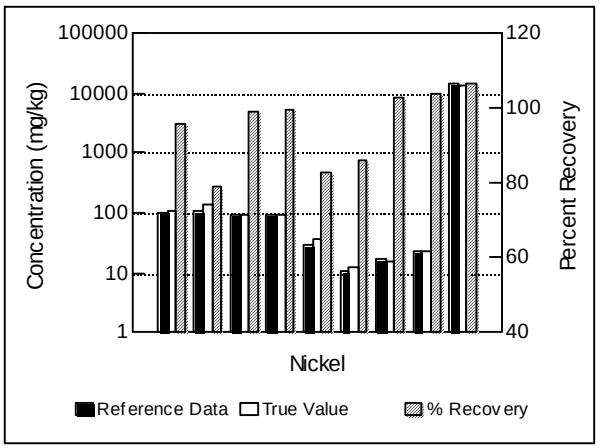


Figure 3-2. Reference Method PE and CRM Results: These graphs illustrate the relationship between the reference data and the true values for the PE or CRM samples. The gray bars represent the percent recovery for the reference data. Each set of three bars (black, white, and gray) represents a single PE or CRM sample. Based on this high percentage of acceptable results for the ERA and CRM PE samples, the accuracy of the reference laboratory method was considered acceptable.









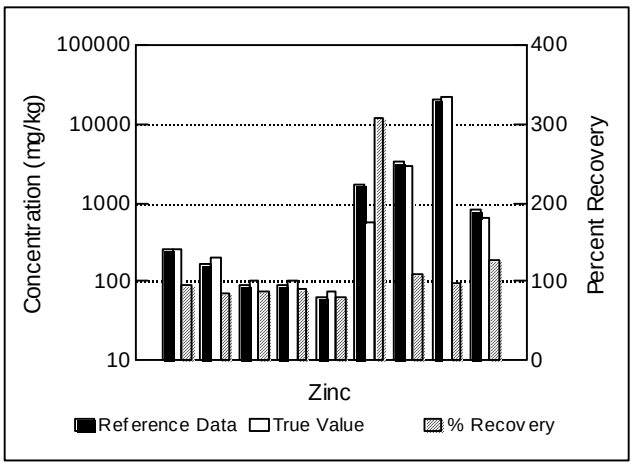


Figure 3-2 (Continued). Reference Method PE and CRM Results: These graphs illustrate the relationship between the reference data and the true values for the PE or CRM samples. The gray bars represent the percent recovery for the reference data. Each set of three bars (black, white, and gray) represents a single PE or CRM sample. Based on this high percentage of acceptable results for the ERA and CRM PE samples, the accuracy of the reference laboratory method was considered acceptable.

Comparability

Comparability of the reference data was controlled by following laboratory SOPs written for the performance of sample analysis using EPA SW-846 Methods 3050A/6010A. QC criteria defined in the SW-846 methods and the demonstration plan (PRC 1995) were followed to ensure that reference data would provide comparable results to any laboratory reporting results for the same samples.

Reference results indicated that EPA SW-846 Methods 3050A/6010A did not provide comparable results for some analytes in the SRM samples. SRM performance data for target analytes is summarized in Table 3-4 and displayed in Figure 3-3. As with the PEs, the analyte concentrations spanned up to 3 orders of magnitude in the SRMs. The percentage of acceptable (80 - 120 percent recovery) SRM results and mean percent recovery was less than 50 percent for the analytes antimony, barium, chromium, iron, and nickel. The low recoveries for these five analytes reflect the lesser tendency for them to be acid-extracted (Kane and others 1993).

Under contract to the EPA, multiple laboratories analyzed NIST SRMs 2709, 2710, and 2711 by EPA SW-846 Methods 3050A/6010A. A range, median value, and percent leach recovery based on the median value for each detectable element were then published as an addendum to the SRM certificates. These median values are not certified but provide a baseline for comparison to other laboratories analyzing these SRMs by EPA SW-846 Methods 3050A/6010A. Table 3-5 presents the published percent leach recovery for the 10 primary and secondary analytes and the reference laboratory's results for these three NIST SRMs. Table 3-5 shows that the results produced by the reference laboratory were consistent with the published results indicating good comparability to other laboratories using the same analytical methods on the same samples.

Table 3-4. SRM Performance Data for Target Analytes

Analyte	n	Percent Within Acceptance Range	Mean Percent Recovery	Range of Percent Recovery	SD of Percent Recovery	Concentration Range (mg/kg)
Antimony	5	0	22	15 - 37	9	3.8 - 171
Arsenic	11	72	84	67 - 106	10	18 - 626
Barium	8	12	41	21 - 89	21	414 - 1,300
Cadmium	10	50	80	43 - 95	15	2.4 - 72
Chromium	10	0	45	14 - 67	16	36 - 509
Copper	17	88	82	33 - 94	17	35 - 2,950
Iron	7	14	62	23 - 84	25	28,900 - 94,000
Lead	17	82	83	37 - 99	17	19 - 5,532
Nickel	16	19	67	25 - 91	17	14 - 299
Zinc	16	75	81	32 - 93	14	81 - 6,952

Notes:
n Number of SRM samples with detectable analyte concentrations.
SD Standard deviation.
mg/kg Milligrams per kilogram.

Table 3-5. Leach Percent Recoveries for Select NIST SRMs

Analyte	NIST SRM 2709		NIST SRM 2710		NIST SRM 2711	
	Published Result[a]	Reference Laboratory Result	Published Result[a]	Reference Laboratory Result	Published Result[a]	Reference Laboratory Result
Antimony	–	–	21	–	–	20
Arsenic	–	106	94	87	86	91
Barium	41	37	51	45	28	25
Cadmium	–	–	92	84	96	87
Chromium	61	–	49	–	43	49
Copper	92	85	92	92	88	90
Iron	86	84	80	78	76	66
Lead	69	87	92	96	95	90
Nickel	89	76	71	69	78	70
Zinc	94	78	85	88	89	85

Notes:
[a] Published results found in an addendum to SRM certificates for NIST SRMs 2709, 2710, and 2711.
NIST National Institute of Standards and Technology.
SRM Standard reference materials.
– Analyte not present above the method LRL.

The inability of EPA SW-846 Methods 3050A/6010A to achieve the predetermined 80 - 120 percent recovery requirement indicated that the methods used to determine the certified values for the SRM samples were not comparable to EPA SW-846 Methods 3050A/6010A. Differences in the sample extraction methods and the use of different analytical instruments and techniques for each method were the major factors of this noncomparability. Because of these differences, it was not surprising that the mean percent recovery was less than 100 percent for the target analytes. The lack of comparability of EPA SW-846 Methods 3050A/6010A to the total metals content in the SRMs did not affect the quality of the data generated by the reference laboratory.

The assessment of comparability for the reference data revealed that it should be comparable to other laboratories performing analysis of the same samples using the same extraction and analytical methods, but it may not be comparable to laboratories performing analysis of the same samples using different extraction and analytical methods or by methods producing total analyte concentration data.

Use of Qualified Data for Statistical Analysis

As noted above, the reference laboratory results were reported and validated, qualified, or rejected by approved QC procedures. Data were qualified for predigestion matrix spike recovery and pre- and postdigestion laboratory duplicate RPD control limit outliers. None of the problems were considered sufficiently serious to preclude the use of coded data. Appropriate corrective action identified in the demonstration plan (PRC 1995) was instituted. The result of the corrective action indicated that the poor percent recovery and RPD results were due to matrix effects. Since eliminating the matrix effects would require additional analysis using a different determination method such as atomic absorption spectrometry, or the method of standard addition, the matrix effects were noted and were not corrected.

PARCC parameters for the reference laboratory data were determined to be acceptable. It was expected that any laboratory performing analysis of these samples using EPA SW-846 Methods 3050A/6010A would experience comparable matrix effects. A primary objective of this demonstration was to compare sample results from the FPXRF analyzers to EPA SW-846 Methods 3050A/6010A, the most widely used approved methods for determining metal concentrations in soil samples. The comparison of FPXRF and the reference methods had to take into account certain limitations of both methods, including matrix effects. For these reasons, qualified reference data were used for statistical analysis.

The QC review and QA audit of the reference data indicated more than 98 percent of the data either met the demonstration QAPP objectives or was QC coded for reasons not limiting its use in the data evaluation. Less than 2 percent of the data were rejected based on QAPP criteria. Rejected data were not used for statistical analysis. The reference data were considered as good as or better than other laboratory analyses of samples performed using the same extraction and analytical methods. The reference data met the definitive data quality criteria and was of sufficient quality to support regulatory activities. The reference data were found to be acceptable for comparative purposes with the FPXRF data.

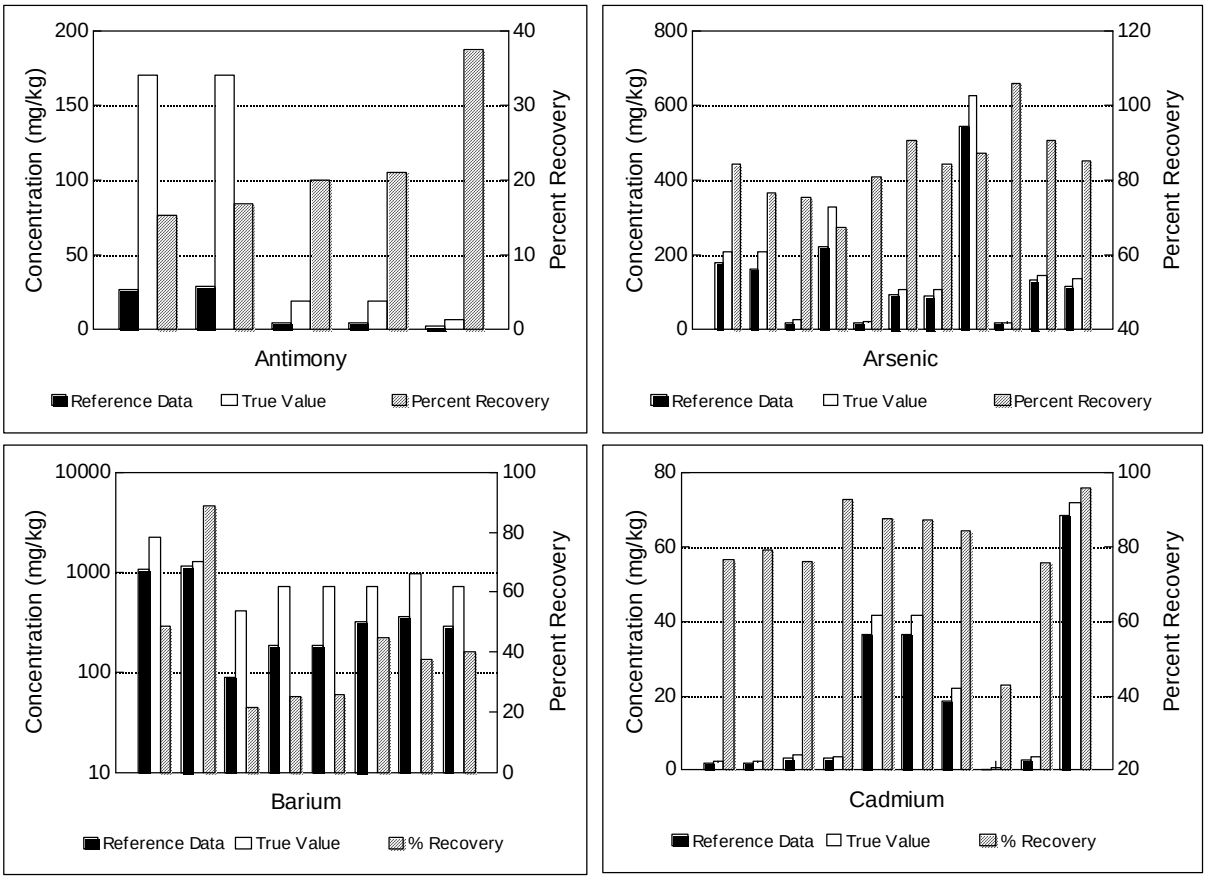


Figure 3-3. Reference Method SRM Results: These graphs illustrate the relationship between the reference data and the true values for the SRM samples. The gray bars represent the percent recovery for the reference data. Each set of three bars (black, white, and gray) represents a single SRM sample.

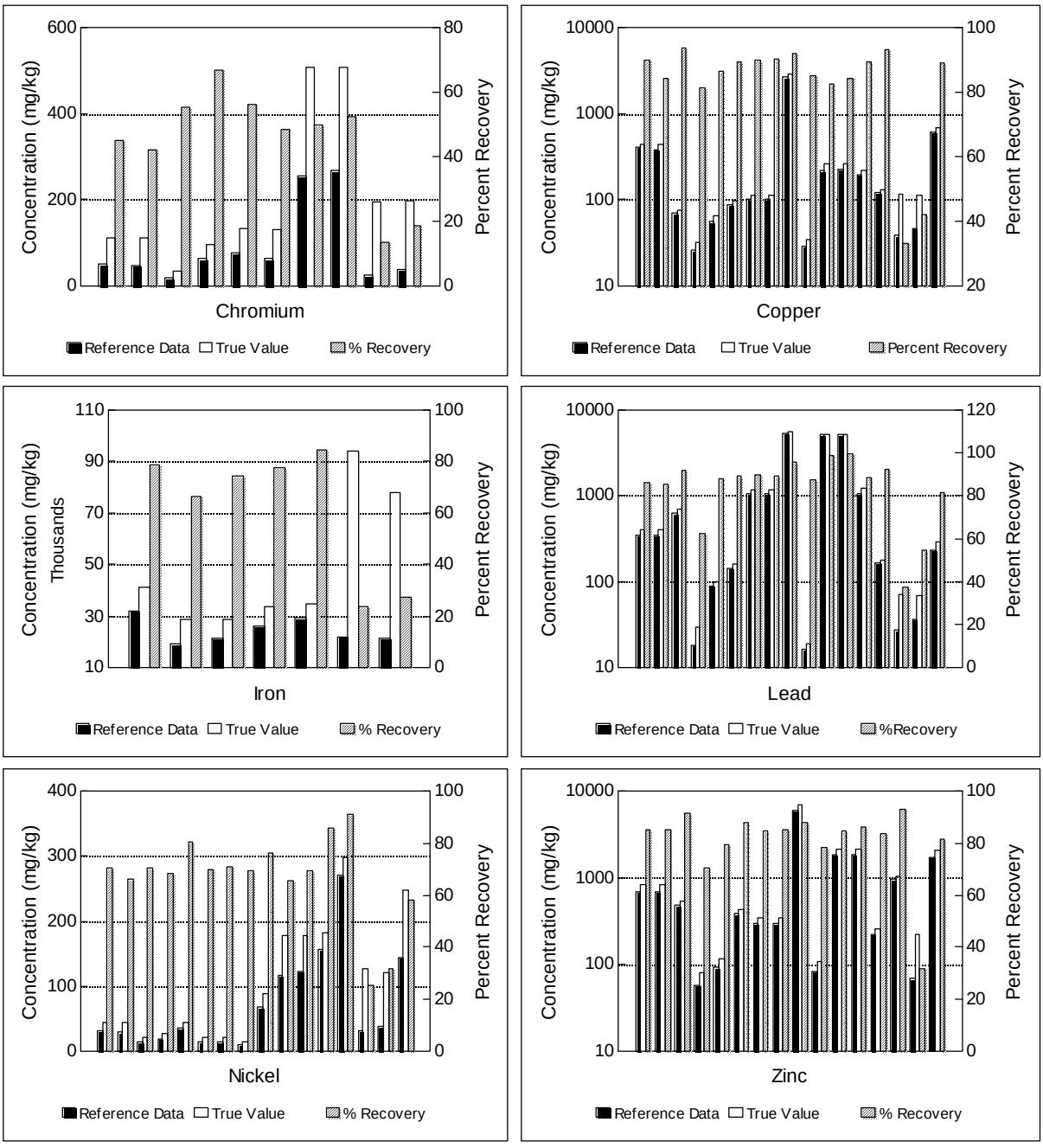


Figure 3-3 (Continued). Reference Method SRM Results: These graphs illustrate the relationship between the reference data and the true values for the SRM samples. The gray bars represent the percent recovery for the reference data. Each set of three bars (black, white, and gray) represents a single SRM sample.

Section 4
TN Pb Analyzer

This section provides information on the Spectrace TN Pb Analyzer, including the theory of FPXRF, operational characteristics, performance factors, a data quality assessment, and a comparison of results with those of the reference laboratory.

Theory of FPXRF Analysis

FPXRF analyzers operate on the principle of energy dispersive XRF spectrometry. This is a nondestructive qualitative and quantitative analytical technique that can be used to determine the metals composition in a test sample. By exposing a sample to an X-ray source having an excitation energy close to, but greater than, the binding energy of the inner shell electrons of the target element, electrons are displaced. The electron vacancies that result are filled by electrons cascading in from the outer shells. Electrons in these outer shells have higher potential energy states than inner shell electrons, and to fill the vacancies, they give off energy as they cascade into the inner shell vacancies (Figure 4-1). This release of energy results in an emission of X-rays that is characteristic to each element. This emission of X-rays is termed XRF.

Because each element has a unique electron shell configuration, each will emit unique X-rays at fixed wavelengths called "characteristic" X-rays. The energy of the X-ray is measured in electron volts (eV). By measuring the peak intensity of X-rays emitted by a sample, it is possible to identify and quantify the elemental composition of the sample. A qualitative analysis can be made by identifying the characteristic X-rays produced by the sample. The intensity of each characteristic X-ray is proportional to the concentration of the target and can be used to quantitate each element.

Three electron shells are generally involved in the emission of characteristic X-rays during FPXRF analysis: the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given element has multiple peaks generated from the emission X-rays by the K, L, or M shell electrons. The most commonly measured X-ray emissions are from the K and L shells; only elements with an atomic number of 58 (cerium) or greater have measurable M shell emissions.

Each characteristic X-ray peak or line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α) or beta (ß), which indicates the next outermost shell from which electrons fell to fill the vacancy and produce the X-ray. For example, a K_α-line is produced by a vacancy in the K shell filled by an L shell electron, whereas a $K_ß$-line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is between 7 and 10 times more probable than the $K_ß$ transition. The K_α-line is approximately 10 times more intense than the $K_ß$-line for a given element, making the K_α-line analysis the preferred choice for quantitation purposes. Unlike the K-lines, the L-lines (L_α and

$L_ß$) for an analyte are of nearly equal intensity. The choice of which one to use for analysis depends on the presence of interfering lines from other analytes.

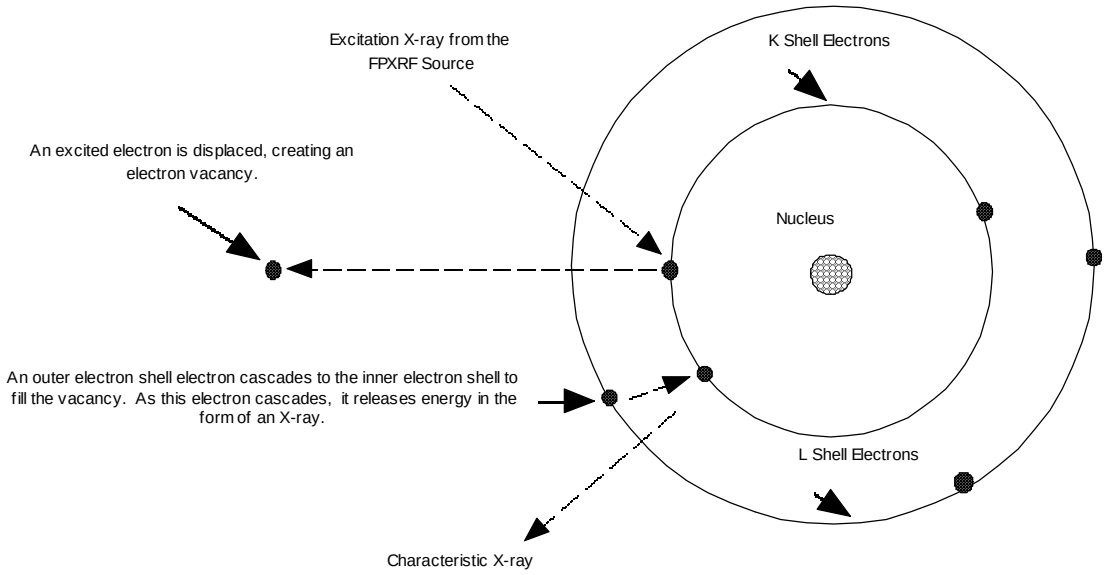


Figure 4-1. Principle of Source Excited X-ray Fluorescence: This figure illustrates the dynamics of source excited X-ray fluorescence.

An X-ray source can excite characteristic X-rays from an analyte only if its energy is greater than the electron binding energies of the target analyte. The electron binding energy, also known as the absorption edge energy, represents the amount of energy an electron has to absorb before it is displaced. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K-absorption edge energy is approximately the sum of the K-, L-, and M-line energies of the particular element, and the L- absorption edge energy is approximately the sum of the L- and M-line energies. FPXRF analytical methods are more sensitive to analytes with absorption edge energies close to, but less than, the excitation energy of the source. For example, when using a Cd^{109} source, which has an excitation energy of 22.1 kiloelectron volts (keV), an FPXRF analyzer would be more sensitive to zirconium, which has a K-line absorption edge energy of 15.7 keV, than to chromium, which has a K-line absorption edge energy of 5.41 keV.

Background

Since 1988, TN Spectrace has produced field portable and laboratory-grade XRF technologies for a broad range of applications. The TN Pb Analyzer was released in 1993 specifically for analyzing lead in a variety of matrices such as soil, paint, paint chips, surface dust, and air filters. Using the "Soils Application" software supplied with the analyzer, it can also identify and quantify arsenic, chromium, iron, copper, zinc, and manganese in soils.

The TN Pb Analyzer uses an HgI_2 semiconductor detector that achieves a manganese-K_α X-ray resolution of approximately 300 eV. The detector is operated at a subambient temperature using a low power thermoelectric (Peltier) cooler in the measurement probe.

To perform either an *in situ* or intrusive analysis, a sample is positioned in front of the plastic film probe window and the sample measurement sequence is initiated. This exposes the sample to primary radiation from the source. Fluorescent and backscattered X-rays from the sample re-enter the analyzer through the window and are counted in the high resolution HgI_2 detector. When analyzing intrusive samples, the probe is placed upright in a stand and the sample, which is contained in a thin-windowed plastic cup, is placed over the probe measurement window beneath a swing-down safety shield.

Analyte concentrations are computed using a fundamental parameter (FP) calibrated algorithm that is part of the TN Pb Analyzer's software package. The TN Pb Analyzer uses FPs to calibrate its detector. The FPs are based on the physics of the excitation of target analytes and the emission of X-rays. The FP method does not require site-specific calibration samples; however, site specific samples can be used to customize the calibration to a particular site or matrix. The software package supports multiple XRF calibrations. Each application requires a complete analysis configuration, including target analytes to be measured, interfering target analytes in the sample, and a set of FP calibration coefficients.

Operational Characteristics

This section discusses equipment and accessories, operation of the analyzer in the field, background of the operator, training, reliability of the analyzer, health and safety concerns, and representative operating costs.

Equipment and Accessories

The TN Pb Analyzer comes with all the accessories needed for both *in situ* and intrusive operation (Table 4-1). A hard-shell carrying case containing the equipment protected by foam inserts is provided for transportation and storage.

Two main components make up the analytical system: a probe and an electronics unit. The probe contains the radioisotope source, Cd^{109}, for sample excitation and the HgI_2 detector for analyte detection, identification, and quantitation. The source is encapsulated and housed in a metal turret with additional lead shielding inside the probe. The source exposes the sample to excitation radiation through a sealed 1-inch-diameter Mylar™ window in the face of the probe. The X-ray-induced fluorescence from the sample passes back through the window and is intercepted by the HgI_2 detector. This signal is then transferred to the electronics unit, which identifies and measures the energy of each X-ray and builds a spectrum of analyte peaks on a 2,048-channel multichannel analyzer (MCA). This spectrum contains the peak lines for all the metals present in the sample.

Spectral data is communicated from the probe to the electronics unit through a flexible cable of 6, 12, or 20 feet in length. The standard cable length is 6 feet. X-ray emission peaks are integrated and metal concentrations in milligrams per kilogram or percentage values are calculated. The electronics unit will store and display both numerical results and spectra from a measurement. A maximum of 600 sets of numerical results and 100 spectra can be stored before downloading to a personal computer (PC) using an RS-232 cable.

