SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION PROGRAM

FINAL DEMONSTRATION PLAN FOR THE EVALUATION OF FIELD PORTABLE X-RAY FLUORESCENCE TECHNOLOGIES

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89193

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The purpose of this demonstration is to evaluate field portable x-ray fluorescence technologies in how well they identify and quantify concentrations of metals in soils at hazardous waste sites. The demonstration will take place under the Monitoring and Measurement Technologies Program of the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation Program.

This document is intended to ensure that all aspects of the demonstration are documented, scientifically sound, and that operational procedures are conducted within quality assurance and quality control specifications and health and safety regulations.

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

FINAL DEMONSTRATION PLAN

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APPROVAL SIGNATURES

The signatures of the developers below indicate that they have reviewed the experimental design of the demonstration plan and agree that the design will fairly represent and evaluate the performance of their technologies.

FINAL DEMONSTRATION PLAN

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John Moore Date
HNU Systems, Inc.

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DISCLAIMER NOTICE

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LIST OF ACRONYMS

AC Alternating Current
ACES Automated Contaminant Evaluation Software
Am^{241} Americium-241
ASTM American Society for Testing Materials
CCS Continuing Calibration Standard
Cd^{109} Cadmium-109
CFR Code of Federal Regulations
cm Centimeter
cm^3 Cubic Centimeters
cm/s Centimeter per Second
Co^{57} Cobalt 57
CRZ Contamination Reduction Zone
Cm^{244} Curium-244
DQO Data Quality Objective
eV Electron Volt
EMSL-LV Environmental Monitoring Systems Laboratory - Las Vegas
EPA Environmental Protection Agency
ERC Enviro-Recovery Consultants
Fe-55 Iron-55
FPXRF Field Portable X-ray Fluorescence
HASP Health and Safety Plan
HgI_2 Mercuric Iodide
HSD Health and Safety Director
ICS Interference Check Standard
ICV Initial Calibration Verification
IDW Investigation-Derived Waste
IOLM International Organization of Legal Metrology
ITER Innovative Technology Evaluation Report
keV Kiloelectron Volt
Kg Kilogram
LCD Liquid Crystal Display
LCS Laboratory Control Samples
MCA Multichannel Analyzer
mCi millicuries
MDL Method Detection Limit
MDNR Missouri Department of Natural Resources
g/L Microgram per Liter
m Micrometers
mg/cm^2 Milligram per Square Centimeter
mg/kg Milligram per Kilogram
mg/m^3 Milligram per Cubic Meter
mL Milliliter
mm Millimeter
MMTP Monitoring and Measurement Technologies Program
MRI Midwest Research Institute
NEMA National Electrical Manufacturers Association
NIOSH National Institute of Occupational Safety and Health
NIST National Institute of Standards and Technology
NPL National Priorities List
ODEQ Oklahoma Department of Environmental Quality
OSHA Occupational Safety and Health Administration
OSW Office of Solid Waste
%D Percent Difference
PAL Pacific Activities Limited

PARCC Precision, Accuracy, Completeness, and Comparability
PC Personal Computer
PE Performance Evaluation
PM Program Manager
PPE Personal Protective Equipment
ppm Parts per million
PRC PRC Environmental Management, Inc.
PSI Pounds Per Square Inch
QA Quality Assurance
QAPP Quality Assurance Project Plan
QC Quality Control
RCRA Resource Conservation and Recovery Act
RPD Relative Percent Difference
RSD Relative Standard Deviation
SHSO Site Health and Safety Officer
Si(Li) Silicon (Lithium)
SITE Superfund Innovative Technology Evaluation
SOP Standard Operating Procedure
SRM Standard Reference Materials
SSC Site-Specific Calibration
TER Technology Evaluation Report
TPM Technical Project Manager
VGA Video Graphics Array
XPCS X-MET Personal Computer System
XRF X-ray Fluorescence

EXECUTIVE SUMMARY

This demonstration was developed under the U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program. The purpose of this document is to provide the information needed to fairly and thoroughly evaluate how well field portable x-ray fluorescence (FPXRF) technologies identify and quantitate concentrations of metals in soils.

The developers involved in this demonstration are as follows: Enviro-Recovery Consultants, Inc.; HNU Systems, Inc.; Metorex, Inc.; Niton Corporation; Scitec Corporation; and TN Spectrace. The FPXRF technologies being demonstrated are either in situ or intrusive, or capable of both modes of operation. Together these developers are supplying nine different instruments for evaluation. The FPXRF in situ technologies analyze undisturbed soil samples. The FPXRF intrusive technologies analyze soils that have been removed from their natural matrix and, in some cases, have undergone sample preparation. Some of the developers manufacture both types of FPXRF technologies. After reviewing information on each technology, PRC Environmental Management, Inc. (PRC), and the EPA Environmental Monitoring Systems Laboratory (EMSL) determined that the FPXRF technologies manufactured by these developers were suitable for this demonstration.

These technologies were developed to provide rapid, real-time, relatively low cost analysis of the metals content of soil samples at hazardous waste sites. They are designed to quickly distinguish contaminated areas from noncontaminated areas to allow investigation and remediation decisions to be made more efficiently on site, and to reduce the number of samples that need to be submitted for costly confirmatory analyses.

The primary objectives of this demonstration are (1) to determine how well each technology performs in comparison to conventional analytical methods, (2) to identify the effects of sample matrix variations on the performance of each technology, (3) to determine the logistical and economic resources needed to operate each technology, and (4) to produce an SW-846 method for the use of intrusive and in situ FPXRF technologies. Secondary objectives for this demonstration are to evaluate FPXRF technologies for their (1) reliability, ruggedness, cost, and range of usefulness, (2) data quality, and (3) ease of operation. The performances of the FPXRF technologies will not be compared against each other. Instead, their performances will be compared to the performances of conventional analytical methods used in performing site characterization activities. The calibration and operational procedures for each technology will follow the developer's recommendations.

Two sites have been selected for this demonstration: the RV Hopkins site and the Asarco Tacoma Smelter site (Asarco). 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 the location of a former copper and lead smelter and is located in Tacoma, Washington. These sites represent different manufacturing processes that commonly generate heavy metals waste. The soils at the two sites range in texture from sand to silty clay.

After completing the demonstration, a technical evaluation report (TER) will be prepared. The TER will present objective results of the demonstration and provide supporting documentation. In addition, an innovative technology evaluation report (ITER) will be prepared and published that summarizes the findings presented in the TER. A separate ITER will be published for each developer. These reports will help data users and technology reviewers assess the performance of each technology for possible use on future site characterization or remediation projects at hazardous waste sites.

The November 1994 draft demonstration plan was made available to the demonstrates for review and comment. Comments received from the demonstration participants were addressed and are reflected in the final demonstration plan. Appendix A contains the comments from the demonstration participants and PRC's responses to those comments.

XRF Chapter 1

This chapter provides an overview of the Superfund Innovative Technology Evaluation (SITE) Program and introduces elements of the field portable x-ray fluorescence technologies (FPXRF) demonstration, such as the purpose of the demonstration, the technologies to be demonstrated, the developers of the technologies, and where and when the demonstration will take place.

1.1 SITE PROGRAM OVERVIEW

The SITE Program evolved in response to the Superfund Amendments and Reauthorization Act of 1986, which recognized the need for a program to explore alternative or innovative technologies for treating hazardous waste at Superfund sites. The two primary goals of the SITE Program are to develop and implement (1) treatment technologies for hazardous waste remediation, and (2) monitoring and measurement technologies for evaluating the nature and extent of hazardous waste contamination.

The SITE Program consists of four related programs: Demonstration, Emerging Technologies, Monitoring and Measurement Technologies, and Technology Transfer. This demonstration will be conducted under the supervision and guidance of the Monitoring and Measurement Technologies Program (MMTP). The goal of MMTP is to encourage the development, demonstration, and use of innovative monitoring, measurement, and characterization technologies at Superfund sites. The MMTP focuses on new technologies that can provide more cost effective, faster, and safer ways to assess the nature and extent of contamination than current technologies. The EPA Environmental Monitoring Systems Laboratory (EMSL) in Las Vegas, Nevada, implements the MMTP portion of the SITE Program. The EPA Office of Solid Waste (OSW) provides technical support and method validation for all SW-846 analytical methods.

1.1.1 Selecting Technologies

Technologies are selected by the U.S. Environmental Protection Agency (EPA) based on their potential use at Superfund sites, as well as EPA regional interest in a technology. Each technology is evaluated for its ability to meet one or more of the following criteria:

- Capable of being used in the field or in a mobile laboratory
- Applicable to a variety of Superfund sites
- High potential for resolving problems for which current methods are not satisfactory
- Costs are significantly less than current methods
- Performance is significantly better than current methods in areas such as data quality, sample preparation, or analysis time
- Uses techniques that are easier and safer to perform than current methods

1.1.2 Demonstrating Technologies

After a technology has been accepted into the SITE Program, a cooperative agreement between EPA and the developer is made. The purpose of the agreement is to specify responsibilities for conducting the demonstration and evaluating the technology. The following issues are settled at this time:

- Assessing the maturity of the technology
- Estimating the potential benefits and limitations of the technology
- Identifying demonstration sites that will provide the appropriate analytes in the desired environmental sample media or matrices (contaminants must be present in concentrations amenable to the technology being evaluated)
- Identifying and defining the roles of appropriate demonstration participants, observers, and reviewers
- Arranging analytical support for comparative testing (for example, confirmatory analysis)

- Supplying standard operating procedures (SOP), analysis methodologies, and other relevant protocols
- Preparing a demonstration plan that addresses the experimental design, sampling design, quality assurance/quality control (QA/QC), health and safety considerations, scheduling of field and laboratory operations, data analysis procedures, and data output format
- Determining logistical requirements and support (for example, field equipment, power and water sources, mobile laboratory, communications network)
- Anticipating possible corrective actions that may be required during the actual demonstration and providing this information to the demonstration participants

1.1.3 Evaluating Technologies

Innovative technologies are evaluated independently and, when possible, against conventional technologies. Data resulting from this demonstration will be used to evaluate the capabilities, limitations, and field applications of each technology. Following the demonstration, a detailed evaluation of the results will be presented in a technology evaluation report (TER) and in technology-specific innovative technology evaluation reports (ITER). These reports will be reviewed by EPA and technology developers for technical quality.

1.2 DEMONSTRATION PURPOSE

The purpose of this demonstration is to provide the information needed to fairly and thoroughly demonstrate and evaluate how well FPXRF in situ and intrusive technologies identify and quantify concentrations of metals in soils.

These two types of FPXRF technologies, in situ and intrusive, were developed to provide real time, relatively low cost analyses of metals contamination. They were designed to provide information that will allow investigation and remediation decisions to be made more efficiently on site, and provide information that will reduce the number of samples that need to be submitted for confirmatory analyses.

The primary objectives of this demonstration are (1) to determine how well each of the technologies perform in comparison to conventional analytical methods, (2) to identify the effects, if any, of sample matrix variations on each technology's performance, (3) to create an SW-846 method for the use of in situ and intrusive FPXRF technologies, and (4) to identify the logistical and economic resources needed to operate each technology.

Secondary objectives for this demonstration are to evaluate the FPXRF technologies for their (1) reliability, ruggedness, cost, and range of usefulness, (2) data quality, and (3) ease of operation. The performances of the FPXRF technologies will not be compared against each other. Their performances will be compared to the performances of conventional analytical methods used in performing site characterization activities. PRC also will examine the potential for loss of metals from soil samples by volatization during the drying of samples using a microwave. The conventional analytical methods will be referred to as confirmatory methods throughout this demonstration plan. The data they produce will be referred to as confirmatory data.

1.3 DEMONSTRATION TECHNOLOGIES AND DEVELOPERS

To determine which technologies to include in this demonstration, PRC and the SITE Program referred to the International Organization of Legal Metrology (IOLM) 1993 document "Portable and Transportable X-ray Fluorescence Spectrometers for Field Measurements of Hazardous Elemental Pollutants." IOLM defines an FPXRF in situ technology as being self contained, as capable of battery operation for at least 4 hours, and as weighing less than 23 pounds. IOLM defines FPXRF intrusive technologies as being self contained, as capable of battery operation for at least 4 hours, and as weighing between 23 and 68 pounds. In general, in situ technologies take measurements on the soil surface or below the ground surface, and intrusive technologies take measurements from samples removed from their natural setting.

A total of nine technologies will be demonstrated. Eight of these technologies have the dual capability of analyzing both in situ and intrusively; each capability will be demonstrated. Table 1-1 shows the nine technologies, their capabilities, and who developed them.

1.4 DEMONSTRATION PARTICIPANTS

Participants in this demonstration are listed in Table 1-2. Participants include contacts from EPA offices in Regions 3, 7, and 10, several PRC offices, the confirmatory laboratory, the developers, and the site contacts. The specific responsibilities of each demonstration participant are outlined in greater detail in Chapter 2.

1.5 DEMONSTRATION SITES

This demonstration will be conducted at two sites: the RV Hopkins site in Davenport, Iowa, and the Asarco Tacoma Smelter (Asarco) site in Tacoma, Washington.