The electronics unit can be operated from a battery or from an alternating current (AC) electric line using a plug-in adaptor unit. The TN Pb Analyzer is supplied with two nickel-cadmium batteries and a battery charger. The batteries last approximately 8 hours and require a minimum of 14 hours to fully recharge. For *in situ* analysis, the developer provided a water-resistant carrying case and a strap for easy

portability on-site. The carrying case has a flap on top that can be closed to protect the unit from adverse weather conditions.

Table 4-1. Analyzer Instrument Specifications—TN Pb Analyzer

Characteristic	Specification
Resolution	< 300 eV (Manganese-K_α)
Source	30 millicuries (mCi) Cd^{109} (with shim inserts)
Detector	HgI_2-Peltier cooled
Probe Size	12.7 cm x 7.6 cm x 21.6 cm
Probe Weight	1.9 kilograms
Probe Operating Temperature	0 to 49 °C
Electronics Unit Size	32 cm x 30 cm x 10 cm
Electronics Unit Weight	6.7 Kilograms
Electronics Unit Operating Temperature	0 to 49 °C
Electronics Unit Storage Capacity	600 sets of numerical results and 100 spectra
Power Source	120V or 220V (alternating current) or internal batteries
Operational Checks	3 NIST SRMs, silicon dioxide (SiO_2) and Teflon® blanks, pure element check sample kit
Intrusive Operation	Uniblock probe stand
Computer Interface Operation	RS 232 serial input/output cable, operators manual, application and results software, and training video
Contact: Raj Natarajan 2555 N. Interstate Hwy. 35 Round Rock, TX 78664 (800) 736-0801 (512) 388-9200 (FAX)	

Other equipment and supplies that are helpful when using the TN Pb Analyzer, which is not supplied by the developer, include a PC for downloading the FPXRF data, protective gloves, paper towels, and a permanent marking pen.

Operation of the Analyzer

For this demonstration, the TN Pb Analyzer was operated on battery power only. The *in situ* analysis was performed with the analyzer in the carrying case. The probe was pointed at the soil surface and analysis was started by pressing a trigger on the back of the probe. For intrusive analysis, the probe was placed in the "uniblock" pointed upward with the safety shield attached. The "uniblock" is a free standing support for the probe. All intrusive analyses at both sites were performed by setting the analyzer on a table top located indoors. At the ASARCO site, the room was not heated or cooled so analysis occurred at ambient temperatures. At the RV Hopkins site, the area where the analyzers were operated was maintained at 25 °C.

Background of the Technology Operator

The PRC operator chosen for analyzing soil samples using the TN Pb Analyzer has a bachelor's degree in environmental science. Prior to conducting this work, this operator worked for a year and a half in a

pharmaceutical laboratory as an analytical chemist and a half year as an environmental scientist. The operator received approximately 8 hours of training by the developer prior to the start of the demonstration. The training covered the theoretical background of XRF technology and specific operation of the TN Pb Analyzer.

Training

The training included step-by-step instructions on how to set up and use the TN Pb Analyzer. These instructions covered connecting the nickel-cadmium battery, attaching the probe to the electronics unit, setting up the "Soils Applications" software, operating the keyboard and analyzer software, modifying the count times for the Cd^{109} source, setting the probe in the "uniblock" and attaching the safety shield for intrusive analysis, downloading results to a PC, and performing instrument maintenance, for example, replacing the probe window.

The TN Pb Analyzer was calibrated prior to the training using an FP algorithm and fine tuned with site-specific soil samples supplied from the predemonstration activities. Part of the training included a discussion of QC requirements, such as the analysis of a pure iron energy calibration check, a silicon dioxide (SiO_2) blank, and at least one NIST SRM. Possible interferences that could be encountered and recommended procedures for preparing both *in situ* and intrusive soil samples for analysis were discussed in detail. At the conclusion of the training, the developer was confident that the operator was ready to operate the TN Pb Analyzer. The developer accompanied the PRC operator during the first morning at the ASARCO site and observed the operator analyzing soil samples. No problems were encountered and the developer left the site.

Reliability

A reliability check of the TN Pb Analyzer was carried out by a daily measurement of a reference sample. The reliability check involved a 50-second measurement of a pure iron sample. This measurement verified (1) fluorescent element sensitivity; (2) spectrometer energy resolution; and (3) spectrometer energy calibration. To be acceptable, the measured relative X-ray intensity of iron had to be greater than 0.95 and the equivalent intensity of manganese and cobalt had to be less than 0.006. Relative intensity refers to the measured value relative to that obtained at the time of the initial instrument calibration. If the intensity conditions were not met, then the iron sample was reanalyzed. No energy calibrations were required during the demonstration based on the iron sample results.

During the demonstration, there were frequent light to moderate rains while the analyzer was performing the *in situ* measurements. The developer recommended that samples analyzed by the TN Pb Analyzer have less than 20 percent moisture content by weight. The samples collected during this demonstration contained up to 30 percent moisture content by weight. This increased moisture content did not appear to reduce the analyzer's data comparability. During the ASARCO site sampling, there was a period of heavy rain for approximately 1.5 hours. After the rain, it was common for the soil surface to be saturated. This did not pose an operational problem for the analyzer in the *in situ* mode. At the ASARCO and the RV Hopkins sites, the temperatures ranged approximately from 5 to 16 °C and from 6 to 22 °C, respectively. Despite the less than ideal weather conditions, there were no mechanical or electronic problems experienced with the TN Pb Analyzer during the course of the demonstration. The only maintenance required was the replacement of the probe window cover once due to contamination and damage from small pebbles. The replacement of the probe window cover took approximately 2 to 3 minutes. A spare probe window was included with the analyzer.

Health and Safety

The potential for exposure to radiation from the excitation source is the greatest health and safety consideration while using the analyzer. Radiation was monitored with a radiation survey meter. Background radiation at the two sites was between 0.006 and 0.012 millirems per hour (mrem/hr). Radiation exposure was monitored in the *in situ* and intrusive modes while the probe's source was exposed (during a measurement), obtaining a worst-case scenario. The radiation was measured within 5 cm of the probe face while the analyzer was analyzing a sample. Radiation exposure was also monitored at a point on the probe where the operator's hand was located during analysis to provide a realistic value of operator exposure. The TN Pb Analyzer is sold under a general license, meaning that the analyzer is designed and constructed in such a way that anybody operating it, as instructed by the developer, will not be exposed to harmful radiation levels set by the Nuclear Regulatory Commission. Many states still recommend that radiation from survey instruments be below a certain level. For example, in the State of Kansas, the permissible occupational exposure is 5,000 millirems per year, which equates to approximately 2 to 3 mrem/hr assuming constant exposure for an entire work year.

While taking *in situ* measurements, radiation values of 0.40 - 0.45 mrem/hr at the probe face and 0.05 to 0.06 mrem/hr at the probe handle were obtained for the TN Pb Analyzer with the Cd^{109} source exposed. While collecting intrusive measurements with the TN Pb Analyzer, radiation values of 0.50 - 0.60 mrem/hr directly above the protective cover and 0.05 to 0.06 mrem/hr 1.0 foot from the protective cover were obtained with the Cd^{109} source exposed. All measured radiation values were less than the occupational level of 2.0 mrem/hr. The operator noted, however, there was no safety feature on the analyzer that would prevent a person from accidental exposure by pushing the trigger on the rear of the probe to start an analysis while the probe was pointed at the operator or another person.

Cost

At the time of the demonstration, the cost of a new TN Pb Analyzer was $39,500. This included all of the equipment necessary to operate the analyzer. The analyzer is warranted for a full year with an optional extended warranty. The TN Pb Analyzer can be rented from the developer for $5,000 per month or $3,000 for 2 weeks. Additional field packs can be purchased for $200 and external batteries, charger, and adapter for $750. A 12-month or 24-month extended warranty can be purchased for $2,750 or $4,750, respectively. Periodic maintenance includes replacement and disposal of the Cd^{109} source every 2 years at a cost of $3,500 - $3,800. For optimum performance, the Cd^{109} source must be "deshimmed" every 6 - 10 months at a cost of $1,500. Deshimming is the process of removing shielding around the source to keep emissions nearly constant. Because the TN Pb Analyzer contains a radioisotope, a wipe test must be conducted once every 6 months at a cost of $40.

The developer offers a training course at its offices or on-site. The cost of a 2-day training course at the developer's office is only the cost of travel per student. The cost of an on-site course is $1,000 per day, plus travel expenses for the developer's instructor. Costs associated with the operator vary depending on the technical knowledge and experience of the operator.

The primary cost benefit of field analysis is the quick access to analytical data. This allows the process dependent on the testing to move efficiently onto the next phase. Costs associated with field analysis are very dependent on the scope of the project. Since most of the mobilization costs are fixed, analyzing a large number of samples lowers the per sample cost. This is a key advantage that field analysis has over a conventional laboratory. Furthermore, more samples are usually taken for field analysis since

questions raised in the preliminary findings may be resolved completely without the need to return for another sample collection event.

A representative list of costs associated with the operation of the TN Pb Analyzer is presented in Table 4-2. Also included in this table is the measured throughput and the per sample charge of the reference laboratory. Given the special requirements of this demonstration, it was not considered fair or reasonable to report a per sample cost for the field analysis. However, some estimate can be derived from the data provided in the table.

Table 4-2. Instrument and Field Operation Costs

Item	Amount	
TN Pb Analyzer	$ 39,500	Purchase Price
	5,000	Per Month Lease
Replacement Source	3,500	For Cd^{109}
Operator Training (Vendor Provided)	—	—
(On-site Training)	1,000	Per day
Radiation Safety License (State of Kansas)	500	—
Periodic Source Maintenance	1,500	"Deshimming" required every 6 - 10 months
Field Packs for Batteries and Charger	750	—
Field Operation Costs		
Supplies and Consumables (Sample cups, window film, sieves, standards)	300 - 500	(Varies, depending on sample load)
Field Chemist (Labor Charge)	100 - 150	Per day
Per diem	80 - 120	Per day
Travel	200 - 500	Per traveler
Sample Throughput	20 - 25	Samples per hour
Cost of Reference Laboratory Analysis	150	Per sample

Performance Factors

The following paragraphs describe performance factors, including detection limits, sample throughput, and drift.

Detection Limits

MDLs, using SW-846 protocols, were determined by collecting 10 replicate measurements on site-specific soil samples with metals concentrations 2 to 5 times the expected MDL value. These data were obtained during the precision study. Based on these results, a standard deviation was calculated and the MDLs were reported at 3 times the standard deviation for each analyte. All the precision-based MDLs were calculated for soil samples that had been dried, ground, and placed in a sample cup, the intrusive mode of sample preparation. The precision-based MDLs for the TN Pb Analyzer are shown in Table 4-3.

Another method of determining MDLs involved the direct comparison of the FPXRF data and the reference data. When these sets of data were plotted against each other, the resultant plots were linear. As

the plotted line approached zero for either method, there was a point at which the FPXRF data appeared to correspond with the same reading of the reference data. Figure 4-2 shows an example data plot for copper for the TN Pb Analyzer to illustrate this effect. By determining the mean values of this data point, it was possible to determine a field or performance-based MDL for the analyzer. For the TN Pb Analyzer these field-based MDLs are shown in Table 4-3.

Table 4-3. Method Detection Limits—TN Pb Analyzer

Analyte	Developer-based MDL[a] (mg/kg)	Precision-based MDL (mg/kg)	Field based MDL (mg/kg)
Arsenic	46	50	77
Chromium	330	460	2,400
Copper	80	115	216
Lead	25	40	44
Zinc	64	95	168

Notes: [a] Corrected to reflect 60-second count time for the Cd^{109} source.

Mg/kg Milligrams per kilogram.

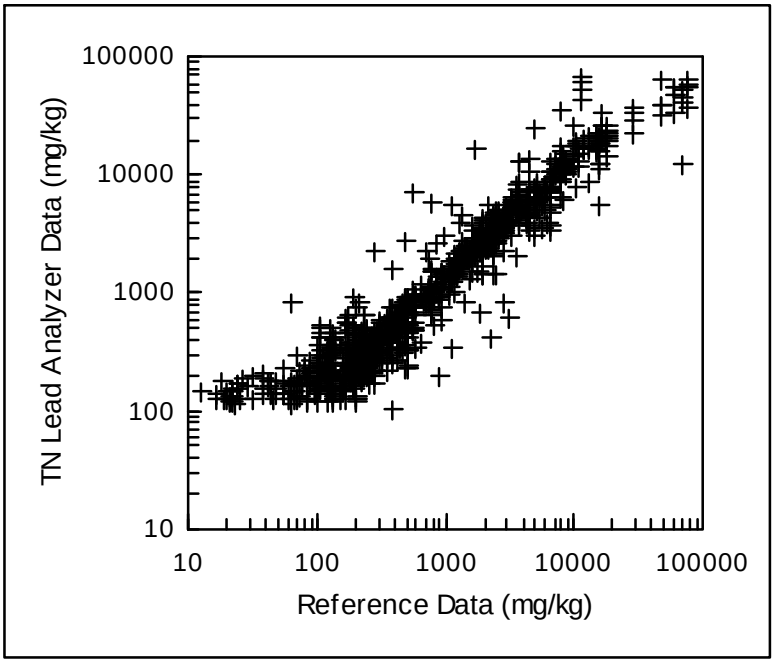


Figure 4-2. Critical Zone for the Determination of a Field-based Method Detection Limit for Copper: Between 100 and 300 mg/kg for the reference data, the linear relationship between the two data sets changes. This point of change identified the point at which field-based MDLs for the analyzer were determined.

Throughput

The TN Pb Analyzer used a Cd^{109} source count time of 60 seconds. With the additional "dead" time of the system and the time required to label each sample and store data between sample measurements, the time required to analyze one soil sample was 2 to 2.5 minutes. This resulted in a throughput of 20 - 25 samples per hour. The minimum number of samples analyzed in a 10-hour day, during the demonstration, was 195 samples. This was for *in situ* measurements in the field at the ASARCO site where the operator sometimes had to traverse distances of up to 0.5 miles between samples. The maximum number of samples analyzed in a 12-hour day was 330 samples for intrusive measurements at the ASARCO site.

This throughput took into account the time necessary to analyze three QC samples, one SiO_2 blank, one pure iron sample calibration check, and one NIST SRM. These QC sample analyses are recommended by the developer. The sample analysis time did not include the time required for sample handling and preparation, or for data downloading, printing, and documentation. Considerable time was spent preparing the *in situ* homogenized samples and the intrusive samples. Homogenization required an average of approximately 5 minutes per sample (*in situ*-prepared), 20 minutes per sample were required for No. 10 sieving (intrusive-unprepared), and 10 minutes per sample were required for grinding and sieving (intrusive-prepared). Approximately 30 minutes were spent daily downloading the data to a PC and printing out a hard copy.

Drift

Drift is a measure of an analyzer's variability in quantitating a known amount of a standard over time. For the TN Pb Analyzer, drift was evaluated by reviewing results from the analysis of NIST SRM 2710. This SRM contained quantifiable levels of arsenic, copper, lead, zinc, and iron. It was analyzed four times by the TN Pb Analyzer during the demonstration. This data was reduced to RSDs for the target analytes and the percent drift from the mean recovery of the true value. The percent drift from the mean recovery for each day is shown in Figure 4-3. The RSD values for all analytes were less than 8 percent, and the mean percent recoveries were between 90 and 100 percent. The RSD values for copper, lead, zinc, and iron were all less than 3 percent and 8 percent for arsenic. These low RSD values and high percent recoveries indicate that for the analytes found in the SRM, the TN Pb Analyzer displayed little drift during the demonstration. The minimal drift that did occur was less than the 10 percent limit noted in the demonstration QAPP.

Intramethod Assessment

Intramethod measures of the analyzer's performance include results on analyzer blanks, completeness, precision, accuracy, and comparability. The following paragraphs discuss these characteristics.

Blanks

Analyzer blanks for the TN Pb Analyzer consisted of SiO_2 blocks. These blanks were routinely analyzed at the beginning and end of each day or at the beginning and in the middle of the day. They were used to monitor for contamination by material such as residual soil left on the face of the probe. A total of 20 SiO_2 blanks was analyzed during the demonstration. None of the target analytes were detected in any of the 20 blanks.

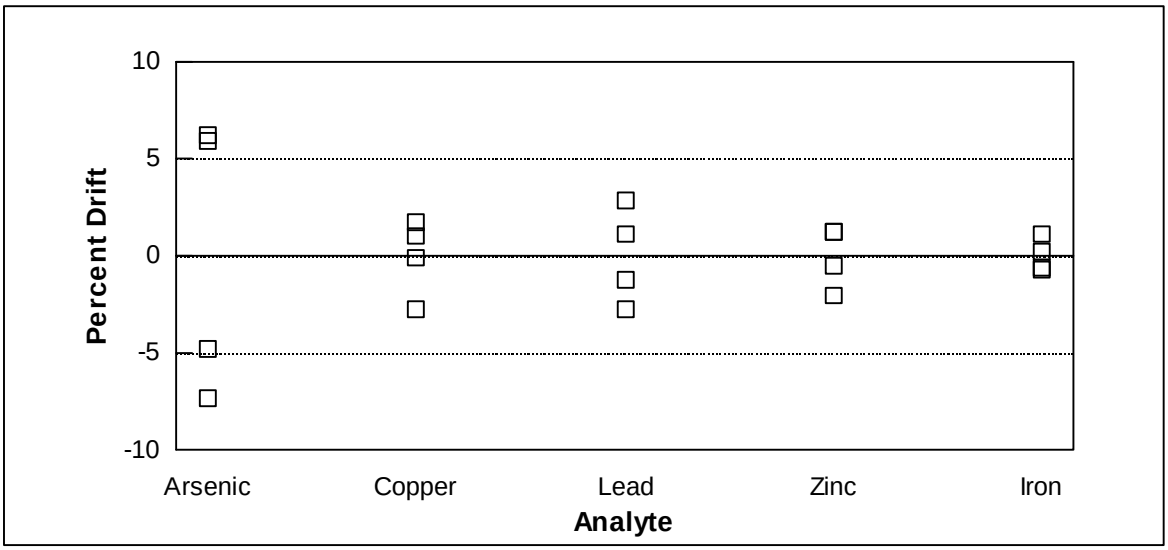


Figure 4-3. Drift Summary—TN Pb Analyzer: This graph illustrates the drift experienced by the analyzer at the two demonstration sites.

Completeness

A total of 315 soil samples was analyzed four times (four preparation steps) resulting in 1,260 sample results. The TN Pb Analyzer produced results for all 1,260 samples for a completeness of 100 percent, above the demonstration objective of 95 percent.

Precision

Precision was expressed in terms of the percent RSD between replicate measurements. The precision data for the target analytes reported by the TN Pb Analyzer are shown in Table 4-4. The results reported at 5 to 10 times the MDL reflects the precision generally referred to in analytical methods, such as SW-846.

Table 4-4. Precision Summary—TN Pb Analyzer

Analyte	Mean % RSD Values by Concentration Range			
	5 - 10 Times MDL[a] (mg/kg)	50 - 500 (mg/kg)	500 - 1,000 (mg/kg)	>1,000 (mg/kg)
Arsenic	4.11 (16)	16.47 (8)	3.47 (12)	2.30 (8)
Chromium	ND	ND	21.73 (12)	24.62 (4)
Copper	9.11 (8)	18.00 (24)	5.82 (4)	2.60 (12)
Iron	ND	ND	ND	2.18 (48)
Lead	5.93 (12)	8.93 (12)	5.02 (8)	2.52 (20)
Zinc	7.48 (16)	13.42 (24)	7.12 (16)	ND

Notes:
[a] The MDLs referred to in this column are the precision-based MDLs shown in Table 4-3.
mg/kg Milligrams per kilogram.
ND No data.
( ) Number of samples, each consisting of 10 replicate analyses.

The TN Pb Analyzer performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from less than 50 mg/kg to greater than 10,000 mg/kg. Each of the 12 soil samples underwent the four different sample preparation steps described previously in Section 2.0. Therefore, there was a total of 48 precision points for the TN Pb Analyzer. The replicate measurements were taken using the source count times discussed in the previous section of this report. For each analyte in each precision sample, a mean concentration, SD, and RSD were calculated.

In this demonstration, the analyzer's precision or RSD for a given analyte had to be less than or equal to 20 percent to be considered quantitative screening level data and less than or equal to 10 percent to be considered definitive level data. With the exception of chromium, the analyzer's precision data, reflected in the 5 to 10 times MDL range, were below the 10 percent RSD required for definitive level data quality classification. Chromium data was not represented in this range. The lower precision for chromium was expected because chromium is a problematic analyte for FPXRF analysis, especially at 60-second count times.

Figure 4-4 shows an asymptotic relationship between concentration and precision. In this figure, precision shows little improvement at concentrations greater than 250 ppm; however, at concentrations below 250 ppm, precision is highly concentration dependent. Although only lead is shown in this figure, this trend was true for all of the reported analytes. These samples were purposely chosen to span a large concentration range to test the effect of analyte concentration on precision.

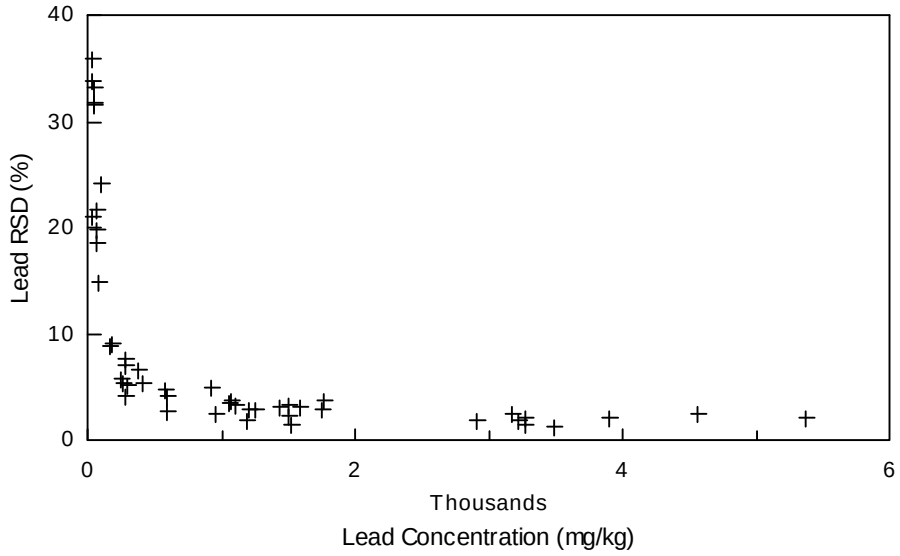


Figure 4-4. Precision vs. Concentration—TN Pb Analyzer: This graph illustrates the analyzer's precision as a function of analyte concentration.

Accuracy

Accuracy refers to the degree to which a measured value for a sample agrees with a reference or true value for the same sample. Intramethod accuracy was assessed for the TN Pb Analyzer by using site-specific PE samples and SRMs. Accuracy was evaluated by comparing percent recoveries for each target analyte reported by the TN Pb Analyzer. The TN Pb Analyzer analyzed six site-specific PE samples and 14 SRMs. The operator knew the samples were PE samples or SRMs, but did not know the true

concentration or the acceptance range. These PE samples and SRMs were analyzed the same way as all other samples.

The six site-specific PE samples included three from each of the two demonstration sites. These samples were collected during the predemonstration activities and were sent to six independent laboratories for analysis by laboratory-grade XRF analyzers. The mean measurement for each analyte was used as the true value concentration. The 14 SRMs included seven soil, four stream or river sediment, two ash, and one sludge SRM. The SRMs were obtained from NIST, USGS, Commission of European Communities-Community Bureau of Reference, National Research Council-Canada, and the South African Bureau of Standards. The SRMs contained known certified concentrations of certain target analytes reported in this demonstration.

These PEs and SRMs did not have published acceptance ranges. As specified in the demonstration plan, an acceptance range of 80 - 120 percent recovery of the true value was used to evaluate accuracy for the six site-specific PEs and 14 SRMs. Table 4-5 summarizes the accuracy data for the target analytes for the TN Pb Analyzer. Figures 4-5 and 4-6 show the true value, the measured value, and percent recovery for the individual SRMs and PEs, respectively. No figure was presented for chromium because only one sample produced a detectable concentration of chromium. True value results from the site-specific PEs and SRMs with concentrations less than the precision-based MDLs listed in Table 4-3 were also excluded from the accuracy assessment.

Overall, the TN Pb Analyzer produced 20 out of 28 results or 71.4 percent within the 80 - 120 percent recovery acceptance range for all analytes in the six site-specific PE samples. Seven of the eight results falling outside of the acceptance range were below the lower limit of 80 percent recovery. Only the 129 percent recovery for chromium in one sample was above the upper limit of 120 percent recovery. For all six site-specific PEs, only three out of 28 percent recoveries were above 100 percent. Table 4-5 also shows that the mean percent recoveries for all six analytes in the PEs were less than 100 percent. This indicates that, in general, the TN Pb Analyzer was producing results that were biased slightly low.