These sites were chosen because they exhibit different climates, modes of waste deposition, soil textures, and because they are contaminated with a variety of heavy metals, including lead, chromium, cadmium, arsenic, copper, and zinc. These metals will be the primary target analytes for this demonstration because they are frequently detected at hazardous waste sites. Detailed descriptions of each site are provided in Chapter 5.

1.6 DEMONSTRATION SCHEDULE

Predemonstration sampling for this demonstration was conducted between December 5 and 14, 1994. PRC analyzed 100 samples during the predemonstration sampling activities. Thirty-nine samples collected during this activity were submitted to the confirmatory laboratory for analysis. These 39 samples included nine field duplicates and one performance evaluation (PE) sample. The 29 soil samples (excluding duplicates and the PE sample) were used by the developers to test and possibly recalibrate their technologies using the site-specific soils. PRC used this data to select specific sampling areas for the demonstration and to verify the magnitude and distribution of contaminants at each site. The field duplicate sample analyses by the confirmatory laboratory were conducted to evaluate the sample homogenization procedures planned for the demonstration. Specifics of the predemonstration sampling and other predemonstration activities are discussed further in Chapter 3.

Demonstration activities, including sampling and analysis, are scheduled to occur in April 1995. Details of the planned demonstration activities are provided in subsequent chapters.

TABLE 1-1

TECHNOLOGY CAPABILITIES

Technology	In Situ	Intrusive	Developer
ATX-100	Yes	Yes	Enviro-Recovery Consultants
SEFA-P Analyzer	No	Yes	HNU Systems, Inc.
SEFA-Px Analyzer	Yes	Yes	HNU Systems, Inc.
X-MET 920 (Si(Li) detector)	Yes	Yes	Metorex, Inc.
X-MET 920 (gas-filled proportional detector	Yes	Yes	Metorex, Inc.
XL Spectrum Analyzer	Yes	Yes	Niton Corporation
MAP Spectrum Analyzer	Yes	No	Scitec Corporation
TN Spectrace 9000	Yes	Yes	TN Spectrace
TN Spectrace Lead Analyzer	Yes	Yes	TN Spectrace

TABLE 1-2

DEMONSTRATION PARTICIPANTS

Agency/Company	Point of Contact
Asarco North 51st and Baltimore St. Tacoma, WA 98407	-- Tom Aldridge, Environmental Director (206) 756-0203 (phone) (206) 756-0250 (fax)
Enviro-Recovery Consultants, Inc. 150 South 600 East, Suite 5B Salt Lake City, UT 84102	-- Alan Seelos, President (801) 328-3659 (phone) (801) 328-3672 (fax)
EPA Environmental Monitoring Systems Laboratory 944 East Harmon Las Vegas, NV 89193	-- Steve Billets, Program Manager/Technical Project Manager (702) 798-2232 (phone) (702) 798-2261 (fax)
EPA Office of Solid Waste 401 M St. SW Washington, DC 20460	-- Oliver Fordham, Technical Advisor (202) 260-4778 (phone) (202) 260-0225 (fax)
EPA Region 7 Resource Conservation and Recovery Act (RCRA) Iowa Section 726 Minnesota Ave. Kansas City, KS 66101	-- Brian Mitchell, EPA Contact for RV Hopkins (913) 551-7633 (phone) (913) 551-7525 (fax)
EPA Region 10 Superfund Section 1200 Sixth Avenue	-- Piper Peterson, Project Manager (206) 553-4951 (phone)

Seattle, WA 98101	
HNU Systems, Inc. 160 Charlemont Street Newton Highlands, MA 02161-9987	-- John Moore, Director of Marketing (617) 964-6690, Ext. 106 (phone) (617) 558-0056 (fax)
Metorex, Inc. 1900 N.E. Division St., Suite 204 Bend, OR 97701	-- James R. Pasmore, Director of Sales and Marketing (800) 229-9209 (phone) (503) 385-6750 (fax)
Midwest Research Institute 425 Volker Blvd. Kansas City, Missouri 64110	-- Gary Wester, Staff Chemist (816) 753-7600 ext. 1713 (phone) (816) 753-5359 (fax)
Niton Corporation 74 Loomis Street, P.O. Box 368 Bedford, MA 01730-0368	-- Stephen Shefsky, Physicist (617) 275-9275 (phone) (617) 275-2397 (fax)
PRC 233 N. Michigan Avenue, Suite 1621 Chicago, IL 60601	-- Harry Ellis, Lead Statistician (312) 856-8700 (phone) (312) 938-0118 (fax) -- Rob Foster, SITE Program Manager (312) 856-8700 (phone) (312) 938-0118 (fax) -- Kurt Sorensen, Health and Safety Director (312) 856-8700 (phone) (312) 938-0118 (fax)
PRC 650 Minnesota Avenue Kansas City, KS 66101	-- Eric Hess, Project Manager (913) 573-1822 (phone) (913) 281-5383 (fax) -- Patrick Splichal, Lead Chemist (913) 573-1826 (phone) (913) 281-5383 (fax) -- Kathleen Homer, QC Manager (913) 573-1836 (phone) (913) 281-5383 (fax)
RV Hopkins 743 Schmidt Rd. Davenport, IA 52808	-- Harold Abdo, President (319) 323-5419 (phone)
Scitec Corporation 415 N. Quay Kennewick, WA 99336-7735	-- Bill Boyce, Vice President of Research & Development (800) 466-5323 (phone) (509) 735-9696 (fax)
TN Spectrace 2555 N. IH 35 P.O. Box 800 Round Rock, TX 78680-0800	-- Margo Myers, Product Manager (512) 388-9100 (phone) (512) 388-9200 (fax)

XRF Chapter 2

DEMONSTRATION RESPONSIBILITIES AND COMMUNICATION

This chapter identifies the participants involved in this demonstration and describes the primary roles of each participant. It also describes the methods and frequencies of communication that will be used in coordinating the demonstration.

2.1 DEMONSTRATION PARTICIPANTS AND ROLES

All demonstration participants are shown in Table 1-2. Roles for each participant are briefly discussed in the following paragraphs.

This demonstration is being conducted by PRC under contract to the EPA EMSL. EMSL's role is to administer the MMTP portion of the SITE Program. PRC's role is to provide technical and administrative leadership and support in conducting the demonstration. This support will include subcontracting analytical services for the demonstration. The EPA EMSL program manager and technical program manager for this demonstration is Mr. Steve Billets.

The EPA OSW will provide technical support on the experimental design of the demonstration and the guidance necessary to produce a demonstration that can result in the submittal and validation of an SW-846 method for in situ and intrusive FPXRF technologies. The EPA OSW technical advisor for this demonstration is Mr. Oliver Fordham.

The developers selected for this demonstration include: Enviro-Recovery Consultants, HNU Systems, Inc., Metorex, Inc., Niton Corporation, Scitec Corporation, and TN Spectrace. The developers will participate in the review and development of the demonstration plan, operator training, and other technical support as required.

Other participants in this demonstration include the EPA Region 7 Iowa Section, which has regulatory authority over the RV Hopkins site, and the EPA Region 10 Superfund Section, which has regulatory authority over the Asarco site. The EPA Region 7 point of contact for the RV Hopkins site is Mr. Brian Mitchell. The EPA Region 10 point of contact for the Asarco site is Ms. Piper Peterson.

2.2 SPECIFIC RESPONSIBILITIES

PRC, in consultation with the EPA EMSL program manager/technical project manager (TPM) and the OSW technical advisor is responsible for the following elements of this demonstration:

- Designing, preparing, overseeing, and implementing all elements of this demonstration plan
- Providing needed logistical support, establishing a communication network, and scheduling and coordinating the activities of all demonstration participants
- Ensuring that an appropriate site and appropriate analytes and matrices are selected for use in the demonstration
- Performing on-site sampling activities including collecting and homogenizing samples, dividing them into replicates, and bottling, labeling, and shipping them as necessary
- Providing monitoring, oversight, or operation of the technologies during the demonstration and documenting the experimental methodology and operation of each technology
- Developing a quality assurance project plan (QAPP) and a health and safety plan (HASP) for the demonstration activities
- Acquiring the necessary confirmatory analysis data
- Managing, evaluating, interpreting, and reporting on data generated by the demonstration

- Evaluating and reporting on the performance of the technologies
- Performing other tasks as assigned by the EPA EMSL program manager/TPM

Each developer is responsible for providing the following:

- Detailed protocols for using their respective technologies
- Complete, field-ready systems for demonstration
- Operation of the technologies during the demonstration or training on the operation of the technologies. Operation of the technologies will only be necessary if a developer's instrument is not marketed as equipment to be purchased and operated by private individuals or organizations
- Data reduction and interpretation support, as required
- Logistical, troubleshooting, and other support, as required

The site owners and the EPA contacts for each site will provide the following support:

- Site access
- Site characterization information on the site
- Health and safety information on the site
- Other logistical information and support needed for PRC to coordinate access to the site for the field portion of the demonstration

PRC has subcontracted the analytical support for confirmatory chemical analyses. The subcontract was issued to Midwest Research Institute (MRI) and it was solicited and issued under the requirements of the Federal Acquisition Regulations. PRC will oversee confirmatory analyses and provide independent QA/QC checks of the confirmatory laboratory.

2.3 COMMUNICATION

PRC will communicate regularly with all participants involved in the demonstration to coordinate activities and to resolve any logistical, technical, or QA issues that arise as the demonstration progresses. Communication will take place through the points of contact for each organization listed in Table 1-2 in Chapter 1. The organizational structure for the demonstration showing lines of communication is provided on Figure 2-1.

FIGURE 2-1 ORGANIZATIONAL CHART
(not available)

XRF Chapter 3

PREDEMONSTRATION ACTIVITIES

Several activities have been conducted by EPA EMSL, EPA OSW, PRC, and other demonstration participants prior to the demonstration. These activities included identifying developers, selecting demonstration sites, selecting a confirmatory laboratory and analytical methods, and performing predemonstration sampling and analysis. This chapter summarizes these activities.

3.1 IDENTIFYING DEVELOPERS

At EPA EMSL's request, PRC began a search for developers of FPXRF technologies capable of identifying and quantifying concentrations of heavy metals in soils. This search was conducted from September 1994 to November 1994. PRC contacted research and academic institutions and manufacturers of analytical and environmental equipment, followed leads from EPA EMSL and EPA regional offices, and reviewed available literature on FPXRF technologies.

PRC initially identified ASOMA Instruments; Enviro-Recovery Consultants, Inc. (ERC); HNU Systems, Inc.; Metorex, Inc.; Niton Corporation; Scitec Corporation; Oxford Instruments, Inc.; and TN Spectrace, as potential demonstration participants. After reviewing information on each of their technologies, EPA EMSL, EPA OSW, and PRC determined that they were suitable for this demonstration. The decision process used by EPA EMSL, EPA OSW, and PRC to accept these technologies for evaluation is briefly described in Chapter 1. Prior to the predemonstration activities, both ASOMA Instruments and Oxford Instruments, Inc., withdrew from the demonstration.

3.2 SELECTING SITES

PRC conducted a search for suitable sites between September 1994 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 mineralized metals deposits will not be assessed during this 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 used EPA EMSL, regional EPA offices, state environmental agencies, and metals fabrication and smelting contacts to create an initial list of potential demonstration sites. PRC received considerable assistance from 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 data base to search for appropriate sites. Table 3-1 contains a listing of the candidate sites that PRC identified.

Based on the site-selection criteria listed above and the assistance of the various state and federal agencies and others listed above, EPA EMSL, EPA OSW, and PRC selected the RV Hopkins and Asarco sites as the demonstration sites.

These sites are contaminated with a variety of heavy metals. The RV Hopkins site is contaminated primarily with chromium and lead. The Asarco site is contaminated primarily with lead, arsenic, and copper.

These sites also exhibit a variety of soil textures and methods of waste deposition, and they exist in vastly different climatological regions. The surface soil at the RV Hopkins site consists of silty and clayey loams. The surface soil at the Asarco site consists of sands, loams, and isolated areas of silt. The variety of heavy metal contaminants, climatological regions, modes of waste deposition, and soil matrices will allow a fair and thorough evaluation of how well each technology performs relative to conventional analytical methods. This diversity also meets the EPA OSW requirements for sample matrices for potential method validation.

3.3 CONFIRMATORY LABORATORY AND ANALYTICAL METHODS

To assess the performance of the FPXRF technologies, the data obtained using the technologies will be compared to data obtained using conventional analytical methods. PRC has subcontracted confirmatory laboratory services. This subcontracting has been carried out under the guidance of the Federal Acquisition Regulations. MRI has been awarded the subcontract for analytical services for this demonstration. MRI will abide by the requirements of the QAPP presented in Chapter 8.