Table 4-5 summarizes the accuracy data for the SRMs. A more detailed analysis of the SRM data is presented in Figure 4-5. A graph is not presented for chromium because no samples produced a detectable chromium concentration. The iron concentrations in the SRMs were in the tens of thousands of milligrams per kilogram which is in a concentration range where the TN Pb Analyzer should perform well. Some analytes such as copper, lead, and zinc had concentrations spanning 1 or more orders of magnitude in the SRMs. Overall, the TN Pb Analyzer produced 31 out of 42 results within the 80 - 120 percent recovery acceptance range for an accuracy of 73.8 percent. Of the 11 results that fell outside of the acceptance range, six results were low and five were high. This nearly equal ratio of high results to low in addition to the mean percent recoveries shown in Table 4-5 indicates that the TN Pb Analyzer was not showing a high or low bias for copper, iron, lead, and zinc. The TN Pb Analyzer did appear to show a slightly low bias for arsenic concentrations. Except for chromium, the TN Pb Analyzer produced percent recoveries ranging from 38 percent for copper in one sediment SRM to 151 percent for zinc in the one sludge SRM.

A more detailed analysis of the SRM data showed that there was a matrix effect on the TN Pb Analyzer's accuracy. The TN Pb Analyzer produced 16 out of 16 results or 100 percent within the acceptance range for all target analytes in the seven soil SRMs. This demonstrated that the TN Pb Analyzer was more accurate when analyzing SRMs that closely matched the matrix used to set the fundamental parameters (FP) of the analyzer. The TN Pb Analyzer showed the lowest comparability to the one sludge SRM by overestimating all analyte concentrations by a factor of 1.3 to 1.5. The overall

accuracy was 60 percent for the four sediment SRMs and 75 percent for the two ash SRMs. Specifically, two sediment, one ash, and the one sludge SRM accounted for all 11 results that fell outside of the acceptance ranges. This indicates that SRMs of a different matrix (sediment, ash, or sludge) than that of soil may not serve as adequate accuracy checks when the FP calibration is based on soil SRMs.

The TN Pb Analyzer was the least accurate for chromium when assessing the site-specific PEs and SRMs. This was expected for two reasons. First, two of the three samples shown in Table 4-6 had concentrations less than 2 times the precision-based MDL for chromium, which may have negatively affected the results. Second, the developer did not design this analyzer for chromium and was not certain what the TN Pb Analyzer's capabilities for chromium would be. The overall accuracy for the remaining five analytes for the PEs and SRMs combined was similar, ranging from 71 percent for zinc to 83 percent for iron. The TN Pb Analyzer was expected to perform well for iron given that the iron concentrations in the PEs and SRMs were well above MDLs yet in a linear range for the TN Pb Analyzer.

Table 4-5. Accuracy Summary for Site-Specific PE and SRM Results—TN Pb Analyzer

Analyte	n	Percent Within Acceptance Range	Mean Percent Recovery	Range of Percent Recovery	SD of Percent Recovery	Concentration Range (mg/kg)
Site-Specific Performance Evaluation Samples						
Arsenic	3	100	89	87 - 92	2.5	424 - 22,444
Chromium	2	0	65	0 - 129	NA	939 - 3,800
Copper	5	100	92	83 - 107	8.9	300 - 7,132
Iron	6	67	87	70 - 98	12	27,320 - 70,500
Lead	6	67	87	70 - 101	12	292 - 14,663
Zinc	6	67	82	70 - 90	7.0	164 - 4,205
Soil Standard Reference Materials						
Arsenic	3	100	89	85 - 97	6.3	105 - 626
Copper	1	100	92	92	NA	2,950
Iron	3	100	94	89 - 99	4.7	28,900 - 35,000
Lead	5	100	101	87 - 116	12	101 - 5,532
Zinc	4	100	101	83 - 118	15	350 - 6,952
Sediment Standard Reference Materials						
Arsenic	1	0	44	44	NA	211
Chromium	1	0	0	0	NA	509
Copper	4	75	85	38 - 106	32	99 - 452
Iron	1	100	99	99	NA	41,100
Lead	4	50	100	75 - 131	23	161 - 5,200
Zinc	4	75	97	81 - 126	21	264 - 2,200
Ash & Sludge Standard Reference Materials						
Arsenic	2	50	87	73 - 101	NA	136 - 145
Copper	1	0	141	141	NA	696
Iron	2	100	86	85 - 86	NA	77,800 - 94,000
Lead	3	67	106	88 - 133	23	68 - 286
Zinc	3	33	109	68 - 151	41	210 - 2,122

Notes: n Number of samples with detectable analyte concentrations.
SD Standard deviation.
mg/kg Milligrams per kilogram.

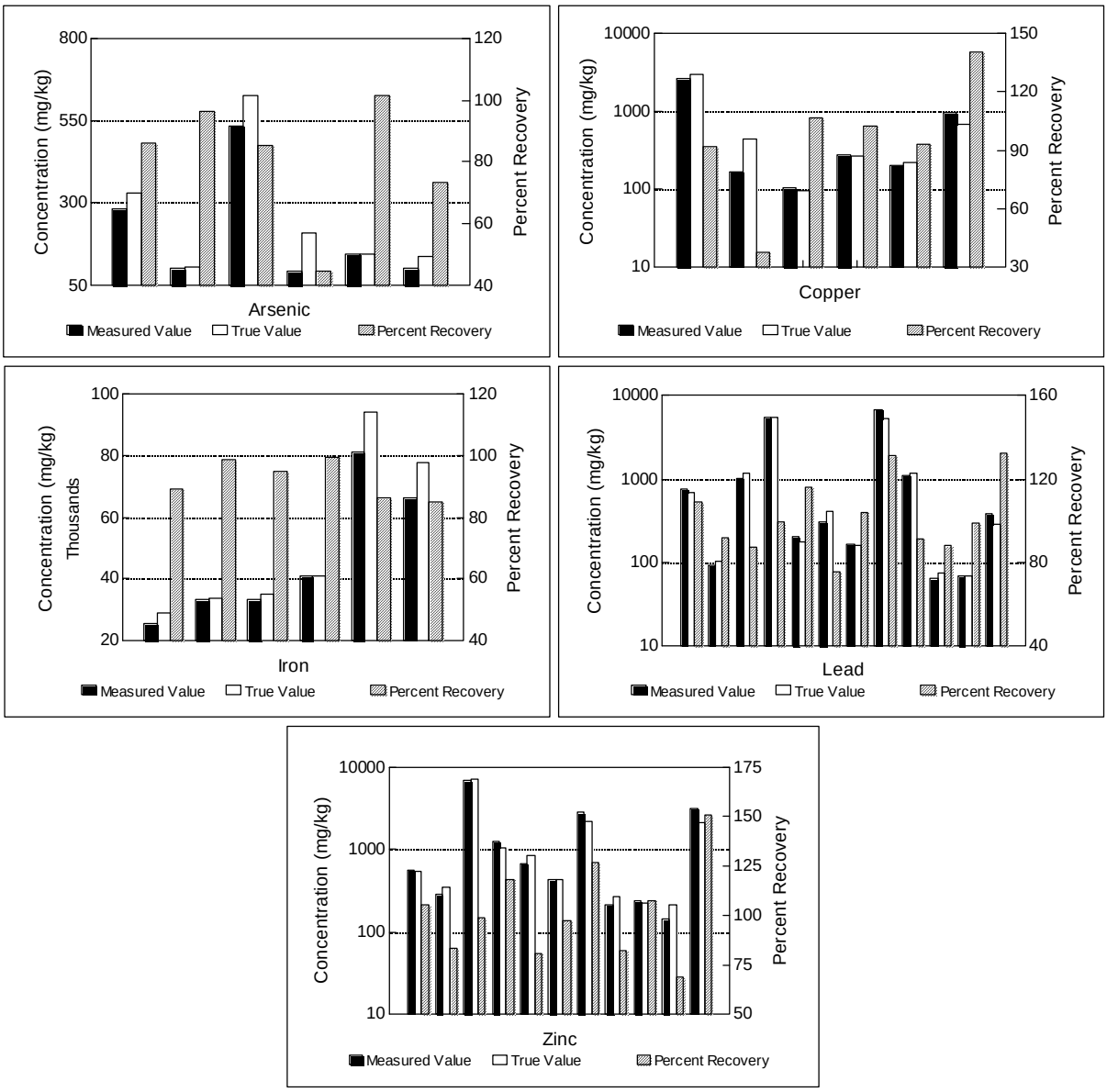


Figure 4-5. SRM Results–TN Pb Analyzer: These graphs illustrate the relationship between the analyzer's data (measured values) and the true values for the SRMs. The gray bars represent the percent recovery for the analyzer. Each set of three bars (black, white, and gray) represents a single SRM sample.

NA Not applicable. Standard deviation not calculated for two or fewer results.

Comparability

Intramethod comparability for the TN Pb Analyzer was assessed through the analysis of four ERA PEs and four CRM PEs. This was done to present potential users additional information on data comparability relative to different commercially available QC samples. The eight PEs were analyzed in the same way as all other samples. As described in Section 3, these eight PE samples had certified analyte values determined by EPA SW-846 Methods 3050A/6010A. Therefore, since these methods do not necessarily determine total metals concentrations in a soil, it was expected that the analyzer would overestimate analyte concentrations relative to PALs. The ability of the TN Pb Analyzer to produce results within the PALs and

the percent recovery for each of the analytes was used to evaluate the TN Pb Analyzer's intramethod comparability. True value analyte concentrations in the ERA and CRM PEs that were below the precision-based MDLs in Table 4-3 were excluded from the intramethod comparability assessment.

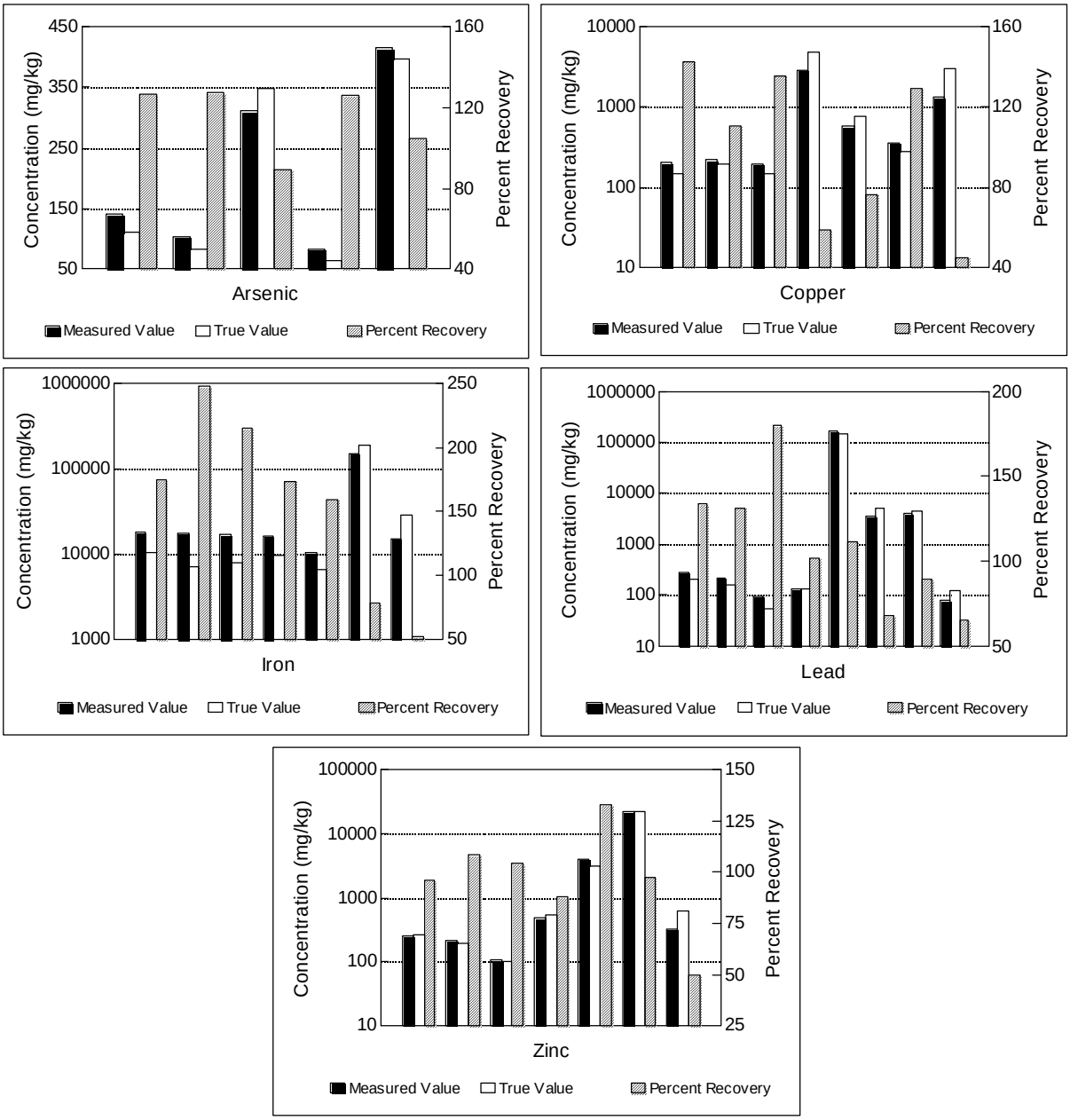


Figure 4-6. Site-specific PE Sample Results—TN Pb Analyzer: These graphs illustrate the relationship between the analyzer's data (measured values) and the true values for the site-specific PE samples. The gray bars represent the percent recovery for the analyzer. Each set of three bars (black, white, and gray) represents a single site-specific PE sample.

The TN Pb Analyzer performance data for all target analytes for the eight CRMs and PEs are summarized in Table 4-6. The measured values, true values, and percent recoveries for all detectable analytes are shown in Figure 4-7. No figure is shown for chromium because there was only one detect for chromium. For the ERA PEs, the TN Pb Analyzer produced 12 out of 18 results or 66.7 percent within the

acceptance range. For the CRMs, the TN Pb Analyzer produced 8 out of 17 results or 47.0 percent within the acceptance range. With the ERA and CRM PEs combined, the TN Pb Analyzer produced 20 out of 35 results or 57.1 percent within the acceptance range. Based on the data presented in Table 4-7, the TN Pb Analyzer's results were more comparable to the ERA PEs than the CRMs. The better comparability to the ERA PEs versus the CRMs was unexpected because the ERA PEs had lower analyte concentrations than the CRMs. With the exception of iron, the analyte concentrations in the ERA PEs were all less than 350 mg/kg, which is less than 5 times the MDL for most of the analytes.

Table 4-6. Accuracy Summary for PE and CRM Results—TN Pb Analyzer

Analyte	n	Percent Within Acceptance Range	Mean Percent Recovery	Range of Percent Recovery	SD of Percent Recovery	Concentration Range (mg/kg)
ERA Performance Evaluation Samples						
Arsenic	4	100	117	89 - 127	19	65 - 349
Copper	3	67	129	110 - 142	17	144 - 196
Iron	4	0	203	174 - 248	36	7,130 - 10,400
Lead	4	75	137	102 - 180	32	52 - 208
Zinc	3	100	103	96 - 104	6.3	101 - 259
Certified Reference Materials						
Arsenic	1	100	104	104	NA	397
Chromium	1	0	121	121	NA	161,500
Copper	4	50	77	45 - 129	37	279 - 4,792
Iron	3	33	96	52 - 159	56	6,481 - 191,650
Lead	4	50	84	65 - 112	22	120 - 144,740
Zinc	4	50	92	50 - 133	34	546 - 22,217

Notes:
n Number of samples with detectable analyte concentrations.
SD Standard deviation.
mg/kg Milligrams per kilogram.
NA Not applicable. Standard deviation not calculated for two or fewer results.

The TN Pb Analyzer produced only two out of 18 percent recoveries that were less than 100 percent for the ERA PEs. All mean percent recoveries for the analytes in the ERA PEs were greater than 100 percent. This indicates that the TN Pb Analyzer was overestimating the results compared to the certified values. This is consistent with the fact that FPXRF is a total metals technique whereas EPA SW-846 Methods 3050A/6010A used to certify the results in the ERA PEs are not.

Intermethod Assessment

The comparison of the analyzer's results to the reference method was performed using the statistical methods detailed in Section 2. The purpose of this statistical evaluation was to determine the comparability between data produced by the analyzer and that produced by the reference laboratory. If the $\log_{10}$ transformed FPXRF data were statistically equivalent to the $\log_{10}$ transformed reference data and had acceptable precision (10 percent RSD), the data met the definitive level criteria. If the data did not meet the definitive level criteria but could be mathematically corrected to be equivalent to the reference data, they met the quantitative screening level criteria. If the analyzer did not meet the definitive level criteria, and the

statistical evaluation could not identify a predictable bias in the data, but the analyzer identified the presence or absence of contamination with at least a 90 percent accuracy rate, the data were classified as qualitative screening level quality.

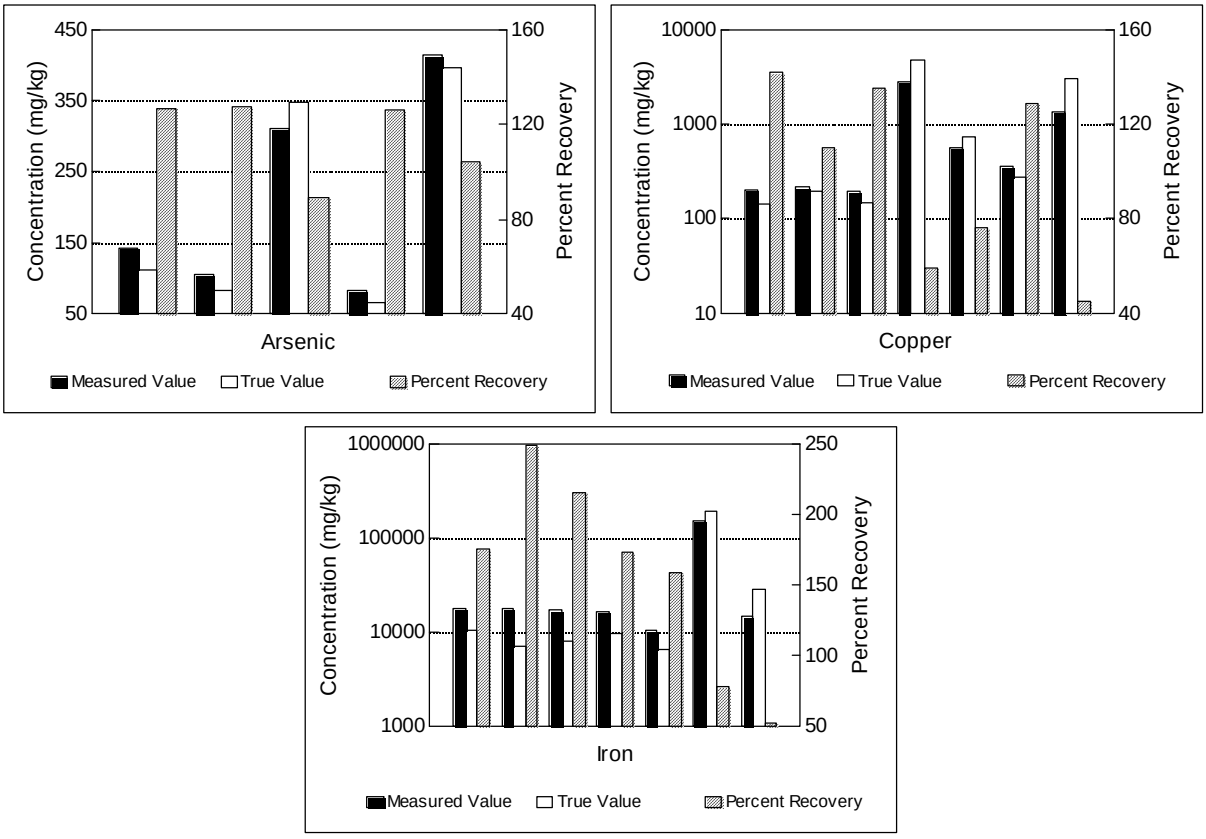


Figure 4-7. PE and CRM Results—TN Pb Analyzer: These graphs illustrate the relationship between the analyzer's data (measured values) and the true values for the PE and CRM samples. The gray bars represent the percent recovery for the analyzer. Each set of three bars (black, white, and gray) represents a single PE or CRM sample.

The TN Pb Analyzer was configured to report concentrations for five of the six primary analytes, and one of the secondary analytes. The primary analytes it reported were arsenic, chromium, copper, lead, and zinc. Iron was the only secondary analyte reported by this analyzer; however, since appropriate precision and detection limit data could not be obtained, no data quality level could be assigned for iron.

The regression analysis on the entire $\log_{10}$ transformed data set indicated that arsenic, copper, lead, and zinc all exhibited r^2 values of 0.90 or greater. In all of these cases, the slopes and y-intercepts were not significantly different from their ideal values of 1 and 0, respectively. This leads to the conclusion that all these analytes can be measured at the definitive data quality level.

Additional data evaluation involved the assessment of the potential influence of the variables site, soil texture, and sample preparation on the regression analysis of the $\log_{10}$ transformed data. Analysis indicated no apparent impact of the site variable on the regression. The sample preparation variable exhibited the greatest influence on the regression analysis (Table 4-8). In all cases, the greatest shift in the r^2 was exhibited between the *in situ*-unprepared and the *in situ*-prepared samples. This is consistent with the fact that the homogenization step increased the possibility that the analyzer and the reference

Table 4-7. Regression Parameters[a] by Primary Variable—TN Pb Analyzer

Arsenic					Variable	Chromium				
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
815	0.952	0.15	0.20	0.95	All Data	136	0.548	0.16	2.31	0.39
806	0.958	0.14	0.18	0.95	ASARCO Site	5	0.017	0.07	3.10	0.03
8	ND	ND	ND	ND	RV Hopkins Site	131	0.585	0.15	2.03	0.49
357	0.966	0.14	0.16	0.95	Sand Soil	2	ND	ND	ND	ND
449	0.950	0.14	0.20	0.95	Loam Soil	3	ND	ND	ND	ND
8	ND	ND	ND	ND	Clay Soil	131	0.585	0.15	2.03	0.49
211	0.884	0.22	0.45	0.83	In Situ-Unprepared	28	0.237	0.17	2.71	0.27
200	0.973	0.11	0.11	0.97	In Situ-Prepared	35	0.564	0.15	2.59	0.29
204	0.984	0.08	0.10	0.99	Intrusive-Unprepared	40	0.671	0.15	2.13	0.46
201	0.981	0.09	0.16	0.98	Intrusive-Prepared	33	0.807	0.12	1.16	0.77

Copper					Variable	Lead				
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
957	0.94	0.17	0.48	0.89	All Data	1168	0.950	0.14	0.30	0.92
746	0.961	0.14	0.19	0.98	ASARCO Site	780	0.943	0.15	0.22	0.95
145	0.516	0.15	1.44	0.48	RV Hopkins Site	385	0.964	0.11	0.43	0.87
366	0.948	0.13	0.14	0.98	Sand Soil	347	0.951	0.14	0.21	0.93
443	0.951	0.13	0.42	0.92	Loam Soil	430	0.943	0.14	0.25	0.95
145	0.516	0.15	1.44	0.48	Clay Soil	385	0.964	0.11	0.43	0.87
246	0.866	0.26	0.67	0.82	In Situ-Unprepared	296	0.849	0.23	0.48	0.83
251	0.942	0.17	0.59	0.85	In Situ-Prepared	300	0.960	0.12	0.36	0.89
242	0.967	0.13	0.38	0.92	Intrusive-Unprepared	298	0.978	0.09	0.23	0.94
225	0.975	0.11	0.21	0.99	Intrusive-Prepared	293	0.976	0.10	0.21	0.96

Zinc					Variable
n	r^2	Std. Err.	Y-Int.	Slope[b]	
1079	0.923	0.12	0.42	0.90	All Data
732	0.914	0.13	0.43	0.89	ASARCO Site
347	0.941	0.11	0.41	0.90	RV Hopkins Site
322	0.947	0.12	0.33	0.91	Sand Soil
411	0.873	0.12	0.56	0.86	Loam Soil
347	0.941	0.11	0.41	0.90	Clay Soil
283	0.825	0.18	0.63	0.81	In Situ-Unprepared
279	0.948	0.10	0.46	0.88	In Situ-Prepared
270	0.946	0.10	0.36	0.93	Intrusive-Unprepared
250	0.962	0.09	0.25	0.97	Intrusive-Prepared

Notes:

[a] Regression parameters based on $\log_{10}$ transformed data. Since the FPXRF data was regressed as the dependent variable, the regression parameters cannot be used to correct the FPXRF data. See Section 6.