All samples collected for confirmatory analysis will be analyzed for heavy metals using SW-846 Methods 3050A and 6010A. PRC anticipates that approximately 400 samples will be analyzed by these methods. This estimate includes field and laboratory QA/QC samples. Thirty percent of these samples also will be extracted using SW-846 Draft Method 3052 (*Microwave Assisted Acid Digestion of Ash and Other Siliceous Wastes - January 1995*) and analyzed by SW-846 Method 6010A. Confirmatory data will meet Level 3 (Definitive) data quality requirements as defined in Chapter 7.

In addition, a quantitative determination of soil moisture content will be achieved by using American Society for Testing and Materials (ASTM) Method D 2216-92 (*Test Method for Laboratory Determination of Water [Moisture] Content of Soil and Rock*) or a similar method. This determination will be made during the field sampling and analysis activities.

3.4 PREDEMONSTRATION SAMPLING AND ANALYSIS

In November 1994, PRC prepared a predemonstration sampling plan for this demonstration. This plan defined the sampling rationale to be used at the two demonstration sites. The predemonstration sampling at both sites was conducted between December 5 and 14, 1994. PRC analyzed 100 soil samples during the predemonstration sampling activities. All of the samples were initially analyzed on site with an FPXRF. Thirty-nine samples were submitted for confirmatory analysis during this activity. All 39 soil samples were submitted to MRI for confirmatory analysis by SW-846 Methods 3050A and 6010A. Ten percent of the samples were also analyzed by SW-846 draft Method 3052 and SW-846 Method 6010A.

These samples were collected from a wide range of concentrations and soil textures. PRC collected surface soil samples (0 to 1 inch) using hand trowels. Samples were homogenized using the procedure described in Chapter 7. Twenty-seven of these samples were split and sent to the developers. Nine field duplicates were collected and submitted for confirmatory analysis to assess PRC's sample homogenization procedures. One performance evaluation (PE) sample was submitted to the confirmatory laboratory to provide an initial check of accuracy. This predemonstration sampling had the following objectives:

- To provide or verify data on the extent of surface contamination at each site and to locate sampling areas for the demonstration

To allow the developers to analyze samples from the demonstration sites in advance, and, if necessary, refine and recalibrate their technologies and revise their operating instructions

To allow an evaluation of any unanticipated matrix effects or interferences that may occur during the demonstration

To check the QA/QC procedures of the confirmatory laboratory

TABLE 3-1

SURVEY OF POTENTIAL DEMONSTRATION SITES

Site Name and Location	Contact	Status and Comments
St. Charles Metal Finishing Company St. Charles, Missouri	Ruben McCullers-EPA Region 7 (913) 551-7455	Plating facility, already characterized, moist climate; lead, chromium, zinc, cadmium; access not granted
Asarco Lead Smelter El Paso, Texas	Traci Fambrou-EPA Region 6 (214) 665-2246	Lead, arsenic, some characterization, dry climate, middle of Consent Order negotiations; EPA does not want site used
Asarco Lead Smelter Tacoma, Washington	Piper Peterson-EPA Region 10 (206) 553-4951	National Priorities List (NPL) site, arsenic, lead, copper, already characterized, moist climate; access granted
RV Hopkins Site Davenport, Iowa	Brian Mitchell-EPA Region 7 (913) 551-7633	Active drum recycling facility, partially characterized, high lead and chromium contamination; access granted
Pacific Activities Limited (PAL) Site Davenport, Iowa	Jeff Weatherford-EPA Region 7 (913) 551-7695	Abandoned nickel-alloy pig manufacturer, partially characterized, high concentrations of all target analytes except arsenic; access denied
Smeltertown Salida, Colorado	Victor Ketellaper-EPA Region 8 (303) 294-7146	Mining and smelting site, some characterization, elevation above 7,000 feet, dry climate, lead, arsenic, zinc, copper, barium; access granted; likely snow covered for demo
East Helena Superfund Site Helena, Montana	Scott Brown-EPA Region 8 (406) 449-5720	Asarco smelter, lead, arsenic, cadmium, zinc, copper; EPA does not want demonstration at this site
Silver Bow Creek Butte, Montana	Neil Marsh-Montana Department of Health and Environment (406) 444-1420	Well characterized, mine tailings along a creek and river, ARCO facility, tailings generally saturated
Wicks Smelter Site Helena, Montana	Dave Donahue-PRC (406) 442-5588	Lead smelter, some characterization, lead, arsenic, zinc, and copper; Bureau of Mines site; likely snow covered for demo
West Dallas Lead Site Dallas, Texas	Stan Hitt-EPA Region 6 (214) 665-6735	Lead smelter, some characterization, primarily residential contamination, mostly remediated
Border Steel El Paso, Texas	Traci Fambrou-EPA Region 6 (214) 665-	Lead smelter, facility going bankrupt, only known contamination associated with an

	2246	on-site landfill; access denied
Kennecott Remediation Salt Lake City, Utah	Eva Hoffman-EPA Region 8 (303) 293-1534	Many subsites, old cobalt refinery, already characterized, lead, arsenic, cadmium, copper, cobalt, cold and dry climate; access granted; likely snow covered during demo
Tri-state Mining Jasper County, Missouri	Mark Doolan-EPA Region 7 (913) 551-7169	Some characterization, lead, moist environment; access granted; too limited contaminant constituents
Tucson International Airport Tucson, Arizona	Dennis Gott-U.S. Air Force (513) 255-0258	Former plating operation, chrome waste in unlined pond, wastes have been capped, dry environment
Oracle Ridge Mining Partners Arizona	Susan Johnson-EPA Region 9 (415) 744-2361	Only copper and zinc contamination; site has been remediated
Portland Cement Utah	No contact	Some characterization, too low metals concentrations
Apache Powder Arizona	Andrea Benner-EPA Region 9 (415) 744-2361	Well characterized, too low metals concentrations; access could be a problem
Phelps-Dodge Reduction Works Bisby, Arizona	Caroline Douglas-EPA Region 9 (415) 744-2343	NPL site; site has been remediated
ILCO Lead Smelter Alabama	Kim Lanterman-EPA Region 4	Lead and arsenic, NPL site, wet climate; access denied
Sherwin Williams Coffeyville, Kansas	Mark Matthews-EPA Region 7 (913) 551-7635	Lead, zinc, barium, residential contamination, moist environment, limited area of gross contamination
Cleveland Mill Silver City, New Mexico	Kathleen Aisling-EPA Region 6 (214) 665-8500	EPA does not want a demonstration at this site
Reeves Southeastern Corporation Tampa, Florida	Anita Davis-EPA Region 4 (404) 347-5054	Electroplating operation, contamination in lagoons that have not been drained
Yakima Plating Yakima, Washington	Joe Mollusky-PRC (206) 624-2692	Site has been remediated
Goldere Junkyard Morristown, New Jersey	Dennis Santella-EPA Region 2 (212) 264-8677	Site does not have target analytes in high enough concentrations for this demonstration
NAVBASE Charleston Charleston, North Carolina	Todd Haverkast-EnSafe (803) 747-7937	Site includes a former abrasives blasting area; contamination in this area is too low for the demonstration
Tar Creek Site Oklahoma	Nowell Bennet-EPA Region 6 (214) 665-8514	This mining area is contaminated with lead and zinc; access is granted; not sufficient constituent variety
Eagle Picher Smelter Joplin, Missouri	Mark Doolan-EPA Region 7 (913) 551-7169	This is part of the Tri-state mining site, the contaminants are lead and zinc; access is granted; not sufficient constituent variety
Peerless Plating	Mike Johnson-PRC	Well characterized, sandy soil, lead,

Muskegon, Minnesota	(312) 856-8700	chromium, zinc; access is possible; snow covered during demo
Asarco Lead Smelter Glover, Missouri	Kathy Flippin-MDNR (314) 751-3176	High lead, copper, and zinc concentrations, some characterization, moist site; access MDNR was not interested in demo
Eagle Picher Smelter Henryetta, Oklahoma	Dennis Datin-ODEQ (405) 271-7097	Arsenic, lead, cadmium, and zinc contamination, some characterization, moist site; access is possible; site now owned by City of Henryetta; ODEQ was not interested in demo
National Zinc Bartlesville, Oklahoma	Scott Thompson-ODEQ (405) 271-7213	Zinc, lead, and cadmium contamination, wet site, remediation in progress, probably finished by Spring 1995
Harbor Island Tacoma, Washington	Keith Rose-EPA Region 10 (206) 553-7721	Privately-owned, lead, arsenic, cadmium, chromium contamination, 400 acres, record of decision (ROD) completed; access may be problematic, wet site, remedial action end of next year
Bunkerville Mining District Southeastern Nevada	Paul Lechler-Nevada Bureau of Mines-Geology (702) 784-6691	Copper, chromium, nickel, no soil data only data for ores and rocks, dry site
Boss Mine Clark County, Nevada	Paul Lechler-Nevada Bureau of Mines-Geology (702) 784-6691	Copper, lead, zinc, gold, silver, platinum, only data for ores and rocks, no soil data, dry site
Weldon Springs, Missouri	Cecilia Tapia-EPA Region 7 (913) 551-7733	Limited constituent variety; only lead present; wet site
Mare Island Naval Shipyard-IR04 Vallejo, California	Curt Enos-PRC (913) 573-1827	Primarily chromium contamination, some copper, lead, nickel, and zinc, contamination in "green sands," well characterized, wet site; access possible; too low of contaminant concentrations for demo
Hanover Whitewater Mine New Mexico	Bert Gorrod-EPA Region 6 (214) 665-6779	No response to request for information
Helvetia Mining District Arizona	Rick Trapp-Arizona Bureau of Geology (602) 882-4795	Lead, zinc, copper, possibly cadmium, smelter on site, arid site, south of Tucson, no analytical data; access may be a problem
Phelps Dodge Smelter Ajo, Arizona	Rick Trapp-Arizona Bureau of Geology (602) 882-4795	Copper mine, arid location, no analytical data; little known about site
Smelter Site Cortland Gleason, Arizona	Rick Trapp-Arizona Bureau of Geology (602) 882-4795	Lead and zinc smelter, good access, arid site, no analytical data; little known about site
Combined Metals Twilla, Utah	No contact	No information
Midvail Superfund Site Suburb of Salt Lake	No contact	No information

City, Utah		
Indian Reservation Santa Clara, New Mexico	Barb Everett-PRC (505) 246-9192	Metals concentrations too low; access may be a problem
General Electric Facility Albuquerque, New Mexico	Vince Malloy-EPA Region 6 (214) 665-8313	Lead contamination, soil sampling during excavation, no information received on this site
Flagstaff Smelter South of Salt Lake City, Utah	Joel Hebdon-SAIC (801) 539-0500	State lead, Superfund site, less than 20 acres, lead, arsenic, copper, zinc; dry, likely snow covered during demo
Big River Desloge-St. Francois Co. Missouri	Paul Doherty-EPA Region 7 (913) 551-7924	Mine tailings, lead and zinc contamination, NPL site; tailings stay wet, too limited constituent variety

XRF Chapter 4

TECHNOLOGY DESCRIPTIONS

This chapter describes the FPXRF technologies manufactured by each developer. The descriptions are based on the information provided by the developers and on information PRC obtained from reports and journal articles written about the FPXRF technologies. The descriptions include background information and a description of the equipment. General operating procedures, training and maintenance requirements, and the cost of each technology also are discussed. References to XRF technologies below refer to both field portable technologies and laboratory-grade technologies.

FPXRF technologies operate on the concept of energy dispersive x-ray fluorescence spectrometry. Energy dispersive x-ray fluorescence spectrometry is a nondestructive qualitative and quantitative analytical technique used to determine the metals composition of samples. The field portable XRF technologies described in this chapter use sealed radioisotope sources to irradiate samples with x-rays. Laboratory-grade XRF technologies use an x-ray tube to irradiate the samples with x-rays. Both the field portable and laboratory-grade technologies produce x-rays of known energies. By exposing a sample to an x-ray excitation source having energy close to, but greater than, the binding energy of the inner shell electrons of the metals, an inner shell electron is discharged. The electron vacancies that result are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, therefore, to fill the vacancies, the outer shell electrons give off energy as they cascade down into the inner shell vacancies. There are three electron shells generally involved in the emission of x-rays during the FPXRF analysis of environmental samples: K, M, and L shell electrons. The emission of x-rays is termed x-ray fluorescence. Each metal gives off x-rays of different energy levels. The specific type or energy of the emitted x-ray is unique to a given metal and is called a "characteristic" x-ray. By measuring the different energies of x-rays emitted by a sample exposed to an x-ray source, it is possible to identify and sometimes quantify the metals composition of a sample. A qualitative analysis of the samples can be made by observing the characteristic x-rays produced by the sample. The quantity or intensity of each energy of x-rays emitted is proportional to the concentration of the target analytes.

The x-ray fluorescence from excited metals span a range of measurable energies. This energy is measured in kiloelectron volts (keV). A typical emission pattern, also called an emission spectrum, from a given metal will have multiple intensity peaks generated from the emission of K, L, or M shell electrons. Most metals contaminants have characteristic K and L electron shell emissions, however, only metals with an atomic number greater than 57 have measurable M emissions. These characteristic electron shell emissions generally consist of at least two unique intensity peaks, identified as alpha and beta. These peaks are commonly described as lines and each metal produces a unique fluorescence energy at each of these lines. For example, lead has the following characteristic lines that can be detected in an emission spectra for lead: L-alpha (10.549 keV), L-beta (12.611 keV), K-alpha (74.957 keV), K-beta (84.922 keV), M-alpha (2.346 keV), and M-beta (2.443 keV).