[b] Slope values determined with FPXRF data plotted on y-axis and the reference data plotted on the x-axis.

Y-Int. Y-Intercept.

Std. Err. Standard error.

n Number of data points.

ND Analytes not present in significant quantities to provide meaningful regression.

Table 4-8. Regression Parameters[a] for the Sample Preparation Variable and Soil Texture — TN Pb Analyzer

Arsenic						Barium				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Soil Texture	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
93	0.920	0.20	0.34	0.86	Sand Soil	3	ND	ND	ND	ND
114	0.876	0.21	0.38	0.87	Loam Soil	3	ND	ND	ND	ND
4	ND	ND	ND	ND	Clay Soil	28	0.237	0.17	2.71	0.27
In Situ-Prepared					Soil Texture	In Situ-Prepared				
89	0.981	0.10	0.09	0.97	Sand Soil	3	ND	ND	ND	ND
109	0.973	0.10	0.17	0.96	Loam Soil	3	ND	ND	ND	ND
4	ND	ND	ND	ND	Clay Soil	31	0.600	0.14	2.18	0.43
Intrusive-Unprepared					Soil Texture	Intrusive-Unprepared				
89	0.987	0.08	0.09	0.98	Sand Soil	3	ND	ND	ND	ND
113	0.987	0.07	0.13	0.99	Loam Soil	3	ND	ND	ND	ND
3	ND	ND	ND	ND	Clay Soil	39	0.703	0.14	1.94	0.53
Intrusive-Prepared					Soil Texture	Intrusive-Prepared				
88	0.981	0.10	0.15	0.98	Sand Soil	3	ND	ND	ND	ND
113	0.984	0.08	0.17	0.99	Loam Soil	3	ND	ND	ND	ND
3	ND	ND	ND	ND	Clay Soil	33	0.807	0.12	1.16	0.77

Chromium						Lead				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Soil Texture	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
89	0.911	0.16	0.35	0.88	Sand Soil	85	0.871	0.21	0.35	0.84
112	0.818	0.27	0.58	0.87	Loam Soil	110	0.834	0.23	0.49	0.84
42	0.619	0.15	1.40	0.53	Clay Soil	99	0.845	0.22	0.74	0.77
In Situ-Prepared					Soil Texture	In Situ-Prepared				
90	0.958	0.12	0.09	0.99	Sand Soil	89	0.959	0.13	0.23	0.93
113	0.957	0.12	0.54	0.87	Loam Soil	111	0.956	0.12	0.39	0.90
45	0.524	0.11	1.58	0.38	Clay Soil	99	0.976	0.09	0.45	0.85
Intrusive-Unprepared					Soil Texture	Intrusive-Unprepared				
96	0.962	0.11	0.10	1.00	Sand Soil	88	0.980	0.09	0.14	0.97
114	0.982	0.08	0.36	0.93	Loam Soil	109	0.983	0.08	0.12	1.00
35	0.487	0.14	1.51	0.44	Clay Soil	100	0.986	0.07	0.37	0.89
Intrusive-Prepared					Soil Texture	Intrusive-Prepared				
93	0.969	0.10	0.01	1.04	Sand Soil	89	0.966	0.12	0.18	0.97
113	0.980	0.09	0.32	0.95	Loam Soil	105	0.985	0.07	0.09	1.03
22	0.470	0.16	0.24	1.05	Clay Soil	98	0.988	0.07	0.29	0.92

Table 4-8. ***Continued***

Zinc										
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared					Soil Texture	Intrusive-Unprepared				
87	0.910	0.14	0.60	0.78	Sand Soil	77	0.972	0.09	0.21	0.97
101	0.720	0.17	0.78	0.75	Loam Soil	106	0.910	0.10	0.49	0.89
96	0.844	0.19	0.61	0.85	Clay Soil	86	0.970	0.08	0.36	0.92
In Situ-Prepared					Soil Texture	Intrusive-Prepared				
84	0.966	0.10	0.33	0.92	Sand Soil	76	0.947	0.13	0.22	0.97
107	0.899	0.10	0.66	0.81	Loam Soil	96	0.960	0.07	0.29	0.97
88	0.971	0.08	0.44	0.88	Clay Soil	79	0.983	0.06	0.17	0.99

Notes:
[a] Regression parameters based on $\log_{10}$ transformed data. These parameters were calculated for FPXRF data as the dependent variable, and thus, cannot be used to correct FPXRF data. See Section 6.

[b] Slope values determined with FPXRF data plotted on the y-axis and the reference data plotted on the x-axis.

n Number of usable matched pairs of data points.

Y-Int. Y-Intercept.

Std. Err. Standard Error.

ND Analyte not present in significant quantities to provide meaningful regression.

methods were analyzing a similar sample. The effect of sample preparation on analysis is illustrated in Figure 4-8. Prior to the initial sample homogenization, only copper met the definitive level criteria. However, its r^2 was at the low end of the acceptability range. The initial sample homogenization step accounted for between 40 and 99 percent of the total increase in the r^2 resulting from all sample preparation steps. This sample preparation pushed lead and arsenic into the definitive level data category and elevated copper's r^2 to the upper end of the acceptability range. The initial sample preparation step improved the regression-based data quality for the zinc analysis; however, the t-test indicated the two data sets were different so the analyzer produced quantitative screening level data for zinc through all sample preparation steps. Since the analyzer's chromium precision was not measured at the required 5 to 10 times MDL, no data quality level could be assigned.

The influence of the site and soil texture variables was assessed for lead and zinc, the only two analytes relatively evenly distributed between both sites and all soil textures, within each of the four sample preparation steps (Tables 4-8 and 4-9). Little influence on the correlation was evident. Zinc appeared to show slightly poorer correlation for the loam soils. Copper appeared to show a site or soil effect, exhibiting much higher comparability for the ASARCO site and soils. However, this was probably an artifact of the low copper concentration at the RV Hopkins site, less than 250 mg/kg. This concentration (250 mg/kg) is near the field-based MDL for this analyzer.

The effect of contaminant concentration on comparability was also examined. The data sets for the primary analytes were divided into the following concentration ranges: 0 - 100 mg/kg, 100 - 1,000 mg/kg, and greater than 1,000 mg/kg as described in the demonstration plan. Regression analysis for each target analyte and for each sample preparation step was performed on $\log_{10}$ transformed data sets sorted by these concentration ranges. No consistent improvement was observed in either the r^2 or the

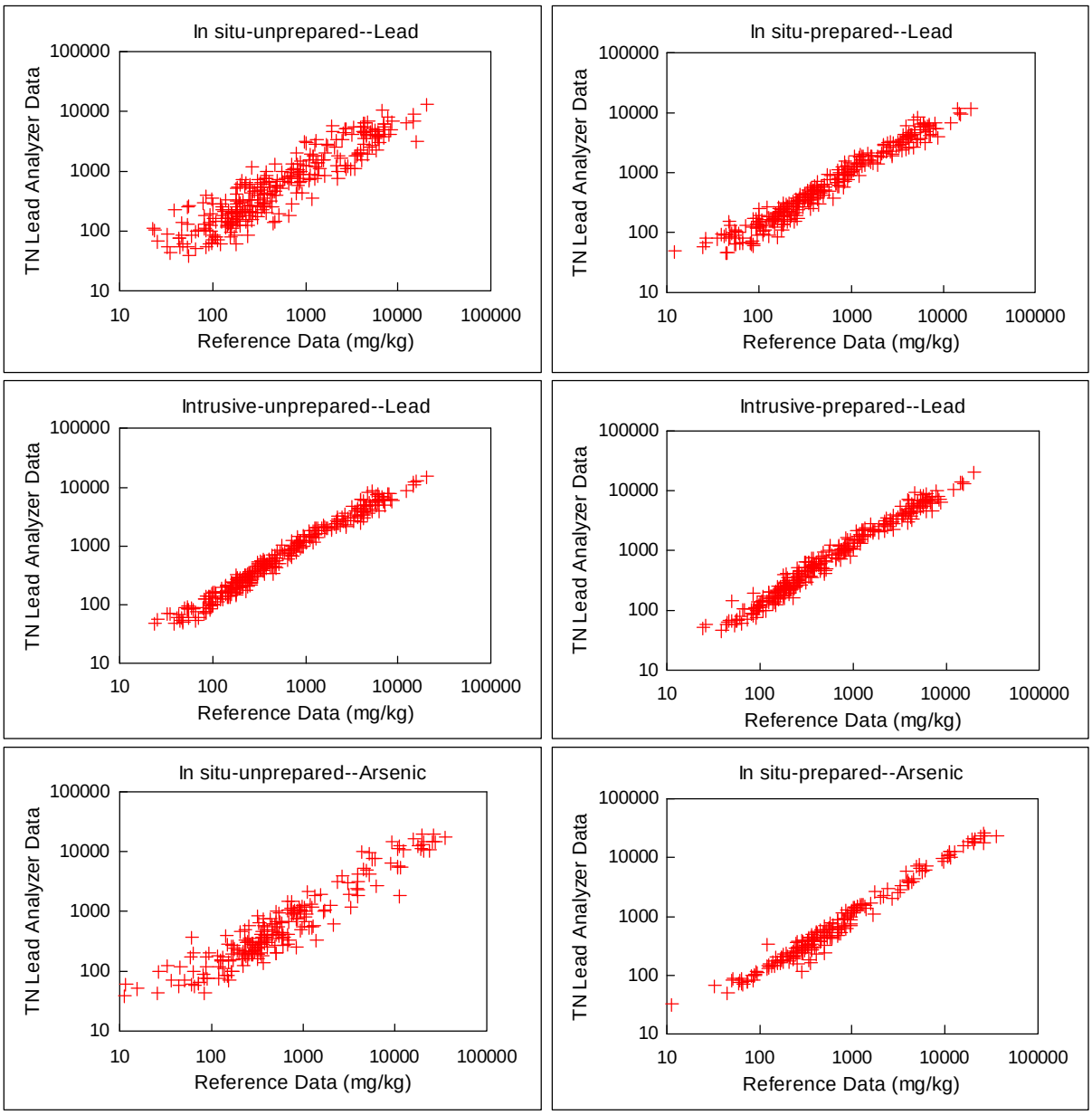


Figure 4-8. Sample Preparation Effect on Lead and Arsenic Results—TN Pb Analyzer: These graphs illustrate the effect of sample preparation on the comparability between the analyzer and the reference data.

standard error for any of the concentration-sorted data sets. This indicates that the correlation is independent of concentration for these ranges, and that the regression analyses associated with the entire $\log_{10}$ transformed data set are representative of the relationship between the analyzer's data and the reference data. The regression parameters based on the $\log_{10}$ transformed data were better, in all cases for the data in the 0 - 2,000 mg/kg concentration range. Lead exhibited the greatest concentration range effect; this analyte did not meet definitive level data quality criteria in the greater than 2,000 mg/kg range. Identification of the exact cause of this concentration effect is beyond the scope of this project. Possible causes include changes in reference method accuracy at higher concentrations due to analyte interferences, and shifts in FPXRF performance at higher concentrations due to detector characteristics, or inherent characteristics of the FP calibration. Whatever the cause, this apparent concentration effect has a minor effect on overall data quality.

Table 4-9. Regression Parameters[a] for the Sample Preparation Variable and Site Name—TN Pb Analyzer

Arsenic						Barium				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Site Name	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
207	0.898	0.21	0.36	0.87	ASARCO	6	ND	ND	ND	ND
4	ND	ND	ND	ND	RV Hopkins	28	0.237	0.17	2.71	0.27
In Situ-Prepared					Site Name	In Situ-Prepared				
199	0.975	0.11	0.11	0.97	ASARCO	6	ND	ND	ND	ND
3	ND	ND	ND	ND	RV Hopkins	31	0.600	0.14	2.18	0.43
Intrusive-Unprepared					Site Name	Intrusive-Unprepared				
202	0.986	0.08	0.10	0.99	ASARCO	5	ND	ND	ND	ND
3	ND	ND	ND	ND	RV Hopkins	39	0.703	0.14	1.94	0.53
Intrusive-Prepared					Site Name	Intrusive-Prepared				
201	0.981	0.09	0.16	0.98	ASARCO	6	ND	ND	ND	ND
3	ND	ND	ND	ND	RV Hopkins	33	0.807	0.12	1.16	0.77

Chromium						Lead				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Site Name	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
200	0.891	0.23	0.24	0.95	ASARCO	196	0.839	0.229	0.440	0.838
42	0.619	0.15	1.40	0.53	RV Hopkins	99	0.845	0.217	0.743	0.765
In Situ-Prepared					Site Name	In Situ-Prepared				
202	0.963	0.13	0.22	0.96	ASARCO	200	0.953	0.129	0.292	0.918
45	0.524	0.11	1.58	0.38	RV Hopkins	99	0.976	0.087	0.449	0.848
Intrusive-Unprepared					Site Name	Intrusive-Unprepared				
210	0.978	0.10	0.19	0.98	ASARCO	198	0.978	0.091	0.126	0.988
35	0.487	0.14	1.51	0.44	RV Hopkins	99	0.987	0.066	0.388	0.881
Intrusive-Prepared					Site Name	Intrusive-Prepared				
203	0.981	0.09	0.07	1.03	ASARCO	194	0.974	0.100	0.120	1.004
22	0.470	0.16	0.24	1.05	RV Hopkins	98	0.988	0.067	0.293	0.923

Zinc										
n	r^2	Std. Err.	Y-Int.	Slope[b]	Site Name	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						Intrusive-Unprepared				
188	0.831	0.163	0.663	0.776	ASARCO	183	0.935	0.112	0.339	0.937
96	0.844	0.188	0.613	0.849	RV Hopkins	86	0.970	0.081	0.360	0.917
In Situ-Prepared					Site Name	Intrusive-Prepared				
192	0.932	0.109	0.470	0.875	ASARCO	172	0.950	0.102	0.262	0.970
88	0.971	0.078	0.436	0.879	RV Hopkins	79	0.983	0.062	0.170	0.990

Notes:

[a] Regression parameters based on $\log_{10}$ transformed data. These parameters were calculated for FPXRF data as the dependent variable, and thus, cannot be used to correct FPXRF data. See Section 6.

[b] Slope values determined with FPXRF data plotted on y-axis and the reference data plotted on the x-axis.

n Number of usable matched pairs of data points.

Y-Int. Y-Intercept.

Std. Err. Standard Error.

ND Analyte not present in significant quantities to provide meaningful regression.

To examine the potential effect of count times on analyzer comparability, a subset of 26 intrusive-prepared samples from the RV Hopkins site was analyzed using doubled count times. This increase in count times increased the r^2 for both chromium and copper 0.02 and 0.14 units, respectively. None of the other target analytes exhibited a count time effect (r^2 values did not change) at the count times evaluated.

Another way to examine the comparability between the two methods involves measuring the average relative bias and accuracy between the FPXRF data and the reference data. The average relative bias indicates the average factor by which the two data sets differ. Concentration effects can affect bias. For example, it is possible for an analyzer to greatly underestimate low concentrations but greatly overestimate high concentrations had a relative bias of zero. To eliminate this concentration effect, the data can be corrected by a regression approach (see Section 6), or only narrow concentration ranges can be analyzed, or average relative accuracy can be examined. The average relative accuracy is the average factor by which each individual analyzer measurement differs from the corresponding reference measurement.

A final decision regarding the assignment of data quality levels derived from this demonstration involves an assessment of both r^2 and the precision RSD. Using the criteria presented in Table 2-2, a summary of the TN Spectrace Pb Analyzer's data quality performance measures from this demonstration is provided in Table 4-10.

Table 4-10. Summary of Data Quality Level Parameters

Target Analytes	Pb Analyzer Analytes	Precision (mg/kg) Mean % RSD 5 - 10 X MDL	Method Detection Limits (mg/kg) (Precision-based)	Coefficient of Determination (r^2 All Data)	Data Quality Level
Arsenic	Arsenic	4.1	50	0.95	Definitive
Barium	Not Reported	—	—	—	—
Chromium	Chromium	Not Determined	460	0.55	Insufficient Data
Copper	Copper	9.1	115	0.94	Definitive
Lead	Lead	5.9	40	0.95	Definitive
Zinc	Zinc	7.5	95	0.92	Definitive
Nickel	Not Reported	—	—	—	—
Iron	Iron	Not Determined	Not Determined	Not Determined	Insufficient Data
Cadmium	Not Reported	—	—	—	—
Antimony	Not Reported	—	—	—	—

Section 5
TN 9000 Analyzer

This section provides information on the Spectrace TN 9000 Analyzer, including the theory of FPXRF, operational characteristics, performance factors, a data quality assessment, and a comparison of results with those of the reference laboratory.

Theory of FPXRF Analysis

FPXRF analyzers operate on the principle of energy dispersive XRF spectrometry. This is a nondestructive qualitative and quantitative analytical technique that can be used to determine the metals composition in a test sample. By exposing a sample to an X-ray source having an excitation energy close to, but greater than, the binding energy of the inner shell electrons of the target element in a sample, electrons are displaced. The electron vacancies that result are filled by electrons cascading in from the outer shells. Electrons in these outer shells have higher potential energy states than inner shell electrons, and to fill the vacancies, they give off energy as they cascade into the inner shell vacancies (Figure 5-1). This release of energy results in an emission of X-rays that is characteristic of each element. This emission of X-rays is termed XRF.

Because each element has a unique electron shell configuration, each will emit unique X-rays at specific wavelengths called "characteristic" X-rays. The energy of the X-ray is measured in electron volts (eV). By measuring the position and intensity of X-rays emitted by a sample, it is possible to identify and quantify the elemental composition of a sample. A qualitative analysis can be made by identifying the characteristic X-rays produced by the sample. The intensity of the characteristic X-rays emitted is proportional to the concentration of a given metal and can be used to quantitate each element.

Three electron shells are generally involved in the emission of characteristic X-rays during FPXRF analysis: the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given element has multiple peaks generated from the emission X-rays by the K, L, or M shell electrons. The most commonly measured X-ray emissions are from the K and L shells; only elements with an atomic number of 58 (cerium) or greater have measurable M shell emissions.

Each characteristic X-ray peak or line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α) or beta (ß), which indicates the next outermost shell from which electrons fell to fill the vacancy and produce the X-ray. For example, a K_α-line is produced by a vacancy in the K shell filled by an L shell electron, whereas a $K_ß$-line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is between 7 and 10 times more probable than the $K_ß$ transition. The K_α-line is approximately 10 times more intense than the $K_ß$-line for a given element, making the K_α-line analysis the preferred choice for quantitation purposes. Unlike the K-lines, the L-lines (L_α and

$L_ß$) for an analyte are of nearly equal intensity. The choice of which one to use for analysis depends on the presence of interfering lines from other analytes.

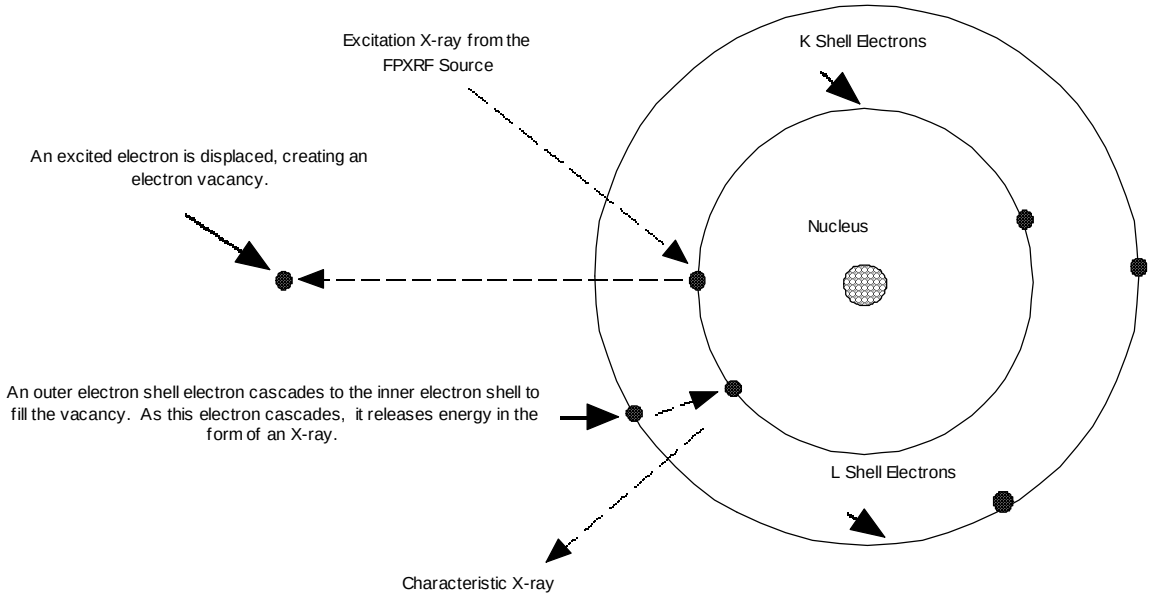


Figure 5-1. Principle of Source Excited X-ray Fluorescence: This figure illustrates the dynamics of source excited X-ray fluorescence.

An X-ray source can excite characteristic X-rays from an analyte only if its energy is greater than the electron binding energies of the target analyte. The electron binding energy, also known as the absorption edge energy, represents the amount of energy an electron has to absorb before it is displaced. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K-absorption edge energy is approximately the sum of the K-, L-, and M-line energies of the particular element, and the L- absorption edge energy is approximately the sum of the L- and M-line energies. FPXRF analytical methods are more sensitive to analytes with absorption edge energies close to, but less than, the excitation energy of the source. For example, when using a Cd^{109} source, which has an excitation energy of 22.1 kiloelectron volts (keV), an FPXRF analyzer would be more sensitive to zirconium, which has a K-line absorption edge energy of 15.7 keV, than to chromium, which has a K-line absorption edge energy of 5.41 keV.

Background

Since 1988, the Spectrace has produced field portable and laboratory-grade XRF technologies for a broad range of applications. The TN 9000 Analyzer was released in 1992 to address environmental applications.

The TN 9000 Analyzer uses a HgI_2 semiconductor detector that achieves a manganese K_α X-ray resolution of approximately 300 eV. The detector is operated at a subambient temperature using a low power thermoelectric (Peltier) cooler in the measurement probe.

The TN 9000 Analyzer uses energy dispersive XRF spectrometry to determine elemental composition of soils, sludges, aqueous solutions, oils, and other waste materials. It uses three radioactive isotopes, iron-55 (Fe^{55}), cadmium-109 (Cd^{109}), and americium-241 (Am^{241}), to produce excitation X-rays. The TN 9000 Analyzer can identify and quantify target metals from sulfur through uranium on the periodic chart of the elements. When more than one source is needed to detect a specific element, the appropriate source is selected according to its excitation efficiency for the target element. Generally, the source with the excitation energy closest to, but above, the absorption edge energy for a given metal is selected for performing an analysis. Interferences sometimes affect this selection.

To analyze a sample with the TN 9000 Analyzer, the sample is positioned in front of a plastic film probe measurement window and sample measurement sequence is initiated. The sample is exposed to primary radiation from the source. Only one of the three sources is exposed at a time. If all three sources are required for a sample's analysis, three source exposures are sequenced automatically. Fluorescent and back-scattered X-rays from the sample re-enter through the window and are counted by the high resolution HgI_2 detector. The surface probe of the HgI_2 detector provides for both *in situ* and intrusive soil analysis. For intrusive analysis, the probe is placed upright in a stand, and the sample, contained in a thin-windowed plastic cup, is placed over the probe measurement window beneath a swing-down safety shield.

Analyte concentrations are computed using a fundamental parameters (FP) calibrated algorithm included in the analyzer's software. The developer uses FPs to calibrate its FPXRF analyzer. The FPs are based on the physics of X-ray excitation and emission. The menu-driven software in the TN 9000 Analyzer supports multiple XRF calibrations in a "Soil Applications" software package. Each application contains a complete analysis configuration including target metals to be measured, interfering target metals in the sample, and a set of FP calibration coefficients. The FP calibration does not require site-specific calibration samples; however, these samples can be used to fine tune the calibration.

Operational Characteristics

This section discusses equipment and accessories, operation of the analyzer in the field, background of operator training, reliability of the analyzer, health and safety concerns, and representative operating costs.

Equipment and Accessories

The TN 9000 Analyzer comes with all the accessories needed for *in situ* and intrusive operation. A hard-shell carrying case containing the equipment protected by foam inserts is provided for transportation and storage. Specifications for the analyzer are provided in Table 5-1.