The energy of each intensity peak is characteristic of the excited metal. The magnitude of the intensity peaks is related to the concentration of the metal. The magnitude of these peaks is measured in "counts," and this unit of measure relates to the number of x-rays emitted per unit of time. For most metals, the K and L emissions are used for identification and quantification.

Along with the K, L, and M electron shell emissions, the x-ray excitation source emits characteristic x-rays of a set energy level. This emission energy can be measured along with the K, L, and M shell emissions during XRF analysis. The emission peak of the excitation source is called the Compton Peak. By selecting an excitation source with a Compton Peak energy close to either the K, L, or M shell emissions of a target metal, the detection sensitivity of the XRF analysis is increased. XRF technologies with x-ray tube sources can tune their excitation emissions to optimize the relationship between the source's characteristic energy (Compton Peak energy) and the characteristic fluorescence energy of the metals. Radioisotope sources, on the other hand, only emit x-rays at one characteristic energy. Because of this, different radioisotope sources may be needed to provide adequate detection sensitivity for a wide range of target analytes. For example, using an Iron-55 (Fe^{55}) radioisotope source would be appropriate for titanium analysis, however, the Compton Peak from this source is too close to chromium to allow accurate or precise quantitation. When the Compton Peak is too close to the characteristic emission energies for a target analyte, it interferes with the resolution of the target analyte's emission peaks. For chromium analysis, a cadmium-109 (Cd^{109}) radioisotope would be more appropriate. The Cd^{109} Compton Peak energy is far enough away from the characteristic energies of chromium, but close enough to allow good resolution and relatively low detection limits.

Another way to increase the sensitivity and precision of an XRF technology is to increase a samples exposure time to an excitation source. This is commonly referred to as increasing count times. The measurement of the x-ray emissions occurs concurrently with the excitation of a sample. By increasing a sample's exposure time, more time is available for measuring the emission counts from the sample. This generally increases the data gathered for a sample, and allows the averaging out of natural variation in emissions, therefore, increasing precision and accuracy.

XRF technologies consist of a source for sample excitation, a detector, a sample chamber, and an emission or fluorescence energy analyzer, such as a multichannel analyzer (MCA). The excitation source types are either x-ray tubes coupled with primary radiation filters or sealed radioisotope sources. The x-ray tube is an evacuated glass envelope comprised of a filament with adjustable current control, a pure metal anode, which is typically rhodium, tungsten, or silver, and a beryllium window through which the x-rays radiate toward the sample. Common radioisotope sources used in source-excited XRF analysis are Fe^{55}, Cobalt-57 (Co^{57}), Cd^{109}, Americium-241 (Am^{241}), and Curium-244 (Cm^{244}). The relative strength of the radioisotope sources is measured in units of millicuries (mCi). The stronger the source, the greater its sensitivity and precision. XRF radioisotope sources undergo constant decay. In fact, it is the process of decay that emits the characteristic x-rays used to excite samples for XRF analysis. The decay of radioisotopes is measured in "half lives." The half-life of a radioisotope is defined as the length of time required to reduce its strength or activity by 50 percent. Developers of XRF technologies recommend source replacement at regular intervals, based on a source's half life. Table 4-1 provides a summary of the characteristics of the radioisotope sources.

The detectors in the XRF technologies can either be solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include lithium drifted silicon Si(Li) or mercuric iodide (HgI_2). The HgI_2 detector can be operated at room temperature. The Si(Li) detector must be cooled to at least -90 C for operation. This can be done with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Proportional counters are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter is not as good as that of a solid-state detector.

The MCA is used to collect and manipulate the data. The MCA receives pulses from the detector and separates every pulse by energy level. The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. Most XRF technologies are menu-driven from software built into the detector or from a personal computer (PC).

XRF technologies can be calibrated using the following methods: internally using fundamental parameters determined by the developer, empirically based on calibration standards, or based on Compton Peak ratios. XRF technologies can generally be calibrated by multiple methods. Technology-specific calibration is described in the following subsections.

Table 4-2 summarizes general operational characteristics for the technologies involved in this demonstration.

4.1 TN SPECTRACE 9000

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of the TN Spectrace 9000.

4.1.1 Background Information

TN Technologies introduced field portable XRF technology in 1966. In 1988, it released the first field portable XRF technologies for mining, chemical plant, and refinery applications. Since then, TN Technologies and Spectrace Instruments together (as TN Spectrace) have been producing field portable and laboratory-grade XRF technologies for a broad range of applications. The TN Spectrace 9000 was released in 1992 for environmental applications.

The HgI_2 detector, also referred to as a spectrometer, uses an HgI_2 semi-conductor x-ray detector that achieves a manganese K-alpha x-ray resolution of 270 electron volts (eV) while operating near ambient temperature.

The TN Spectrace 9000 uses energy dispersive x-ray fluorescence spectrometry to determine elemental composition of soils, sludges, aqueous solutions, oils, and other waste materials. It uses three radioactive isotopes, Fe^{55}, Cd^{109}, and Am^{241} to produce x-rays, which excite a corresponding range of metals in a sample (Table 4-1). The TN Spectrace 9000 can identify and quantify the target metals sulfur through uranium in a sample. When more than one source can excite metals, the appropriate source is selected according to its excitation efficiency for the target metals.

The sample is positioned in front of the source-detector beryllium window and sample measurement is initiated. This exposes the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the source-detector beryllium window and are counted in a high resolution HgI_2 detector. The surface probe of the HgI_2 detector provides for both in situ soil analysis and intrusive soil analysis with the probe in the upright position and the safety shield attached.

Contaminant concentrations are computed using a fundamental parameter backscatter algorithm. The TN Spectrace uses fundamental parameters to calibrate its FPXRF technology. The fundamental parameters are based on the physics of the excitation and emission of x-rays. The menu-driven software in the TN Spectrace 9000 supports multiple XRF calibrations called "applications." Each application is a complete analysis configuration including target metals to be measured, interfering target metals in the sample, and a set of fundamental parameter calibration coefficients. The fundamental parameters method does not require site-specific calibration samples.

4.1.2 Equipment and Accessories

The TN Spectrace 9000 comes with all of the equipment necessary for in situ and intrusive operation. A hard-shell carrying case is provided for transportation and storage.