Two main components make up the analytical system: a probe and an electronics unit. The probe contains three radioisotope sources: Fe^{55} (50 mCi), Cd^{109} (5 mCi), and Am^{241} (5 mCi) for sample excitation and the HgI_2 detector. The sources are encapsulated and housed in a metal turret with additional lead shielding inside the probe. These sources can sequentially expose the sample to excitation radiation through the sealed 1-inch-diameter polypropylene cover over the Mylar™ window in the face of the probe. The source-induced fluorescence from the sample passes back through the window and is intercepted by the HgI_2 detector. The detector quantitates the energy of each characteristic emission X-ray and builds a spectrum of analyte peaks on a 2,048-channel MCA, which is contained in the electronics unit. The standard probe operating temperature is 0 - 49 °C, and the standard probe storage temperature is -40 to 43 °C.

Table 5-1. Analyzer Instrument Specifications—TN 9000 Analyzer

Characteristic	Specification
Resolution	< 300 eV (Manganese-K_α)
Sources	5 mCi Cd^{109}, 50 mCi Fe^{55}, 5 mCi Am^{241}
Detector	HgI_2-Peltier cooled
Probe Size	12.7 cm x 7.6 cm x 21.6 cm
Probe Weight	1.9 kilograms
Probe Operating Temperature	0 to 49 °C
Electronics Unit Size	32 cm x 30 cm x 10 cm
Electronics Unit Weight	6.7 kilograms
Electronics Unit Operating Temperature	0 to 49 °C
Electronics Unit Storage Capacity	300 sets of numerical results and 120 spectra
Power Source	120V or 220V (AC) or internal batteries
Operational Checks	3 NIST SRMs, SiO_2 and Teflon® blanks, pure element check
Intrusive Operation	Uniblock probe stand
Computer Interface Operation	RS 232 serial input/output cable, operators manual, application and results software, and training video
Contact: Raj Natarajan 2555 N. Interstate Hwy. 35 Round Rock, TX 78664 (800) 736-0801 (512) 388-9200 (FAX)	

Spectral data is communicated to the electronics unit through a flexible cable of 6, 12, or 20 feet in length. The standard cable length is 6 feet. X-ray emission peaks are integrated and concentrations in ppm or percentage values are calculated. The electronics unit will store and display both numerical results and spectra from a measurement. A maximum of 300 sets of numerical results and 120 spectra can be stored before being downloaded to a PC using an RS-232 cable.

The electronics unit can be operated from a battery or from an alternating current electric line using a plug-in adaptor unit. The TN 9000 Analyzer is supplied with two nickel-cadmium batteries and a battery charger. The batteries last approximately 4 to 5 hours and require a minimum of 14 hours to fully recharge. For this demonstration, the developer provided two additional batteries and chargers so that analysis could continue for up to 12 hours per day. For *in situ* analysis, the developer provided a water-resistant carrying case and a strap for easy portability on-site. The carrying case has a flap on top which can be closed to protect the analyzer from the environment.

Other equipment and supplies that are helpful when using the TN 9000 Analyzer, which is not supplied by the developer, include a PC to download data, protective gloves, paper towels, and a permanent marking pen.

Operation of the Analyzer

For this demonstration, the TN 9000 Analyzer was operated on battery power during the *in situ* phases of the demonstration. The *in situ* analysis was performed with the analyzer in the carrying case. The probe was placed in contact with the soil surface and analysis was started by pressing a trigger on the back of the probe. For intrusive analysis, the probe was pointed upward with the safety shield attached. All intrusive analyses at both sites were performed by setting the analyzer on a table top located indoors. At the ASARCO site, the room was not heated or cooled so analysis occurred at ambient temperatures which ranged from 5 to 16 °C. At the RV Hopkins site, the area used for the analysis was maintained at approximately 25 °C.

Background of the Technology Operator

The PRC operator selected to analyze soil samples using the TN 9000 Analyzer has a bachelor's degree in zoology, which included 30 hours of undergraduate chemistry, and a master's degree in environmental engineering. This operator worked as a gas chromatography chemist in an environmental analytical laboratory for 3 years and as an assistant chemist at a chemical company for 3 years prior to accepting a position at PRC. His job at PRC, for the past year, has involved performing on-site analyses, conducting site investigations, performing risk assessments, and evaluating remedial design systems.

Training

The operator viewed a 22-minute training video which described the analyzer, applications of the analyzer, instructions on the analysis procedures for *in situ* and intrusive sample measurements, and procedures for downloading data from the analyzer to a PC. The operator then received approximately 6 hours of training at the start of the demonstration by the developer. The training covered the theoretical background of XRF and certain specific applications of the TN 9000 Analyzer as they would relate to this demonstration.

The operator estimated that approximately 80 percent of the training was "hands-on." The training included step-by-step instructions involving the daily setup and use of the TN 9000 Analyzer. The developer had calibrated the TN 9000 Analyzer prior to the training using an FP algorithm based on NIST soil SRMs. Part of the training included a discussion of QC requirements such as the analysis of a pure iron energy calibration check, a SiO_2 blank, and at least one NIST SRM; possible interferences; and procedures for preparing both *in situ* and intrusive soil samples for analysis. At the conclusion of the training, the developer was confident that the operator was ready to operate the TN 9000 Analyzer. The developer accompanied the operator to the ASARCO site during the first morning and observed him analyzing soil samples. No problems were encountered, and the developer left the site.

Reliability

A reliability check of the TN 9000 Analyzer was carried out by a daily measurement of a reference sample. This check required a 50-second measurement of a pure iron sample. By this one measurement, a verification was obtained of (1) fluorescent element sensitivity; (2) spectrometer energy resolution; and (3) spectrometer energy calibration. To be acceptable, the measured relative X-ray intensity of iron had to be greater than 0.95, and the equivalent intensity of manganese and cobalt had to be less than 0.006. Relative intensity refers to the new value relative to that obtained at the time of the initial instrument calibration. No energy recalibrations were required during the demonstration based on the pure iron sample results.

During the demonstration, there were frequent light to moderate rains while the analyzer was collecting the *in situ* measurements. After this rain, it was common for the soil surface to be saturated. The developer recommends that samples analyzed by the TN 9000 have less than 20 percent moisture content by weight. The samples collected during this demonstration contained up to 30 percent moisture content by weight. This increased moisture content did not reduce the analyzer's data comparability. At the ASARCO and RV Hopkins sites, the temperatures ranged from 5 to 16 °C and from 6 to 22 °C, respectively. Despite the less than ideal weather conditions, there were no mechanical or electronic problems experienced with the TN 9000 Analyzer during the course of the demonstration.

Health and Safety

The potential for exposure to radiation from the excitation sources was the largest health and safety consideration while using the analyzer. Radiation was monitored with a radiation survey meter. Background radiation at the two sites was between 0.006 and 0.012 mrem/hr. Radiation exposure was monitored in both the *in situ* and intrusive modes while the shutters of the analyzers were open to obtain a worst-case scenario. The radiation was measured within 5 cm of the probe face while the analyzer was analyzing a sample. Radiation exposure also was monitored at a point on the probe where the operator's hand was located during analysis to provide a realistic value of operator exposure. The TN 9000 Analyzer is sold under a general license, meaning that the analyzer is designed and constructed in such a way that anybody operating it, as per the instruction manual, will not be exposed to harmful radiation levels set by the Nuclear Regulatory Commission. Many states still recommend that radiation from survey instruments be below a certain level. For example, in the State of Kansas, the permissible occupational exposure is 5,000 mrem/year, which equates to approximately 2 to 3 mrem/hr assuming constant exposure for an entire work year.

While taking *in situ* measurements (probe pointing down), the following radiation values were obtained at the probe face for the TN 9000 Analyzer: Cd^{109} source, 0.10 to 0.12 mrem/hr; Fe^{55} source, 0.025 - 0.035 mrem/hr; and Am^{241}, 0.50 - 0.60 mrem/hr. Radiation background levels were recorded at the probe handle while the Fe^{55} and Cd^{109} sources were exposed, while 0.020 - 0.025 mrem/hr were recorded when the Am^{241} source was exposed. While collecting intrusive measurements with the TN 9000 Analyzer, the following radiation values were obtained on top of the protective sample cover: Cd^{109} source, 0.09 to 0.10 mrem/hr; Fe^{55} source, 0.008 - 0.012 mrem/hr; and Am^{241} source, 0.08 to 0.10 mrem/hr. All measured radiation values were less than the permissible 2.0 mrem/hr. The operator noted there was no safety feature on the analyzer that prevented a person from accidentally exposing someone by pushing the button on the rear of the probe to start an analysis while the probe was pointed at the operator or another person.

Cost

At the time of demonstration, the cost of a new TN 9000 analyzer was $58,000. This included all of the equipment necessary for operation of the analyzer. The analyzer has a full-year warranty with an optional extended warranty. The TN 9000 Analyzer can be rented through several companies for $6,000 per month or $3,500 for 2 weeks. Additional field packs can be purchased for $200 and external batteries, charger, and adapter for $750. A 12-month or 24-month extended warranty can be purchased for $2,750 or $4,750, respectively. Periodic maintenance includes replacement of the Cd^{109} source every 2 years at a cost of $3,500 - $3,800. The Fe^{55} source should be replaced every 4 to 5 years. The cost of replacement of the Cd^{109} and Fe^{55} sources together is $6,800. The Am^{241} source has a half-life of 433 years and does not need to be replaced. Because the TN 9000 Analyzer contains a radioisotope, a wipe test must be performed every 6 months at the cost of $60. The developer offers a training course at its offices or on-

site. The cost of the on-site course is $1,000 per day, plus travel expenses. Operator costs will vary depending on the technical knowledge of the operator.

The primary cost benefit of field analysis is the quick access to analytical data. This allows the process dependent on the testing to move efficiently onto the next phase. Costs associated with field analysis are very dependent on the scope of the project. Since most of the mobilization costs are fixed, analyzing a large number of samples lowers the per sample cost. This is a key advantage that field analysis has over a conventional laboratory. Furthermore, more samples are usually taken for field analysis since questions raised in the preliminary findings may be resolved completely without the need to return for another sample collection event.

A representative list of costs associated with the Spectrace TN 9000 is presented in Table 5-2. Also included in this table is the measured throughput and the per sample charge of the reference laboratory. Given the special requirements of this demonstration, it was not considered fair to report a per sample cost for the field analysis. However, some estimate can be derived from the data provided in the table.

Table 5-2. Instrument and Field Operation Costs

Item	Amount	
TN 9000	$ 58,000	Purchase Price
	6,000	Per Month Lease
Operator Training (Vendor Provided)	—	—
Radiation Safety License (State of Kansas)	500	—
Field Packs for Batteries and Charger	750	—
Replacement Sources		
Cd^{109}	3,500	Every 2 years
Fe^{55}	3,000	Every 4 years
Am^{241}	N/A	Lifetime use
Field Operation Costs		
Supplies and Consumables (Sample cups, window film, sieves, standards)	300 - 500	(Varies, depending on sample load)
Field Chemist (Labor Charge)	100 - 150	Per day
Per diem	80 - 120	Per day
Travel	200 - 500	Per traveler
Sample Throughput	9.5 - 10.5	Samples per hour
Cost of Reference Laboratory Analysis	150	Per sample

Performance Factors

The following paragraphs describe performance factors, including detection limits, sample throughput, and drift.

Detection Limits

MDLs were determined using standard EPA SW-846 protocols. Ten replicate measurements were collected on site-specific soil samples having metals concentrations 2 to 5 times the expected MDLs. These data were obtained from the same samples used in the precision assessment. Based on these 10 replicate

measurements, a standard deviation on the replicate analysis was calculated. For the purpose of this demonstration, these precision-based MDLs, presented in Table 5-3, are defined as 3 times the standard deviation for each analyte. The precision-based MDLs were obtained using a 100-second count time and the Cd^{109} source. All the precision-based MDLs were calculated for soil samples that had been dried and ground in a sample cup.

Table 5-3. Method Detection Limits— TN 9000 Analyzer

Analyte	Developer MDL (mg/kg)	Precision-based MDL (mg/kg)	Field based MDL (mg/kg)
Antimony	58	55	68
Arsenic	35	60	100
Barium	16	60	975[a]
Cadmium	255	ND	247
Chromium	164[b]	200[b]	443[b]
	372[c]	500[c]	838[c]
Copper	62	85	195
Iron	157	ND	ND
Lead	20	45	46
Nickel	89	100	286
Zinc	50	80	165

Notes:

[a] This MDL may be an artifact of the reference data at concentrations below 200 mg/kg, or it may be an artifact of barium concentration determination by total analysis method.

[b] Chromium low based on Fe^{55} source.

[C] Chromium high based on Cd^{109} source.

mg/kg Milligrams per kilogram.

ND Not determined.

Table 5-3 also lists MDLs reported by the developer. The developer's MDLs were acquired using a 200-second count time for each source with a SiO_2 blank free of any potential interferences but spiked with the target analytes.

Because the developer's MDLs were based on 200-second count times, while the precision-based MDLs were calculated based on the shorter count times, the developer's MDLs were corrected for comparison purposes. According to XRF counting statistics, the precision-based MDLs will vary by the square root of the count time. Therefore, the developer MDLs for elements reported by the Cd^{109} source were multiplied by a factor of 1.4 (square root 2) and by a factor of 1.82 (square root 3.33) for the elements reported by the Fe^{55} and Am^{241} sources. The developer MDLs listed in Table 5-3 have been corrected by the factors listed above to account for count time differences.

Another method of determining MDLs involves the direct comparison of the analyzer data and the reference method data. When these sets of data are plotted against each other, the resultant plots were linear. As the line approached zero concentration, there was a point at which the analyzer data appeared to

correspond to the reference data. Figure 5-2 illustrates this effect for copper. By determining the concentration value of this data point, it was possible to determine field-based MDLs for the analyzer. These field-based MDLs are shown in Table 5-3.

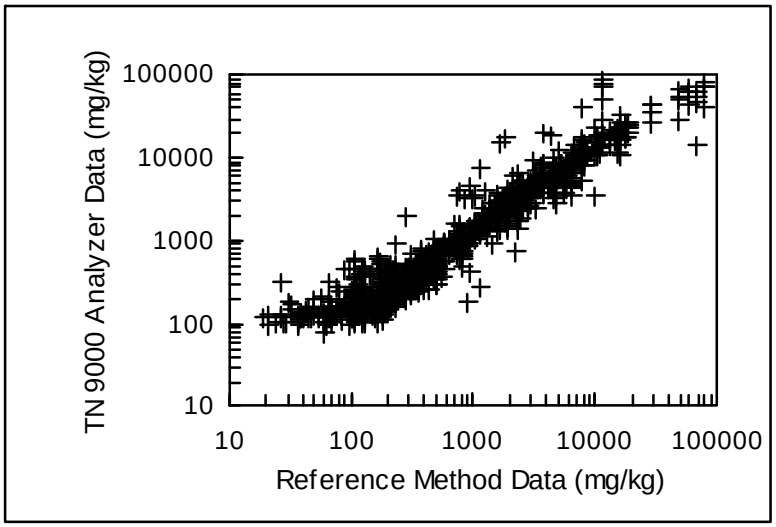


Figure 5-2. Critical Zone for the Determination of a Field-based Method Detection Limit for Copper: Between 100 and 200 mg/kg for the reference data, the linear relationship between the two data sets changes. This point of change identified the point at which field-based MDLs for the analyzer were determined.

Although the TN 9000 Analyzer reported results for 24 analytes, only the target analytes are shown in Table 5-3. Cadmium was reported only at very low concentrations and a precision-based MDL could not be determined. Iron was mostly found at concentrations in the tens of thousands of milligrams per kilogram so that reasonable detection limits could not be calculated. The precision-based MDLs were generally higher than the developer's detection limits, but usually within a factor of 2. The field-based MDLs were generally higher than the precision-based MDLs. The differences between the developer's MDLs and the precision- and field-based MDLs is probably due to increased matrix interferences inherent in environmental soil samples.

Throughput

The TN 9000 Analyzer used a total source live-second count time of 220 seconds or 3.7 minutes. With the additional "dead" time of the analyzer and the time required to label each sample and store data between sample measurements, the time required to analyze one soil sample was between 5 and 6 minutes. At the beginning of the demonstration, the operator was able to analyze 8.5 *in situ* soil samples per hour. As he gained more experience and became more efficient at operating the TN 9000 Analyzer, he was able to analyze 9.5 *in situ* soil samples per hour. In the intrusive mode with the samples already prepared, the throughput was increased to 9.5 to 10.5 samples per hour. The operator found he was capable of analyzing an average of 100 soil samples in a 10-hour day. The maximum number of soil samples analyzed was 128 in a 12-hour day. This throughput did not include the analysis of an average of six QC samples, such as two SiO_2 blanks, two pure iron sample calibration checks, and two NIST SRMs. These QC analyses are recommended by the developer. Sample analysis time did not include the time required for sample handling

and preparation or for data downloading, printing, and documentation. Considerable time was spent preparing the *in situ* homogenized samples and the intrusive samples. The sample homogenization process took approximately 5 minutes per sample, wet sieving took nearly 20 minutes per sample, and grinding and sieving took approximately 10 minutes per sample. Approximately 30 minutes were spent daily downloading data to a PC and obtaining a hard copy.

Drift

Drift is a measure of an analyzer's variability in quantitating a known amount of a standard over time. For the TN 9000 Analyzer, drift was evaluated by reviewing results from the daily analysis of NIST SRM 2710. This SRM contained quantifiable levels of arsenic, barium, copper, iron, lead, and zinc. NIST SRM 2710 data was collected over 18 days, approximately 67 percent at the ASARCO site and 33 percent at the RV Hopkins site. This data was reduced to RSDs for the target analytes, and the percent drift from the mean recovery of the true value. The percent drift from the mean recovery for each of the 18 days is shown in Figure 5-3. The RSD values for barium, copper, iron, lead, and zinc were all less than 8 percent. The RSD for arsenic was much higher at 18.2 percent. This higher RSD for arsenic is probably an artifact of interference from the much greater concentration of lead in the sample. The developer has noted that in past analyses of NIST SRM 2710, the precision of the arsenic analysis in the presence of 5,500 ppm lead was 18 percent in a 100-second measurement. The low RSD values indicate that for the concentrations of analytes found in NIST SRM 2710, the TN 9000 Analyzer exhibited little drift during the demonstration. With the exception of arsenic, the drift that did occur was less than the 10 percent RSD specified in the demonstration plan.

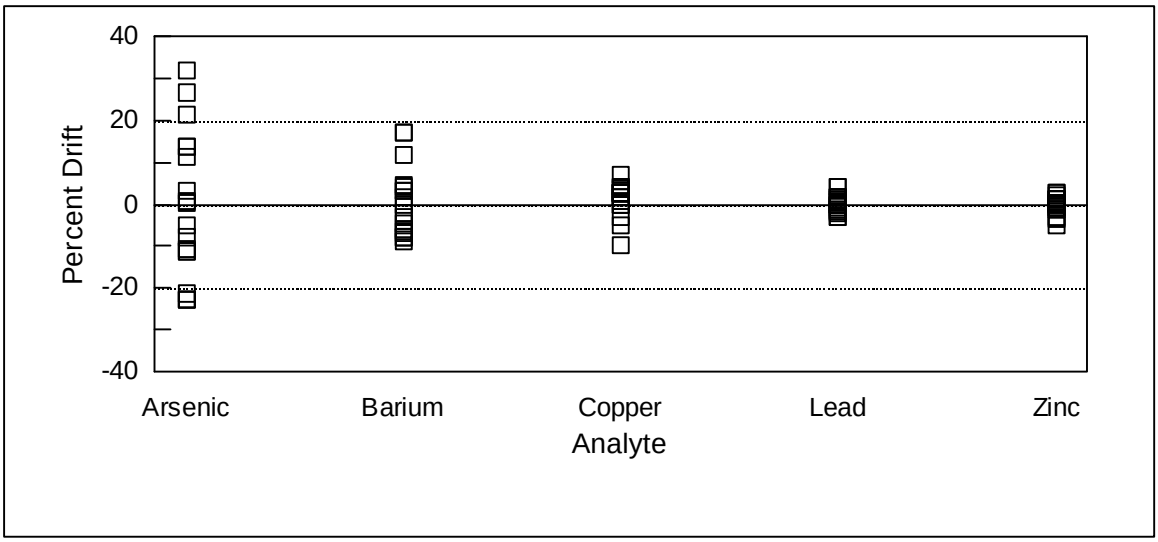


Figure 5-3. Drift Summary—TN 9000 Analyzer: This graph illustrates the analyzer's drift over a period of 18 days. Each bar represents a single measurement on a single day. The same sample was used throughout the demonstration.

Intramethod Assessment

Intramethod measures of the analyzer's performance included results on analyzer blanks, completeness, precision, accuracy, and comparability. The following sections discuss these characteristics.

Blanks

Analyzer blanks for the TN 9000 Analyzer consisted of SiO_2 blocks. These blanks were routinely analyzed at the beginning and end of each day. They were used to monitor contamination due to such factors as residual soil left on the face of the probe. A total of 37 SiO_2 blanks was analyzed during the demonstration. None of the primary analytes were detected in the 37 blanks. Iron was frequently detected at concentrations ranging from 150 to 250 mg/kg. This small amount of iron is actually present in the SiO_2 matrix. These concentrations of iron would not have significantly affected the results of the soil samples because iron concentrations in the soil samples were mostly greater than 20,000 mg/kg.

Completeness

A total of 315 soil samples was analyzed four times (four sample preparation steps) resulting in 1,260 sample results. The TN 9000 Analyzer produced results for 1,259 of the 1,260 samples for a completeness of 99.9 percent, above the demonstration objective of 95 percent. The one missing sample result was due to operator error and was not to an analyzer malfunction. The operator failed to analyze one *in situ* sample at the ASARCO site.

Precision

Precision refers to the degree of repeatability or agreement among individual measurements of the same sample and provides an estimate of analyzer-induced or random error. Precision for this demonstration was expressed in terms of the percent RSD between replicate measurements. The precision data for the target analytes are shown in Table 5-4. The TN 9000 Analyzer performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from less than 50 mg/kg to tens of thousands of milligrams per kilogram. Each of the 12 soil samples underwent the four sample preparation steps providing 480 precision data points for each analyte. Since the replicate analyses were taken without moving the probe or sample, the resulting measurements reflect analyzer precision and not method precision, which would include sample preparation. The replicate measurements were obtained using the source count times discussed previously. For each detectable analyte in each precision sample, a mean concentration, standard deviation, and RSD were calculated.

In this demonstration, the RSD for a given analyte had to be less than or equal to 20 percent to be considered quantitative screening level data and less than or equal to 10 percent to be considered definitive level data. The precision of the analyzer was defined by measurements in the 5 to 10 times the expected MDL range. The analyzer's precision was below the 10 percent RSD required for definitive level data classification for all target analytes except chromium (Table 5-4). Nickel, cadmium, and iron did not have sufficient data to allow data quality conclusions based on precision. Table 5-4 shows that chromium precision in this concentration range was greater than 20 percent placing the chromium data in the qualitative screening level category. The decreased precision for chromium shown in Table 5-4 was expected as chromium is a problematic analyte for FPXRF analysis. The average RSD values for nickel and cadmium shown in Table 5-4 are biased high because of the low inherent nickel and cadmium concentrations in the precision samples.

There was no significant sample preparation effect on precision. This was expected because the method used to assess precision during this demonstration was primarily measuring analyzer precision, not total method precision. There was a concentration effect on the precision data. The precision samples were purposely chosen to span a large concentration range to test the effect of analyte concentration on

precision. As the concentration of the target analyte increased, the precision increased (Figure 5-4). The largest increase in precision occurred at concentrations 2 to 3 times the detection limit for that analyte. The precision continued to increase until 1,000 - 2,000 mg/kg, then stabilized above analyte concentrations of 2,000 mg/kg.

Table 5-4. Precision Summary— TN 9000 Analyzer

Analyte	Mean % RSD Values by Concentration Range			
	5 - 10 Times MDL[a]	50 - 500 (mg/kg)	500 - 1,000 (mg/kg)	>1,000 (mg/kg)
Antimony	6.54 (8)	12.52 (16)	4.54 (4)	ND
Arsenic	5.33 (12)	9.68 (8)	4.39 (12)	2.87 (8)
Barium	4.02 (20)	ND	3.70 (40)	2.67 (8)
Cadmium	ND	29.84[b] (48)	ND	ND
Chromium[c]	22.25 (12)	38.95 (12)	29.10 (4)	ND
Copper	7.03 (8)	19.02 (24)	6.21 (4)	3.35 (12)
Iron	ND	ND	ND	1.78 (48)
Lead	6.45 (12)	9.69 (12)	5.34 (2)	3.68 (20)
Nickel	ND	30.85[b] (16)	ND	ND
Zinc	7.27 (16)	13.59 (24)	7.27 (16)	ND

Notes:

[a] The MDLs referred to in this column are the precision-based MDLs shown in Table 5-3.

[b] These values may be biased high because the concentration of these analytes in the soil samples was near the detection limit.

[c] Values calculated from chromium low results from Fe^{55} source.

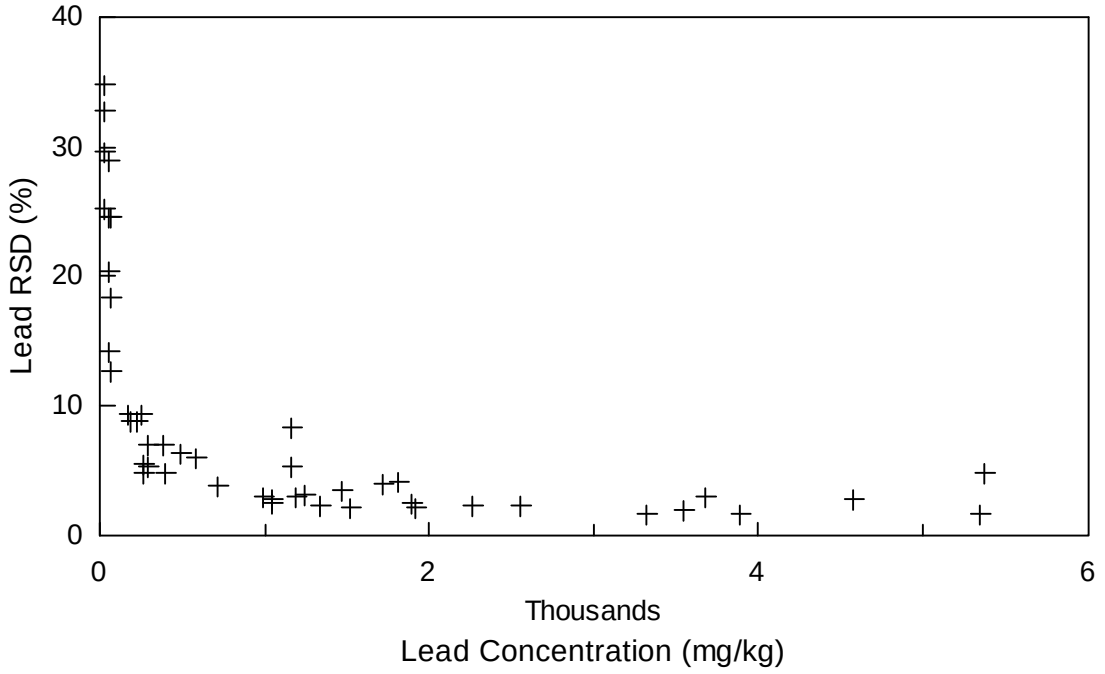
mg/kg Milligrams per kilogram.

ND No data.

( ) Number of samples, including all four preparation steps, each sample represents 10 replicate measurements. Numbers do not always add up to 48 precision points because some samples had analyte concentrations below the analyzer's MDL.

Accuracy

Accuracy refers to the degree to which a measured value for a sample agrees with a reference or true value for the same sample. Intramethod accuracy was assessed for the TN 9000 Analyzer by using site-specific PE samples and SRMs. Accuracy was evaluated through a comparison of percent recoveries for each target analyte. The TN 9000 Analyzer analyzed six site-specific PE samples and 14 SRMs. The operator knew the samples were PE samples or SRMs, but did not know the true concentration or the acceptance range. These site-specific PE samples and SRMs were analyzed in the same way as all other samples.



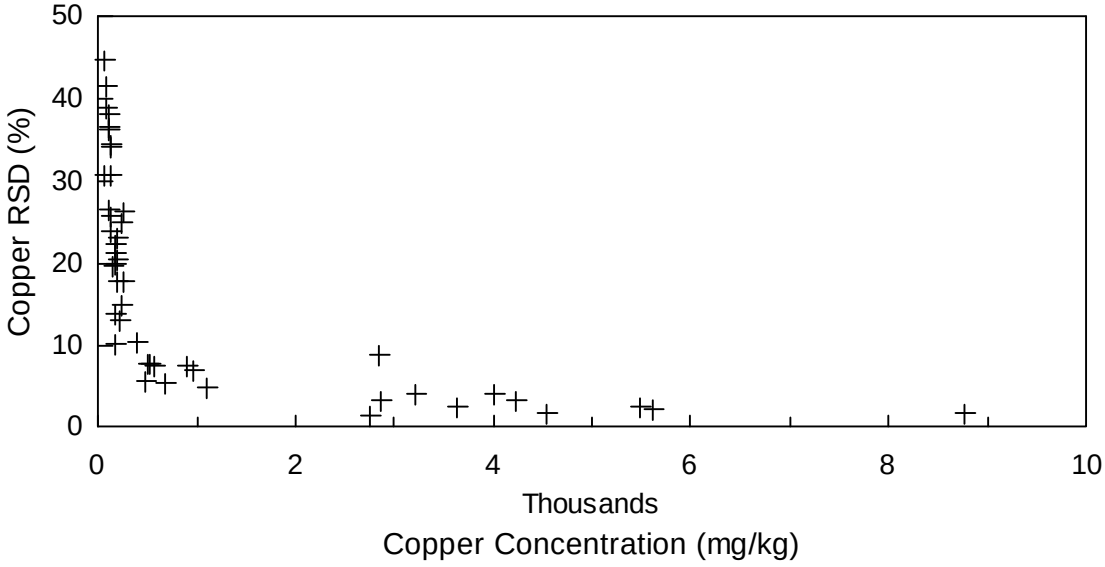


Figure 5-4. Precision vs. Concentration for Lead and Copper—TN 9000 Analyzer: These graphs illustrate the analyzer's precision as a function of analyte concentration.

The six site-specific PE samples included three from each of the two demonstration sites. These samples were collected during the predemonstration activities and sent to six commercial laboratories for analysis by laboratory-grade XRF analyzers. The mean measurement for each analyte was used as the true value concentration. The 14 SRMs included seven soil, four stream or river sediment, two ash, and one sludge SRM. The SRMs were obtained from NIST, USGS, Commission of European Communities-

Bureau of Reference, National Research Council-Canada, and the South African Bureau of Standards. The SRMs contained known certified concentrations of certain target analytes.

These PEs and SRMs did not have published acceptance ranges. As specified in the demonstration plan, an acceptance range of 80 - 120 percent recovery of the true value was used to evaluate accuracy for the six site-specific PEs and 14 SRMs. Table 5-5 summarizes the site-specific PE and SRM accuracy data for the target analytes for the TN 9000 Analyzer. Figures 5-5 and 5-6 show the true values, the measured value, and percent recoveries for the individual site-specific PEs and SRMs, respectively. No figures were presented for analytes that had less than three samples with detectable concentrations. True value results from the site-specific PEs and SRMs with concentrations less than the precision-based MDLs listed in Table 5-3 were excluded from the accuracy assessment.

The TN 9000 Analyzer was 100 percent accurate for all analytes in the site-specific PE samples with the exception of chromium, nickel, and zinc. Overall, the TN 9000 Analyzer produced 37 out of 41 results within the 80 - 120 percent recovery acceptance range for all analytes in the six site-specific PE samples. This translates into a 90.2 percent accuracy for all analytes. Two of the four results were only slightly outside the acceptance range, a nickel recovery of 125 percent in one sample and a zinc recovery of 79.1 percent in one sample. The other two unacceptable results fell far outside the acceptance ranges with a nondetect or 0 percent recovery for chromium in one sample and a zinc recovery of 58.3 percent in one sample. The 58.3 percent recovery for zinc was for a PE sample that contained 164 mg/kg zinc which is less than the field-based MDL and less than 2 times the precision-based MDL. With the exception of chromium, the TN 9000 Analyzer produced mean percent recoveries near 100 percent for all analytes (Table 5-5). These results were for analytes with concentrations spanning 1 or more orders of magnitude in the site-specific PE samples.

A detailed analysis of the SRM data is presented in Figure 5-6. The TN 9000 Analyzer accuracy for the SRMs varied from 0 percent for chromium (only one SRM concentration for chromium above the TN 9000 Analyzer's MDL) to 100 percent for antimony and iron in all SRMs. The iron concentrations in the SRMs were in the tens of thousands of milligrams per kilogram so it was not surprising the TN 9000 Analyzer performed well for iron. Some analytes such as barium, copper, lead, and zinc had concentrations spanning one or more orders of magnitude in the SRMs. Overall, the TN 9000 Analyzer produced 38 out of 58 results within the 80 - 120 percent recovery range for an accuracy of 65.5 percent. Of the 20 results that fell outside of the acceptance range, four results were low, and 16 were high. This ratio of high results to low, in addition to the mean percent recoveries shown in Table 5-5, indicated that, in general, the TN 9000 Analyzer overestimated analyte concentrations in the SRMs, especially for barium. The lowest recovery produced by the TN 9000 Analyzer was 67 percent for copper in the Canadian sediment SRM. The highest recovery was 198 percent for barium in one of the USGS soil SRMs. The TN 9000 Analyzer results for all analytes were less than 2 times the reported SRM true value for all SRMs.

A more detailed analysis of the SRM data showed that there was a matrix effect on the TN 9000 Analyzer accuracy. The TN 9000 Analyzer produced 22 out of 24 or 91.7 percent of the results within the acceptance range for all target analytes in the soil SRMs; 10 out of 19 or 52.6 percent for the sediment SRMs; and 6 out of 15 or 40 percent for the ash and sludge SRMs. The greater accuracy for the soil SRMs is expected since it was using an FP calibration based on the NIST soil SRMs. Only barium recovery in the two USGS soil SRMs was outside (above) the acceptance range. This demonstrates that the TN 9000 Analyzer is more accurate when analyzing SRMs that closely match the matrix used to set its FPs. The TN 9000 Analyzer performed the poorest on the one sludge SRM by overestimating all analyte concentrations by a factor of 1.5 to 1.7. With the sludge SRM removed from the data, the TN 9000

Analyzer had percent recoveries less than 140 percent for all analytes in all SRMs except for barium in one USGS SRM.

Table 5-5. Accuracy Summary for Site-Specific PE and SRM Results—TN 9000 Analyzer

Analyte	n	Percent Within Acceptance Range	Mean Percent Recovery	Range of Percent Recovery	SD of Percent Recovery	Concentration Range (mg/kg)
Site-Specific Performance Evaluation Samples						
Antimony	4	100	96	85 - 105	8.82	51 - 2,253
Arsenic	3	100	94	87 - 101	7.07	424 - 19,584
Barium	6	100	100	94 - 110	5.95	792 - 7,240
Cadmium	1	100	110	110	NA	353
Chromium	2	50	41	0 - 82	NA	939 - 3,800
Copper	5	100	96	85 - 120	14.5	300 - 7,132
Iron	6	100	97	87 - 105	6.43	27,320 - 70,500
Lead	6	100	98	91 - 103	4.34	292 - 14,663
Nickel	2	50	115	105 - 125	NA	312 - 444
Zinc	6	67	85	58 - 103	15.4	164 - 3,490
Soil Standard Reference Materials						
Arsenic	3	100	101	89 - 115	13	105 - 626
Barium	5	60	130	98 - 198	40	707 - 2,240
Copper	2	100	88	80 - 96	NA	131 - 2,950
Iron	3	100	98	95 - 102	3.7	28,900 - 35,000
Lead	5	100	100	80 - 115	13	101 - 5,532
Nickel	1	100	99	99	NA	299
Zinc	5	100	98	93 - 112	8.1	106 - 6,952
Sediment Standard Reference Materials						
Antimony	1	100	100	100	NA	171
Arsenic	1	0	68	68	NA	211
Barium	3	33	125	107 - 139	16	335 - 414
Chromium	1	0	178	178	NA	509
Copper	4	50	100	67 - 139	31	99 - 452
Iron	1	100	99	99	NA	41,100
Lead	4	75	104	82 - 138	25	161 - 5,200
Zinc	4	50	94	74 - 122	18	264 - 2,200
Ash and Sludge Standard Reference Materials						
Arsenic	2	50	107	85 - 127	NA	136 - 145
Barium	2	50	123	117 - 130	NA	709 - 1,500
Copper	3	0	143	124 - 174	27	113 - 696
Iron	2	100	88	86 - 89	NA	77,800 - 94,000
Lead	2	50	122	91 - 153	NA	72 - 286
Nickel	1	0	123	123	NA	247
Zinc	3	33	115	77 - 166	46	210 - 2,122

Notes: n Number of samples with detectable analyte concentrations.
SD Standard deviation.
mg/kg Milligrams per kilogram.

NA Not applicable. Standard deviation not calculated for two or fewer results.

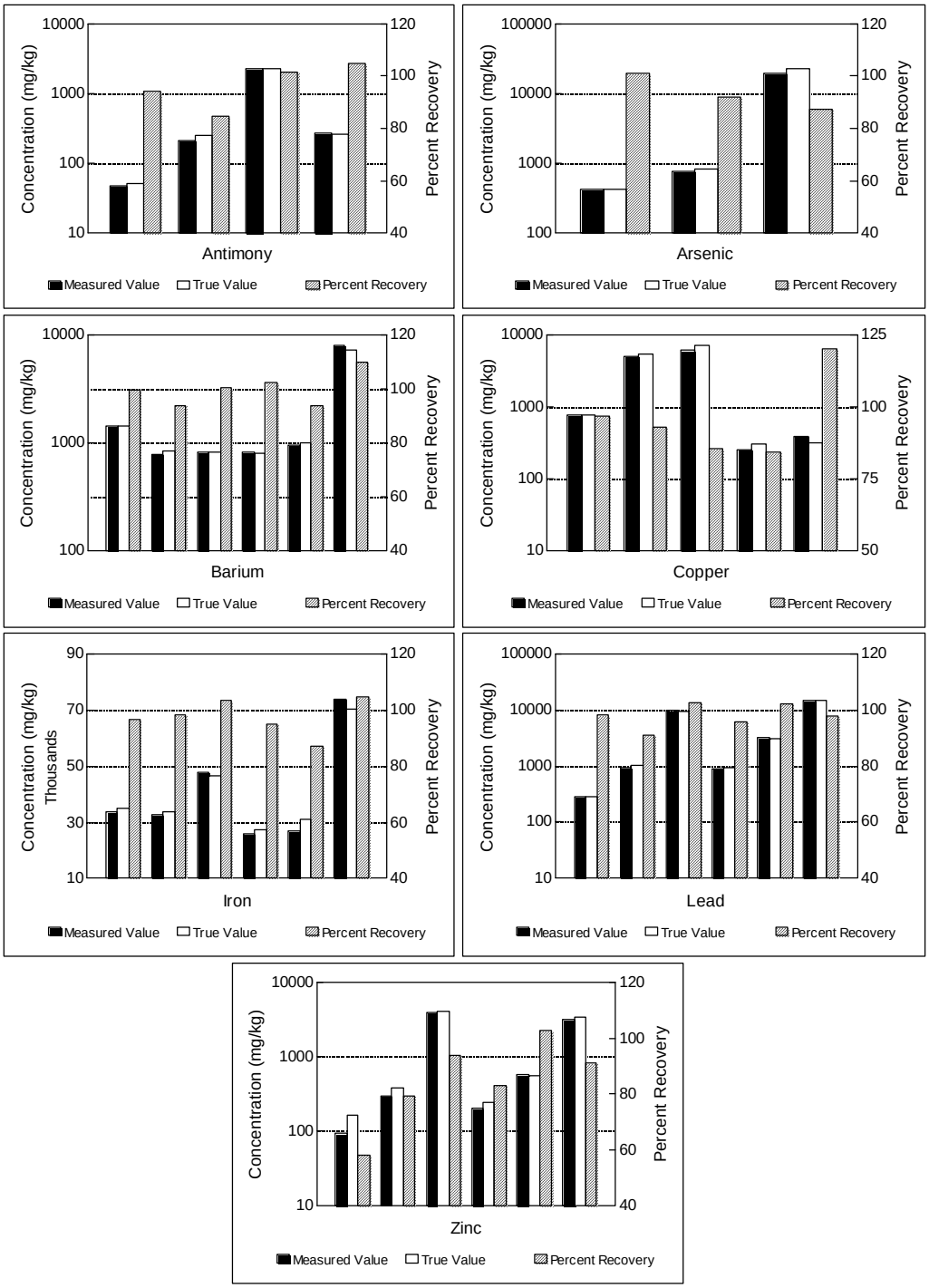


Figure 5-5. Site-specific PE Sample Results—TN 9000 Analyzer: These graphs illustrate the relationship between the analyzer's data (measured values) and the true values for site-specific PE samples. The gray bars represent the percent recovery for the analyzer. Each set of three bars (black, white, and gray) represents a single site-specific PE sample.

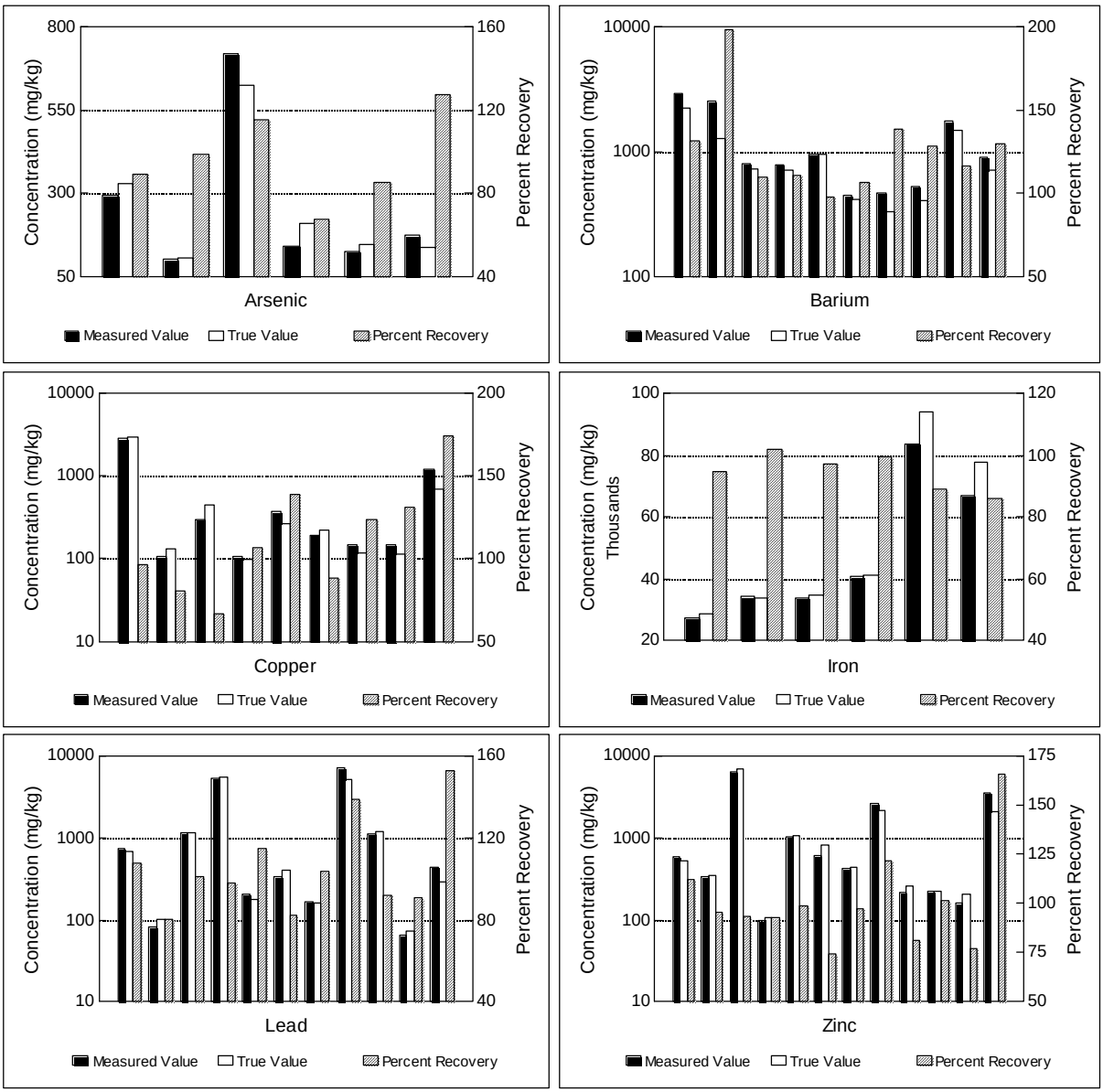


Figure 5-6. SRM Results—TN 9000 Analyzer: These graphs illustrate the relationship between the analyzer's data (measured values) and the true values for the SRMs. The gray bars represents the percent recovery for the analyzer. Each set of three bars (black, white, and gray) represents a single SRM sample.

The TN 9000 Analyzer displayed almost identical accuracy for the soil SRMs and the site-specific PEs (90.2 percent). This indicates that the matrix of the soil SRMs matched the matrix of the site-specific samples well enough such that the FP calibration based on the soil SRMs produced results that were over 90 percent accurate for site-specific samples. It also indicates that SRMs of a sediment, ash, or sludge matrix are not as suitable of accuracy checks when the FP calibration is based on a soil matrix.

Comparability

Intramethod comparability for the TN 9000 Analyzer was assessed through the analysis of four ERA PEs and four CRM PEs. These eight samples were analyzed by the TN 9000 Analyzer in the same manner as all other samples. As described in Section 3, these eight samples had certified analyte concentrations determined by EPA SW-846 Methods 3050A/6010A. The ERA PEs had published PALs based on a 95 percent confidence interval around each certified concentration. The CRMs had a 95 percent confidence interval around each certified concentration. The CRMs had a 95 percent prediction interval (PI) associated with each certified value. The ability of the TN 9000 Analyzer to produce results within the PALs or PIs and the percent recovery for each of the analytes was used to evaluate the TN 9000 Analyzer's intramethod comparability. True value analyte concentrations in the ERA and CRM PEs that were below the precision-based MDLs in Table 5-3 were excluded from the intramethod comparability assessment.

The TN 9000 Analyzer performance data for all primary and secondary target analytes for the PE and CRM samples are summarized in Table 5-6. The measured values, true values, and percent recoveries for all detectable analytes are shown in Figure 5-7. No figure is shown for chromium and nickel because there were only one and two reported certified concentrations, respectively, for these two analytes. For the ERA PEs, the TN 9000 Analyzer produced 15 out of 29 results or 51.7 percent within the acceptance range. For the CRMs, the TN 9000 Analyzer produced 17 out of 23 results or 73.9 percent within the acceptance range. With the ERA and CRMs combined, the TN 9000 Analyzer produced 32 out of 52 results or 61.5 percent within the acceptance range. Based on the data presented in Table 5-6, the TN 9000 Analyzer's results were more comparable to the CRMs than the ERA PEs. Also, the mean percent recovery was nearer 100 percent for all analytes in the CRMs versus the ERA PEs except for arsenic. The better comparability to the CRMs versus the ERA PEs may have been an artifact of the low analyte concentrations in the ERA PEs. With the exception of iron, the analyte concentrations in the ERA PEs were all less than 350 mg/kg which is less than 5 times the precision-based MDL.

The TN 9000 Analyzer overestimated antimony concentrations in the ERA PEs and barium concentrations in the ERA PEs and CRMs. These results were expected because FPXRF techniques (or total metals analytical methods) often produce antimony and barium results much higher than those obtained from EPA SW-846 Methods 3050A/6010A (Kane and others 1993). The TN 9000 Analyzer also produced results for iron and nickel in the ERA PEs that were much higher than the certified values. Again, these are two analytes for which the acid leaching technique of Method 3050A will not achieve 100 percent recovery. Therefore, it was not surprising that the TN 9000 Analyzer's results were higher for iron and nickel. For all analytes in the ERA PEs, only 2 out of 29 recoveries were less than 100 percent. This indicated that the TN 9000 Analyzer generally gave higher results for PEs that had values certified by EPA SW-846 Methods 3050A/6010A, especially when the analyte concentrations were less than 5 times the precision-based MDL.

Intermethod Assessment

The comparison of the TN 9000 Analyzer results to the reference method was performed using the statistical procedures detailed in Section 2. The purpose of this statistical evaluation was to determine the comparability between data produced by the analyzer and that produced by the reference laboratory. If the $\log_{10}$ transformed FPXRF data were statistically equivalent to the $\log_{10}$ transformed reference data and had acceptable precision (10 percent RSD or less), the data met the definitive level criteria. If the data did not meet the definitive level criteria but could be mathematically corrected to be equivalent to the reference

data, they met the quantitative screening level criteria. If the analyzer did not meet the definitive level criteria, and the statistical evaluation could not identify a predictable bias in the data, but the analyzer identified the presence or absence of contamination with at least a 90 percent accuracy rate, the data was classified as qualitative screening level data.

The TN 9000 Analyzer was configured to report concentrations for all of the target analytes. The developer recommends that reported concentrations less than three times their associated standard deviations should not be considered valid data. This analyzer reported two values for chromium. The chromium high values were based on sample analysis by the Cd^{109} source and the chromium low values were based on sample analysis by the Fe^{55} source.

Table 5-6. PE and CRM Results—TN 9000 Analyzer

Analyte	n	Percent Within Acceptance Range	Mean Percent Recovery	Range of Percent Recovery	SD of Percent Recovery	Concentration Range (mg/kg)
ERA Performance Evaluation Samples						
Antimony	3	100	311	270 - 344	38	56 - 99
Arsenic	4	100	101	72 - 120	21	65 - 349
Barium	4	0	762	446 - 1,064	272	111 - 319
Cadmium	2	0	172	156 - 188	NA	90 - 131
Copper	4	75	131	113 - 174	28	88 - 196
Iron	4	0	195	168 - 240	34	7,130 - 10,400
Lead	4	75	112	72 - 146	32	52 - 208
Nickel	1	0	169	169	NA	135
Zinc	3	67	114	107 - 121	9.7	101 - 259
Certified Reference Materials						
Antimony	1	100	149	149	NA	4,955
Arsenic	1	100	108	108	NA	397
Barium	2	0	270	193 - 347	NA	342 - 586
Cadmium	2	100	115	101 - 129	NA	362 - 432
Chromium	1	100	99	99	NA	161,500
Copper	4	100	92	61 - 142	35	279 - 4,792
Iron	3	67	110	78 - 154	40	6,481 - 191,650
Lead	4	75	103	66 - 139	30	120 - 144,740
Nickel	1	100	108	108	NA	13,279
Zinc	4	50	92	41 - 130	38	546 - 22,217

Notes:
n Number of samples with detectable analyte concentrations.
SD Standard deviation.
mg/kg Milligrams per kilogram.
NA Not applicable. Standard deviation not calculated for two or fewer results.

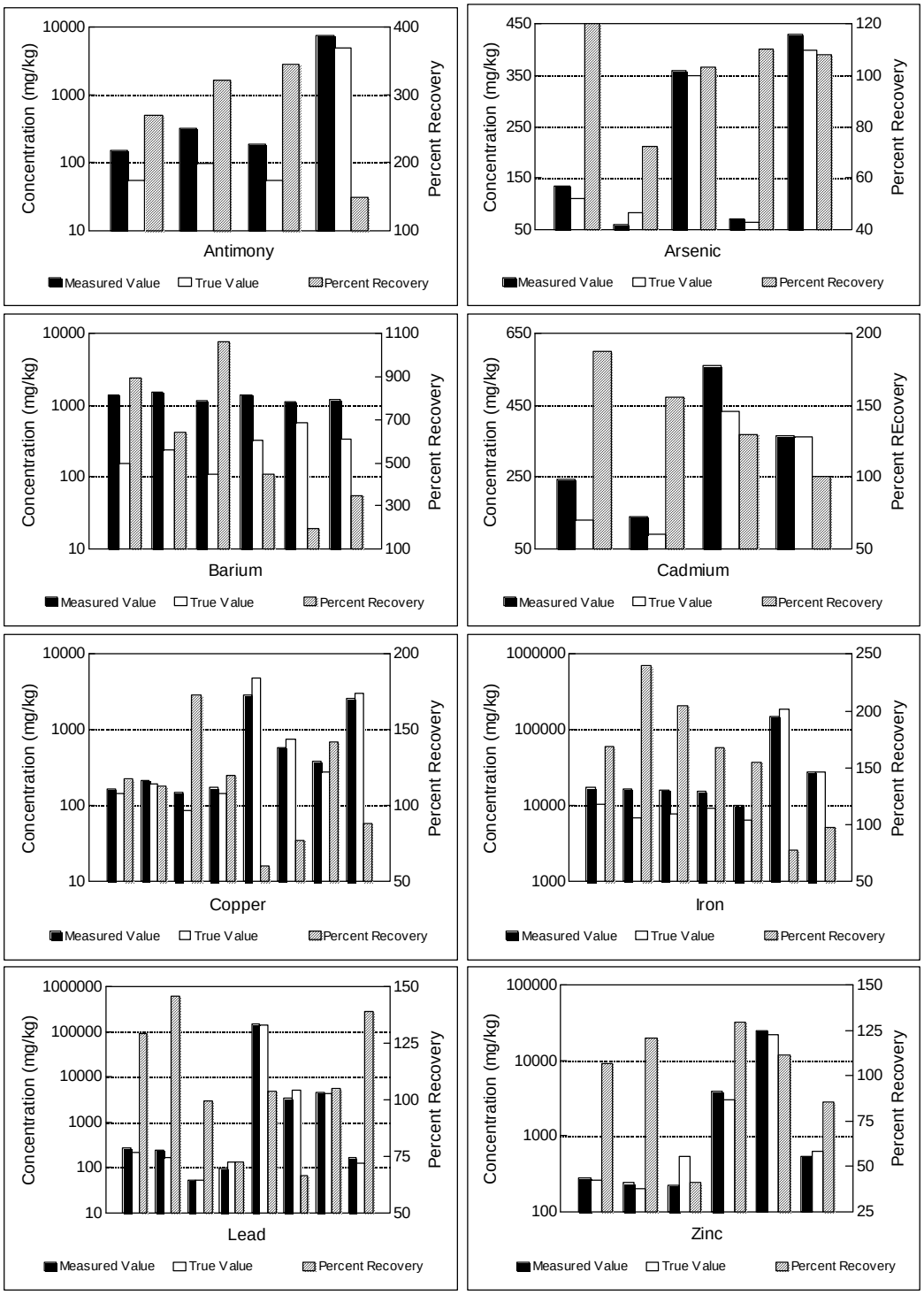


Figure 5-7. PE and CRM Results—TN 9000 Analyzer: These graphs illustrate the relationship between the analyzer's data (measured values) and the true values for the PE and CRM samples. The gray bars represent the percent recovery for the analyzer. Each set of three bars (black, white, and gray) represents a single PE or CRM sample.

The regression parameters for the six primary analytes are shown in Table 5-7. The regression analysis of the entire $\log_{10}$ transformed data set showed that arsenic, copper, lead, and zinc had r^2 values at or above 0.92. In the cases of arsenic, lead, copper, and zinc, the slopes and y-intercepts were not significantly different from 1.0 and 0.0, respectively. Barium and chromium had r^2 values ranging from 0.79 to 0.67. Based on these data, the analyzer tended to overestimate barium and chromium concentrations by a factor of greater than 10.0 relative to the reference method. The slope values in Table 5-7 were determined by plotting the $\log_{10}$ transformed FPXRF data on the y-axis and the $\log_{10}$ transformed reference data on the x-axis.

The next step in the data evaluation involved the assessment of the potential impact of the variables: site, soil texture, and sample preparation step on the regression analysis of the $\log_{10}$ transformed data (Table 5-7). Based on this evaluation, there was no apparent impact of either the site or soil variables on the regression. The sample preparation variable exhibited the greatest impact on the regression analysis. Generally, the largest shift in the r^2 was exhibited between the *in situ*-unprepared and *in situ*-prepared analyses (Figure 5-8). Sample homogenization accounted for between 80 and 100 percent of the total increase in the r^2 experienced across all sample preparation steps. This makes sense since the homogenization step assured that the analyzer and the reference method were analyzing essentially the same sample. Arsenic and copper data met definitive level data quality criteria prior to initial sample homogenization. For lead, the initial sample homogenization (*in situ*-prepared) improved the comparability between the two data sets to the point that the analyzer met the definitive level criteria. The remaining primary target analytes, barium and chromium, never exceeded quantitative or qualitative screening levels, respectively. The chromium data was considered qualitative screening level because the precision was greater than 20 percent.

The impact of the site and soil texture variables was then assessed for each of the four sample preparation steps (Tables 5-8 and 5-9). This evaluation was conducted for lead and zinc only. These were the only primary analytes exhibiting relatively even concentration distribution between the site and soil variables. Copper and barium tended to exhibit site and soil effects. However, a closer examination of the data shows that the reported concentrations were approaching either instrument MDLs or a very narrow range of concentrations. This held for the site and soil variables. No clear relationship was observed for these variables and the comparability of the technology's data with the reference method data. A minor trend was noticed for zinc. The loam soil always produced the poorest correlation; however, these correlations still met the quantitative screening level criteria.

Within the four sample preparation steps, the effect of contaminant concentration was also examined. The $\log_{10}$ transformed data sets for the primary target analytes were sorted into the following concentration ranges: 0 - 100 mg/kg, 100 - 1,000 mg/kg, and greater than 1,000 mg/kg. The regression analysis for each target analyte and for each sample preparation step was rerun on these concentration-sorted data sets. A review of these results showed no consistent improvement in either the r^2 or the standard error for any of the concentration-based data sets. This indicates that there is no concentration effect and that the regression analyses associated with the entire data set are most representative of the relationship between the analyzer data and the reference data. After examining the analyzer and reference data plots, a slight shift in the slope of the plot was noticed at approximately 2,000 mg/kg (Figure 5-8). When the data was assessed in the 0 - 2,000 mg/kg and greater than 2,000 mg/kg concentration ranges, a definite concentration effect was noticed. The regression parameters were generally better for the data in the 0 - 2,000 mg/kg concentration ranges. Lead exhibited the greatest effect, the comparison consistently produced lower r^2 values in the greater than 2,000 mg/kg range. Identification of the exact cause of the concentration effect is beyond the scope of this project. This effect does not appear to strongly effect data quality, and it is less

pronounced for the TN 9000 relative to the TN Pb Analyzer. Possible causes include changes in reference method accuracy at higher concentrations due to analyte interferences, and shifts in FPXRF performance at higher concentrations due to detector characteristics, or inherent characteristics of the FP calibration.

To examine the effect of count times on the analyzer's comparability, a subset of 26 samples from the RV Hopkins site was reanalyzed using twice the original count times. This increased the r^2 values for both chromium and copper measurements from 0.09 to 0.23 units, respectively. Antimony, arsenic, barium, cadmium, lead, nickel, iron, and zinc did not show as great an effect.

A final decision regarding the assignment of data quality levels derived from this demonstration involves an assessment of both r^2 and the precision RSD. Using the criteria presented in Table 2-2, a summary of the Spectrace TN 9000 data quality performance measures from this demonstration are shown in Table 5-10.

Table 5-7. Regression Parameters[a] by Primary Variable—TN 9000 Analyzer

Arsenic					Variable	Barium				
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
816	0.949	0.15	0.16	0.96	All Data	1223	0.787	0.11	1.87	0.50
804	0.964	0.13	0.11	0.98	ASARCO Site	827	0.412	0.09	2.26	0.31
3	ND	ND	ND	ND	RV Hopkins Site	393	0.869	0.12	1.67	0.58
359	0.970	0.13	0.08	0.97	Sand Soil	385	0.078	0.06	2.62	0.12
445	0.962	0.12	0.14	0.97	Loam Soil	444	0.611	0.11	1.78	0.53
3	ND	ND	ND	ND	Clay Soil	393	0.869	0.12	1.67	0.58
204	0.909	0.20	0.34	0.88	In Situ-Unprepared	305	0.675	0.14	1.86	0.50
205	0.981	0.09	0.09	0.96	In Situ-Prepared	306	0.770	0.11	1.91	0.48
202	0.983	0.09	0.02	1.01	Intrusive-Unprepared	306	0.865	0.08	1.91	0.49
201	0.965	0.13	0.14	0.99	Intrusive-Prepared	306	0.853	0.09	1.86	0.52

Copper					Variable	Lead				
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
959	0.951	0.16	0.32	0.94	All Data	1177	0.956	0.14	0.19	0.96
824	0.966	0.13	0.10	1.00	ASARCO Site	792	0.951	0.14	0.16	0.97
135	0.488	0.16	1.16	0.59	RV Hopkins Site	387	0.953	0.13	0.29	0.93
378	0.951	0.13	0.05	1.00	Sand Soil	351	0.957	0.13	0.13	0.96
444	0.963	0.12	0.28	0.96	Loam Soil	440	0.953	0.13	0.20	0.97
135	0.488	0.16	1.16	0.59	Clay Soil	387	0.953	0.13	0.29	0.93
250	0.888	0.24	0.54	0.87	In Situ-Unprepared	296	0.871	0.23	0.38	0.90
241	0.966	0.13	0.28	0.93	In Situ-Prepared	294	0.979	0.09	0.14	0.96
228	0.981	0.10	0.13	0.99	Intrusive-Unprepared	297	0.983	0.09	0.11	0.99
239	0.976	0.11	0.25	0.98	Intrusive-Prepared	294	0.979	0.10	0.14	1.00

Zinc					Variable	Chromium (Low)				
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
1062	0.926	0.13	0.24	0.96	All Data	277	0.782	0.15	1.85	0.41
734	0.918	0.13	0.27	0.94	ASARCO Site	93	0.003	0.08	2.43	0.03
341	0.934	0.13	0.18	1.00	RV Hopkins Site	184	0.673	0.17	1.60	0.49
323	0.945	0.13	0.21	0.94	Sand Soil	40	0.047	0.07	2.67	-0.13
413	0.888	0.12	0.34	0.93	Loam Soil	53	0.032	0.09	2.30	0.12
341	0.934	0.13	0.18	1.00	Clay Soil	184	0.673	0.17	1.60	0.49
281	0.824	0.20	0.49	0.87	In Situ-Unprepared	100	0.865	0.12	8.43	1.31
266	0.959	0.09	0.24	0.94	In Situ-Prepared	77	0.513	0.27	1.91	0.36
265	0.957	0.10	0.07	1.02	Intrusive-Unprepared	47	0.770	0.14	1.79	0.43
265	0.955	0.11	0.11	1.03	Intrusive-Prepared	49	0.748	0.17	1.50	0.56

Chromium (High)					Variable
n	r^2	Std. Err.	Y-Int.	Slope[b]	
160	0.674	0.17	1.93	0.43	All Data
18	ND	ND	ND	ND	ASARCO Site
143	0.692	0.17	1.53	0.57	RV Hopkins Site
10	ND	ND	ND	ND	Sand Soil
8	ND	ND	ND	ND	Loam Soil
143	0.692	0.17	1.53	0.57	Clay Soil
39	0.617	0.19	1.96	0.43	In Situ-Unprepared
35	0.735	0.15	1.93	0.42	In Situ-Prepared
42	0.631	0.18	1.98	0.41	Intrusive-Unprepared
45	0.768	0.17	1.77	0.51	Intrusive-Prepared

Notes:

[a] Regression parameters based on $\log_{10}$ transformed data. These parameters were calculated for FPXRF data as the dependent variable, and thus, cannot be used to correct the FPXRF data. See Section 6.

[b] Slope values determined by plotting FPXRF data on the x-axis and the reference data on the y-axis.

Y-Int. Y-Intercept.

Std. Err. Standard error.

n Number of data points.

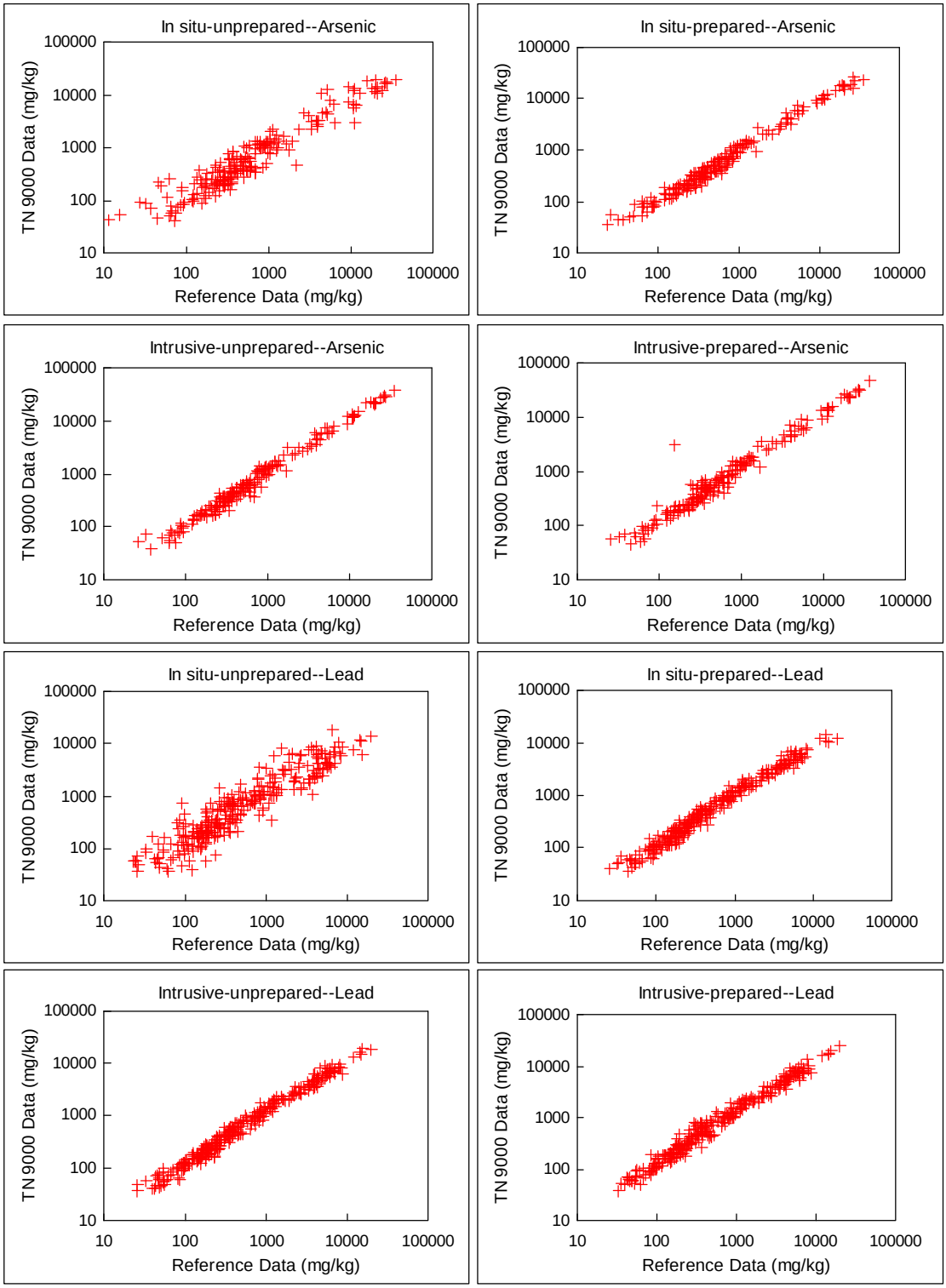


Figure 5-8. Sample Preparation Effect on Arsenic and Lead Results—TN 9000 Analyzer: These graphs illustrate the effect of sample preparation on the comparability between the analyzer and the reference data.

Table 5-8. Regression Parameters[a] by Sample Preparation Variable and Soil Texture—TN 9000 Analyzer

Arsenic						Barium				
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared					Soil Texture	In Situ-Unprepared				
90	0.924	0.19	0.34	0.86	Sand Soil	95	0.015	0.07	2.92	-0.06
112	0.911	0.18	0.26	0.93	Loam Soil	110	0.570	0.12	1.77	0.51
2	ND	ND	ND	ND	Clay Soil	98	0.742	0.17	1.69	0.57
In Situ-Prepared					Soil Texture	In Situ-Prepared				
92	0.986	0.09	0.04	0.97	Sand Soil	97	0.078	0.08	2.55	0.15
112	0.981	0.08	0.15	0.95	Loam Soil	112	0.509	0.15	1.73	0.55
4	ND	ND	ND	ND	Clay Soil	98	0.855	0.11	1.81	0.52
Intrusive-Unprepared					Soil Texture	Intrusive-Unprepared				
87	0.989	0.08	-0.05	1.02	Sand Soil	99	0.304	0.04	2.51	0.18
111	0.987	0.07	0.06	1.01	Loam Soil	111	0.698	0.09	1.82	0.52
3	ND	ND	ND	ND	Clay Soil	98	0.929	0.08	1.72	0.57
Intrusive-Prepared					Soil Texture	Intrusive-Prepared				
90	0.980	0.11	0.09	0.99	Sand Soil	95	0.293	0.03	2.63	0.13
111	0.983	0.08	0.13	1.00	Loam Soil	111	0.742	0.09	2.27	0.79
3	ND	ND	ND	ND	Clay Soil	99	0.938	0.09	1.56	0.63

Copper						Lead				
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared					Soil Texture	In Situ-Unprepared				
94	0.918	0.15	0.34	0.88	Sand Soil	87	0.920	0.17	0.36	0.86
113	0.852	0.25	0.45	0.92	Loam Soil	112	0.879	0.20	0.47	0.87
44	0.494	0.18	1.21	0.61	Clay Soil	96	0.776	0.28	0.74	0.81
In Situ-Prepared					Soil Texture	In Situ-Prepared				
95	0.973	0.09	-0.05	1.03	Sand Soil	89	0.978	0.09	0.04	0.98
113	0.979	0.09	0.27	0.94	Loam Soil	109	0.971	0.10	0.15	0.97
33	0.592	0.11	1.36	0.45	Clay Soil	98	0.982	0.08	0.24	0.93
Intrusive-Unprepared					Soil Texture	Intrusive-Unprepared				
93	0.977	0.09	-0.11	1.07	Sand Soil	88	0.984	0.08	0.01	1.01
114	0.988	0.07	0.26	0.96	Loam Soil	113	0.983	0.08	0.12	1.00
24	0.394	0.15	0.82	0.75	Clay Soil	98	0.989	0.07	0.21	0.95
Intrusive-Prepared					Soil Texture	Intrusive-Prepared				
95	0.970	0.10	0.03	1.04	Sand Soil	87	0.972	0.11	0.11	1.00
112	0.987	0.07	0.24	0.98	Loam Soil	109	0.974	0.10	0.12	1.02
34	0.541	0.16	0.98	0.68	Clay Soil	99	0.988	0.07	0.17	0.98

Table 5-8. ***Continued***

Zinc						Chromium (Low)				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Soil Texture	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
80	0.950	0.11	0.40	0.85	Sand Soil	19	ND	ND	ND	ND
106	0.753	0.17	0.70	0.78	Loam Soil	28	ND	ND	ND	ND
92	0.861	0.20	0.38	0.97	Clay Soil	56	0.688	0.17	1.81	0.43
In Situ-Prepared					Soil Texture	In Situ-Prepared				
81	0.968	0.10	0.23	0.94	Sand Soil	16	ND	ND	ND	ND
101	0.923	0.10	0.37	0.90	Loam Soil	18	ND	ND	ND	ND
84	0.976	0.07	0.18	0.97	Clay Soil	42	0.715	0.15	1.46	0.51
Intrusive-Unprepared					Soil Texture	Intrusive-Unprepared				
79	0.963	0.11	0.00	1.03	Sand Soil	3	ND	ND	ND	ND
101	0.935	0.10	0.21	0.98	Loam Soil	4	ND	ND	ND	ND
86	0.979	0.08	0.06	1.03	Clay Soil	40	0.793	0.12	1.32	0.58
Intrusive-Prepared					Soil Texture	Intrusive-Prepared				
77	0.955	0.12	0.12	1.00	Sand Soil	3	ND	ND	ND	ND
106	0.937	0.10	0.20	1.00	Loam Soil	3	ND	ND	ND	ND
81	0.978	0.08	0.05	1.06	Clay Soil	43	0.842	0.13	0.76	0.80

Chromium (High)										
n	r^2	Std. Err.	Y-Int.	Slope[b]	Soil Texture	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						Intrusive-Unprepared				
3	ND	ND	ND	ND	Sand Soil	3	ND	ND	ND	ND
6	ND	ND	ND	ND	Loam Soil	3	ND	ND	ND	ND
36	0.544	0.19	1.82	0.48	Clay Soil	37	0.779	0.14	1.14	0.69
In Situ-Prepared					Soil Texture	Intrusive-Prepared				
3	ND	ND	ND	ND	Sand Soil	3	ND	ND	ND	ND
4	ND	ND	ND	ND	Loam Soil	3	ND	ND	ND	ND
30	0.816	0.12	1.28	0.63	Clay Soil	39	0.794	0.16	1.44	0.62

Notes:

[a] Regression parameters based on $\log_{10}$ transformed data. These parameters were calculated for FPXRF data as the dependent variable, and thus, cannot be used to correct FPXRF data. See Section 6.

[b] Slope values determined by plotting FPXRF data on the x-axis and the reference data on the y-axis.

Y-Int. Y-Intercept.

Std. Err. Standard Error.

n Number of data points.

ND Not detected. Analyte not present in significant quantities to provide meaningful regression.

Table 5-9. Regression Parameters[a] by Sample Preparation Variable and Site Name—TN 9000 Analyzer

Arsenic						Barium				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Site Name	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
202	0.916	0.19	0.31	0.89	ASARCO Site	206	0.364	0.11	2.19	0.32
2	ND	ND	ND	ND	RV Hopkins Site	98	0.742	0.17	1.69	0.57
In Situ-Prepared						In Situ-Prepared				
204	0.982	0.09	0.08	0.97	ASARCO Site	207	0.477	0.11	2.10	0.38
4	ND	ND	ND	ND	RV Hopkins Site	98	0.855	0.11	1.81	0.52
Intrusive-Unprepared						Intrusive-Unprepared				
198	0.986	0.08	0.00	1.02	ASARCO Site	207	0.600	0.06	2.29	0.30
3	ND	ND	ND	ND	RV Hopkins Site	98	0.929	0.08	1.72	0.57
Intrusive-Prepared						Intrusive-Prepared				
201	0.980	0.10	0.11	1.00	ASARCO Site	206	0.583	0.05	2.35	0.27
3	ND	ND	ND	ND	RV Hopkins Site	99	0.938	0.09	1.56	0.63

Copper						Lead				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Site Name	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
203	0.912	0.21	0.19	0.97	ASARCO Site	200	0.885	0.20	0.38	0.88
44	0.494	0.18	1.21	0.61	RV Hopkins Site	96	0.776	0.28	0.74	0.81
In Situ-Prepared						In Situ-Prepared				
207	0.980	0.10	0.03	1.01	ASARCO Site	196	0.975	0.10	0.09	0.98
33	0.592	0.11	1.36	0.45	RV Hopkins Site	98	0.982	0.08	0.24	0.93
Intrusive-Unprepared						Intrusive-Unprepared				
208	0.984	0.09	0.04	1.02	ASARCO Site	200	0.980	0.09	0.05	1.02
24	0.394	0.15	0.82	0.75	RV Hopkins Site	98	0.989	0.07	0.21	0.95
Intrusive-Prepared						Intrusive-Prepared				
208	0.982	0.09	0.11	1.02	ASARCO Site	197	0.970	0.11	0.12	1.01
34	0.541	0.16	0.98	0.68	RV Hopkins Site	99	0.988	0.07	0.17	0.98

Zinc						Chromium (Low)				
n	r^2	Std. Err.	Y-Int.	Slope[b]	Site Name	n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared						In Situ-Unprepared				
186	0.860	0.16	0.51	0.83	ASARCO Site	47	ND	ND	ND	ND
93	0.867	0.20	0.43	0.95	RV Hopkins Site	56	0.688	0.17	1.81	0.43
In Situ-Prepared						In Situ-Prepared				
183	0.947	0.10	0.28	0.92	ASARCO Site	34	ND	ND	ND	ND
84	0.976	0.07	0.18	0.97	RV Hopkins Site	42	0.715	0.15	1.46	0.51
Intrusive-Unprepared						Intrusive-Unprepared				
181	0.939	0.12	0.13	1.00	ASARCO Site	6	ND	ND	ND	ND
86	0.979	0.08	0.06	1.03	RV Hopkins Site	40	0.793	0.12	1.32	0.58
Intrusive-Prepared						Intrusive-Prepared				
184	0.939	0.12	0.17	1.00	ASARCO Site	5	ND	ND	ND	ND
81	0.978	0.08	0.05	1.06	RV Hopkins Site	43	0.842	0.13	0.76	0.80

Table 5-9. ***Continued***

Chromium (High)										
n	r^2	Std. Err.	Y-Int.	Slope[b]		n	r^2	Std. Err.	Y-Int.	Slope[b]
In Situ-Unprepared					Site Name	Intrusive-Unprepared				
9	ND	ND	ND	ND	ASARCO Site	5	ND	ND	ND	ND
36	0.544	0.19	1.82	0.48	RV Hopkins Site	37	0.779	0.14	1.14	0.69
In Situ-Prepared					Site Name	Intrusive-Prepared				
7	ND	ND	ND	ND	ASARCO Site	6	ND	ND	ND	ND
30	0.816	0.12	1.28	0.63	RV Hopkins Site	39	0.794	0.16	1.44	0.62

Notes:

[a] Regression parameters based on $\log_{10}$ transformed data. These parameters were calculated for FPXRF data as the dependent variable, and thus, cannot be used to correct FPXRF data. See Section 6.

[b] Slope values determined by plotting FPXRF data on the x-axis and the reference data on the y-axis.

Y-Int. Y-Intercept.

Std. Err. Standard Error.

n Number of data points.

ND Not detected. Analyte not present in significant quantities to provide meaningful regression.

Table 5-10. Summary of Data Quality Level Parameters

Target Analytes	TN 9000 Analytes	Precision (mg/kg) Mean % RSD 5 - 10 X MDL	Method Detection Limits (mg/kg) (Precision-based)	Coefficient of Determination (r^2 All Data)	Data Quality Level
Arsenic	Arsenic	6.5	60	0.95	Definitive
Barium	Barium	4.0	60	0.79	Quantitative
Chromium	Chromium	22.2	200	0.78	Qualitative
Copper	Copper	7.0	85	0.95	Definitive
Lead	Lead	6.5	45	0.96	Definitive
Zinc	Zinc	7.3	80	0.93	Definitive
Nickel	Nickel	Not Determined	100	Not Determined	Insufficient Data
Iron	Iron	Not Determined	Not Determined	Not Determined	Insufficient Data
Cadmium	Cadmium	Not Determined	Not Determined	Not Determined	Insufficient Data
Antimony	Antimony	6.54	55	Not Determined	Insufficient Data

Section 6
Applications Assessment and Considerations

Both TN Spectrace analyzers are designed to produce quantitative data on the concentration of metals in soils, sludges, and other solids. The TN Spectrace "Soils Application" software used for calibration and quantitation maximizes instrument performance and accounts for common soil-related matrix interferences. The FP calibrations can be fine tuned with NIST soil SRMs to further improve data comparability. These analyzers are designed for field use and exhibited ruggedness under a variety of operating conditions. Neither analyzer experienced failures resulting in down time throughout the 1-month field demonstration. During this time, more than 1,260 samples were analyzed by each instrument. The short training video provided by the developer was sufficient to allow basic field operation of either analyzer. The developer offered a training class in the use of the analyzers. This training, coupled with on-line technical support, was sufficient to allow uninterrupted operation and no data loss throughout the demonstration.

Comparison of the $\log_{10}$ transformed TN Pb Analyzer and the $\log_{10}$ transformed reference data indicated that the analyzer can provide quantitative screening level quality data for certain metals. In addition, a comparison showed that the FPXRF and reference data are $\log_{10}$-$\log_{10}$ linearly related. This $\log_{10}$-$\log_{10}$ linear correlation appears to hold more than 5 orders of magnitude. The relationship between the analyzer data and the reference data would indicate that this analyzer could be used in most field analytical applications. Analyzer bias could be corrected to more closely match the reference data. In the case of copper, lead, zinc, and arsenic, the TN Pb Analyzer's $\log_{10}$ transformed data was statistically equivalent to the $\log_{10}$ transformed reference data. This analyzer also exhibited analyzer precision similar to the reference method, indicating a high degree of reproducibility.

The TN Pb Analyzer is generally operated with relatively short count times and has only one radioactive source. The single radioactive source limits the number of analytes which can be detected. The TN Pb Analyzer's "Soils Application" software can report concentrations for arsenic, chromium, iron, copper, zinc, and manganese in soil samples. The shorter count times and the single radioactive source combine to generally increase the sample throughput and detection limits but decrease the analyzer accuracy. In a 10-hour day during the demonstration, 200 - 300 samples were analyzed. A summary of this performance information is found in Table 6-1.

Analysis of the TN 9000 and reference data indicated that the TN 9000 produced definitive level quality data for arsenic, copper, lead, and zinc. This indicates that the $\log_{10}$ transformed TN 9000's data was statistically equivalent to the $\log_{10}$ transformed reference data for these analytes. The TN 9000 produced quantitative screening level for barium. As with the TN Pb Analyzer, if 10 - 20 percent of the samples analyzed by the TN 9000 were submitted for reference method analysis, bias in the TN 9000 data could be determined and the data could be corrected to more closely match reference data. In addition, this analyzer exhibited instrument precision similar to the reference method, indicating high instrument reproducibility.

Table 6-1. Summary of Test Results and Operational Features–TN Pb Analyzer

Weighs less than 20 pounds, battery lifetime of 8 hours
Sample throughput — 20 to 25 samples per hour
Can conduct in situ measurements or measure prepared samples in cups
Achieved data completeness of 100 percent during the demonstration
One day training for operation
Measured radiation levels below occupational limits
Drift less than ±10 percent for all but one of the analytes monitored
Produces EPA definitive level quality for zinc, arsenic, copper, and lead
Data is strongly linearly related to Methods 3050A/6010A data
FP calibrations that can be fine tuned with site-specific samples
Percent RSD values less than 10 percent at 5 to 10 times the MDL for all analytes except chromium
Matrix-specific FP calibrations in “Soils Applications” software
Can be used on soils exhibiting more than 30 percent water saturation by weight
Single excitation source

The TN 9000 can use up to three radioactive sources allowing analysis of a large number of metals in soils. The “Soils Application” software can report concentrations for potassium, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, selenium, rubidium, strontium, zirconium, molybdenum, mercury, lead, uranium, thorium, silver, cadmium, antimony, tin, and barium. The TN 9000 generally uses longer count times, which are proportional to the number of sources used in analysis. The longer count times and multiple sources generally increase accuracy and lower detection limits but decrease sample throughput. Eighty to 100 samples were analyzed in a 10-hour day during the demonstration. A summary of this performance information is found in Table 6-2.

For both analyzers, there was no apparent effect of site or soil type on performance. This demonstration identified sample preparation as the most important variable with regard to analyzer performance. The results from this demonstration indicated that when operated in the *in situ* mode, the data did not show a strong correlation between FPXRF and reference data. This may not be due to instrument error, but rather to inherent spacial variability of contamination, even within an area as small as the 4-inch by 4-inch grid sampled during this demonstration. The greatest increase in correlation between the FPXRF data and reference data for both analyzers was achieved after the initial sample homogenization. Further sample preparation, such as sieving or drying and grinding, did not greatly improve the comparability. However, this more involved sample preparation generally improved the quality of chromium data. This was indicative of the general problematic nature and influence of particle size of chromium determination by FPXRF.

Based on this demonstration, both of these analyzers are well suited for the rapid real-time assessment of metals contamination in soil samples. Although in several cases the analyzers produced data statistically equivalent to the reference data, confirmatory analysis is recommended for FPXRF analysis as is indicated in SW-846 Method 6200. If 10 - 20 percent of the samples analyzed by either analyzer are submitted for reference method analysis, instrument bias, relative to standard methods such as Methods 3050A/6010A, can be corrected. The effects of data correction for both analyzers are illustrated in Tables 6-3 and 6-4. These tables illustrate the effects of data correction on the *in situ*- prepared samples. Changes in average relative bias and accuracy are used to show the effects of data correction. This will only hold true if the analyzers and the laboratory analyze similar samples. This was accomplished in this demonstration by thorough sample homogenization. Bias correction allows analyzer data to be corrected so that it

approximates the Methods 3050A/6010A data. The demonstration showed that these analyzers exhibit a strong linear relationship with the reference method data more than a 5 orders of magnitude concentration range. For optimum correlation, samples with high, medium, and low concentration ranges from a project must be submitted for reference method analysis.

Table 6-2. Summary of Test Results and Operational Features—TN 9000 Analyzer

Weighs less than 20 pounds, battery lifetime of 4 to 5 hours
Sample throughput — 8 to 10 samples per hour
Can conduct in situ measurements or measure prepared samples in cups
Data completeness of 99.9 percent during the demonstration
One day training for operator
All measured radiation levels below occupational limits
Produces EPA quantitative screening level quality or better data for most analytes
• Arsenic, copper, lead, zinc — definitive level • Barium — quantitative screening level • Chromium — qualitative level data
Data is linearly related to Methods 3050A/6010A data
FP calibrations that can be fine tuned with site-specific samples
Precision — percent RSD values less than 10 percent at 5 to 10 times the MDL for all analytes except chromium
Accuracy of greater than 90 percent for all analytes in the site-specific PEs and soil SRMs
Three excitation sources allowing for analysis of more than 30 elements
Matrix-specific FP calibrations in “Soils Applications” software
Can be used on soils exhibiting more than 30 percent water saturation by weight

The steps for correcting the FPXRF measurements to more closely match the reference data are as follows:

1. Conduct sampling and FPXRF analysis.
2. Select 10 - 20 percent of the sampling locations for resampling. These resampling locations can be evenly distributed over the range of concentrations measured or they can focus on an action level concentration range.
3. Resample the selected locations. Thoroughly homogenize the samples and have each sample analyzed by FPXRF and a reference method.
4. Tabulate the resulting data with reference data in the x-axis column (independent variable) and the FPXRF data in the y-axis column (dependent variable). Transform this data to the equivalent $\log_{10}$ value for each concentration.
5. Conduct a linear regression analysis and determine the r^2, y-intercept, and slope of the relationship. The r^2 should be greater than 0.70 to proceed.
6. Place the regression parameters into Equation 6-1:

$$Y\ (\log_{10}\ corrected\ FPXRF\ data) = slope * (\log_{10}\ FPXRF\ data) + Y\text{-}intercept \qquad \textbf{(6-1)}$$

7. Use the above equation with the $\log_{10}$ transformed FPXRF results from Step 4 above and calculate the equivalent $\log_{10}$ corrected FPXRF data.

8. Take the anti-$\log_{10}$ (10 [$\log_{10}$ transformed corrected FPXRF data]) of the equivalent $\log_{10}$ corrected FPXRF data calculated in Step 7. These resulting values (in milligrams per kilogram) represent the corrected FPXRF data.

Table 6-3. Effects of Data Correction on FPXRF Comparability to Reference Data for All In Situ-Prepared Samples—TN Pb Analyzer

Target Analyte	Average Relative Bias on Raw Data[a]	Average Relative Bias on Corrected Data[b]	Average Relative Accuracy on Raw Data[c]	Average Relative Accuracy on Corrected Data[d]	Acceptable Relative Accuracy Based on PE Samples[e]
Arsenic	1.07	1.00	1.30	1.28	1.76
Chromium	8.78	1.63	18.58	2.29	1.55
Copper	1.52	1.07	2.29	1.63	1.18
Iron	1.47	1.02	1.55	1.19	1.54
Lead	1.17	1.05	1.48	1.34	1.63
Zinc	1.50	1.03	1.65	1.27	1.64

Notes:

[a] A measurement of average relative bias, measured as a factor by which the FPXRF, on average, over- or underestimates results relative to the reference methods. This measurement of bias is based on raw (not $\log_{10}$ transformed) data. This average relative bias does not account for any concentration effect on analyzer performance.

[b] A measurement of average relative bias on the FPXRF data after it has been corrected using the eight-step regression approach.

[c] A measurement of average relative accuracy at the 95 percent confidence interval, measured as a factor by which the raw FPXRF, on average, over- or underestimates individual results relative to the reference methods. This measurement of accuracy is based on raw (not $\log_{10}$ transformed) data. This average relative accuracy is independent of concentration effects.

[d] A measurement of average relative accuracy at the 95 percent confidence interval, of the corrected FPXRF data obtained using the eight-step regression approach.

[e] A measurement of accuracy represents a factor and 95 percent confidence interval that define the acceptable range of differences allowed between the reference method reported concentrations and the true value concentrations in the PE samples. This bias is included only as a general reference for assessing the improvement on comparability of FPXRF data and reference data after FPXRF data correction.

The average relative bias is calculated as follows:

$$\text{Average relative bias} = ((\sum_i [\text{FPXRF}_i/\text{Reference}_i])/\text{number of paired samples})-1$$

This value represents the percentage that the FPXRF over- or underestimates the reference data, on average, for the entire data set. To convert this calculated value to a factor, 1.0 is added to the calculated average relative bias. The above table presents the average relative bias as a factor.

The average relative accuracy is calculated as follows:

$$\text{Average relative accuracy} = \text{SQRT}\ (\sum_i ([\text{FPXRF}_i/\text{Reference}_i]-1)^2/\text{number of paired sample})$$

This value represents the percentage that an individual FPXRF measurement over- or underestimates the reference data. The relative accuracy numbers in the table are calculated at the 95 percent confidence interval. This is accomplished by adding two standard deviations to the above formula before the square root is taken. To convert this calculated value to a factor, 1.0 is added to the calculated average relative accuracy. The above table presents the average relative bias as a factor.

Table 6-4. Effects of Data Correction on FPXRF Comparability to Reference Data for All In Situ-Prepared Samples—TN 9000 Analyzer

Target Analyte	Average Relative Bias on Raw Data[a]	Average Relative Bias on Corrected Data[b]	Average Relative Accuracy on Raw Data[c]	Average Relative Accuracy on Corrected Data[d]	Average Relative Accuracy Based on PE Samples[e]
Antimony	6.14	1.10	6.78	1.47	2.94
Arsenic	1.00	1.02	1.21	1.21	1.76
Barium	7.25	1.11	8.13	1.49	1.36
Chromium Lo	6.52	1.79	10.22	3.11	1.36
Chromium Hi	3.63	1.30	6.31	2.10	1.55
Copper	1.23	1.05	1.46	1.33	1.18
Iron	1.42	1.02	1.49	1.18	1.54
Lead	1.09	1.02	1.26	1.22	1.63
Nickel	1.66	1.14	1.62	1.18	1.56
Zinc	1.29	1.02	1.40	1.23	1.64

Notes:

[a] A measurement of average relative bias, measured as a factor by which the FPXRF, on average, over- or underestimates results relative to the reference methods. This measurement of bias is based on raw (not $\log_{10}$ transformed) data. This average relative bias does not account for any concentration effect on analyzer performance.

[b] A measurement of average relative bias on the FPXRF data after it has been corrected using the eight-step regression approach.

[c] A measurement of average relative accuracy at the 95 percent confidence interval, measured as a factor by which the raw FPXRF, on average, over- or underestimates individual results relative to the reference methods. This measurement of accuracy is based on raw (not $\log_{10}$ transformed) data. This average relative accuracy is independent of concentration effects.

[d] A measurement of average relative accuracy at the 95 percent confidence interval, of the corrected FPXRF data obtained using the eight-step regression approach.

[e] A measurement of accuracy represents a factor and 95 percent confidence interval that define the acceptable range of differences allowed between the reference method reported concentrations and the true value concentrations in the PE samples. This bias is included only as a general reference for assessing the improvement on comparability of FPXRF data and reference data after FPXRF data correction.

The average relative bias is calculated as follows:

$$\text{Average relative bias} = ((\sum_i [\text{FPXRF}_i/\text{Reference}_i])/\text{number of paired samples})-1$$

This value represents the percentage that the FPXRF over- or underestimates the reference data, on average, for the entire data set. To convert this calculated value to a factor, 1.0 is added to the calculated average relative bias. The above table presents the average relative bias as a factor.

The average relative accuracy is calculated as follows:

$$\text{Average relative accuracy} = \text{SQRT}\ (\sum_i ([\text{FPXRF}_i/\text{Reference}_i]-1)^2/\text{number of paired sample})$$

This value represents the percentage that an individual FPXRF measurement over- or underestimates the reference data. The relative accuracy numbers in the table are calculated at the 95 percent confidence interval. This is accomplished by adding two standard deviations to the above formula before the square root is taken. To convert this calculated value to a factor, 1.0 is added to the calculated average relative accuracy. The above table presents the average relative bias as a factor.

To show the effect of correcting the FPXRF data, the change in average relative bias and accuracy can be examined. The average relative bias between the FPXRF data and the reference data is a measure of the degree to which the FPXRF over- or underestimates concentrations relative to the reference methods. The

relative bias is an average number for the entire data set and may not be representative of individual measurements. An example of this can be seen in an analyzer's data where measurements are underestimated at low concentrations, but overestimated at high concentrations. On average, the relative bias for this analyzer is zero; however, this bias is not representative for high or low concentration measurements. To avoid this dilemma, three approaches can be taken: (1) the evaluation of average relative bias can be focused on a narrow concentration range, (2) the analyzer's data can be corrected using the regression approach described above, or (3) the average relative accuracy can be calculated. Average relative accuracy represents the percentage that an individual measurement is over or underestimated relative to a reference measurement. Tables 6-3 and 6-4 show the average relative bias and accuracy exhibited by the Spectrace analyzers, before and after data correction using the eight-step approach previously discussed.

The average relative bias and accuracy for the analytes falling into the definitive level data quality category were generally small. However, the analytes falling into the quantitative and qualitative screening level data quality categories had generally larger average relative bias and accuracy.

Once the FPXRF data is corrected using the regression approach presented earlier, both the average relative bias and accuracy are greatly reduced. The average relative bias numbers are no longer strongly influenced by a concentration effect since the regression approach used to correct the data used $\log_{10}$ transformed data. The average relative bias and accuracy for the corrected data are similar to the acceptable average relative bias between the reference data and PE samples (true values), as shown by the last column in Tables 6-3 and 6-4.

Based on the findings of this demonstration, both of these analyzers can provide rapid assessment of the distribution of metals contamination at a hazardous waste site. This data can be used to characterize general site contamination, guide critical conventional sampling and analysis, and monitor removal actions. This demonstration suggested that in some applications and for some elements, the data may be statistically similar to the reference data. The approval of SW-846 Method 6200 "Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment" will speed the acceptance of this data for definitive level applications and most quantitative applications. The analyzer data can be produced and interpreted in the field on a daily or per sample basis. This real-time analysis allows the use of contingency-based sampling for any application and greatly increases the potential for meeting project objectives on a single mobilization. These analyzers are powerful tools for site characterization and remediation. They provide a fast and accurate means of analyzing metals contamination in soil.

General Operational Guidance

The following paragraphs describe general operating considerations for FPXRF analysis. This information is derived from SW-846 Method 6200 for FPXRF analysis.

General operation of FPXRF instruments will vary according to specific developer protocols. For all environmental applications, confirmatory or reference sampling should be conducted so that FPXRF data can be corrected. Before operating any FPXRF instrument, the developer's manual should be consulted. Most developers recommend that their instruments be allowed to warm up for 15 - 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems.

Each FPXRF instrument should be operated according to developer's recommendations. There are two modes in which FPXRF instruments can be operated: *in situ* and intrusive. The *in situ* mode involves analysis of an undisturbed soil or sediment sample. Intrusive analysis involves collecting and preparing a

soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

For *in situ* analysis, one requirement is that any large or nonrepresentative debris be removed from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Another requirement is that the soil surface be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. Most developers recommend that the soil be tamped down to increase soil density and compactness. This step reduces the influence of soil density variability on the results. During the demonstration, this modest amount of sample preparation was found to take less than 5 minutes per sample location. The last requirement is that the soil or sediment not be saturated with water. Developers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 - 20 percent, but will not perform well for saturated soils, especially if ponded water exists on the surface. Data from this demonstration did not see an effect on data quality from soil moisture content. Source count times for *in situ* analysis usually range from 30 to 120 seconds, but source count times will vary between instruments and depending on required detection limits.

For intrusive analysis of surface soil or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 grams or 250 cm^3, which is enough soil to fill an 8-ounce jar. The sample should be homogenized, and at a maximum, dried, and ground before analysis. The data from this demonstration indicated that sample preparation, beyond homogenization, does not greatly improve data quality. Sample homogenization can be conducted by kneading a soil sample in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the demonstration, the homogenization procedure using the fluorescein dye required 3 to 5 minutes per sample.

Once the soil or sediment sample has been homogenized, it can be dried. This can be accomplished with a toaster oven or convection oven. A small portion of the sample (20 - 50 grams) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hours in the convection or toaster oven at a temperature not greater than 150 °C. Microwave drying is not recommended. Field studies have shown that microwave drying can increase variability between the FPXRF data and reference data. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag will form in the sample.

The homogenized, dried sample material can also be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally averages 10 minutes per sample.

After a sample is prepared, a portion should be placed in a 31-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be completely filled and covered with a 2.5-micrometer Mylar™ (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived. All equipment, including the mortar, pestle, and sieves, must be thoroughly cleaned so that the method blanks are below the MDLs of the procedure.

Section 7
References

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