Two main components make up the analytical system: a probe and an electronics unit. The main components are discussed in the following paragraphs. A list of all primary and secondary components follow the discussion.

The probe contains three radioisotope sources: Fe^{55} (50 mCi), Cd^{109} (5 mCi), and Am^{241} (5 mCi) for sample excitation. 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 a sealed 1-inch-diameter polypropylene window (probe 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 detector quantitates the energy of each X-ray and builds a spectrum of element peaks on a 2048-channel MCA.

Spectral data is communicated to the electronics unit through a flexible cable of 6, 12, or 20 feet in length. Metal peaks are integrated and parts per million 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 downloading to a PC via a RS-232 cable.

The TN Spectrace 9000 is supplied with four factory-installed fundamental parameter-based applications. The "Soils" application is for analysis of soils in which most of the sample is silica. The TN Spectrace 9000 is programmed for three other applications, "Fine-Mesh Soils," "Thin Film," and "Lead in Paint," which will not be evaluated in this demonstration. TN Spectrace also will develop calibrations to meet new user application requirements, such as adding target analytes to the present "Soil Samples" application.

The TN Spectrace 9000 can be powered from a 115-volt or 220-volt wall outlet or from its 4-hour capacity battery. It can be operated in temperatures ranging from 0 to 49 C. Furthermore, the probe and electronic unit can be exposed to light rain. However, additional protection is provided when the system is contained in the optional water repellant carrying case.

The probe and electronics unit are completely sealed with rubber gaskets and can be decontaminated with soap and water.

Equipment/Optional Accessories/Instrument Specifications

Equipment

The standard TN Spectrace 9000 system includes:

Electronics unit for data acquisition, processing, storage, and display

-- Nickel and cadmium battery pack (4 to 5 hours of continuous use)

Hand-held probe including:

-- HgI_2 detector
-- Three excitation sources (Fe^{55}, Cd^{109}, Am^{241})
-- Safety Cover

Uniblock for table top use (the uniblock is a probe labstand that conveniently allows the operator to analyze samples in cups and thin films, and to perform the check procedure for the Lead in Paint application.)

-- Sample shield
-- Positioning ring for standard 31-millimeter (mm) x-ray sample cups

Interconnecting probe cable (6-foot cable is standard)
Pure element check samples kit
Two blank samples for background setup and check out
Battery charger
RS-232 serial input/output interface cable
System carrying/shipping case
Operators manual, factory applications, and results management software
Training video (22 minutes)
Ten 31-mm-diameter sample cups

1 roll 6.0 micrometers (m) Mylar XRF film (300 feet)
Spare window assembly

Optional Accessories

Field pack with shoulder straps ($245)
Spare battery pack, charger, and adapter ($750)
Battery eliminator for continuous use ($600)
"Applications Generator" software program
National Institute of Standards and Technology (NIST) Soil Standard Kit (NIST No. 2579)
Micromatter Lead Thin Film Standards Kit (for lead in paint measurements)
Dust wipe kit

Instrument Specifications

Probe Dimensions and Weight: 12.7 centimeters (cm) x 7.6 cm x 21.6 cm; 1.9 kilograms (kg)

Cable: standard 6-foot length, optional 12 or 20-foot lengths

Electronics Unit Dimensions and Weight: 32 cm x 30 cm x 10 cm; 6.7 kg

Power: operates from a nickel cadmium battery for 4 to 5 hours of continuous use. Also can use 110 or 220 volt, 50 to 60 Hertz Alternating Current (AC) electricity.

Operating Temperature: 0 to 49 C (32 to 120 F)

Storage Temperature: -40 to 40 C (-40 to 104 F)

4.1.3 General Operating Procedures

To operate the TN Spectrace 9000, the nickel cadmium battery is plugged in, and the probe cable is connected. The detector is turned on by pressing the "On" button. A message on the screen will ask the operator for the date and time and then proceed to the MAIN MENU. It is important to set the date correctly, otherwise errors in source-decay compensation can result.

The TN Spectrace 9000 software is menu driven. From the MAIN MENU, the operator selects a predefined "Application," which is a complete analysis setup that defines the elements of interest, the radioisotope sources to be used, and the matrix type that is being analyzed (soil, water, oil, sludge, metal, and so on). The TN Spectrace 9000 comes with the following four applications installed:

1. Soils Application (analyzes 25 elements in soil with each measurement)
2. Fine-Mesh Soils (for finely ground and cupped soils, 100 mesh or smaller)
3. Thin Samples (25 elements on air filters, wipes, platings, or coatings)
4. Lead in Paint (makes in situ measurements of lead in paint, substrate independent)

A PC-based software program called the "Applications Generator" allows the operator to develop additional XRF applications for use in the electronics unit.

Once the application is selected, each analysis is completely automated by the TN Spectrace 9000 software. To begin measuring samples, the operator selects MEASURE to get to the "Ready Screen." From here the operator initiates an analysis by pressing either the probe trigger or the "Continue" button on the electronics unit. Distinct sounds signal the beginning and end of a measurement to alert the operator to take the next measurement. Results with standard deviations are displayed at the end of each measurement. If desired, results and spectra can be automatically stored on the electronics unit after each measurement. Transferring the results and spectra to a PC allows printing, archiving, spreadsheet, and report generation.

The TN Spectrace 9000 should be allowed to warm up for 30 minutes before performing analysis. This time allows for detector cool down and instrument stabilization. Automatic gain compensation is a feature of the "Soil Samples" application, which allows operation of the technology over a wide range of ambient temperatures and from one day to another without standardization. If the automatic gain control fails or is out of range, an error message will appear on the screen. If the error message continues to appear after repeat analyses, then the Cd^{109} measurement time should be checked or an energy calibration should be performed.

The "Set Store/Send Modes" option is located in the "more" screen, which can be accessed from the main menu. Data or spectrum storage must be enabled for automatic on-board storing to occur. Sufficient memory is available to store up to 300 sets of analytical results and up to 120 spectra. This is adequate for 40 sample analyses since each sample is exposed to all three radiation sources, which results in three spectra for each sample. When the available memory is full, the respective spectra or results storage mode is automatically disabled. The spectra or results memory must be cleared and the respective store mode enabled before results of spectra can be stored again.

The main menu selection displays the application name, revision date, exposure time for each source, and accesses other options. Routine operation for soil sample analysis proceeds with the selection of "Soils Analysis" from the main menu, which leads to a set up of the sample source exposure times per source and initialization of the probe controls for measurement. Source exposure times can vary. Source exposure times for soil samples typically vary from 60 to 300 seconds. Generally, the metals detection limit is reduced by 50 percent for every four-fold increase in source exposure time. This does not consider metal interferences and matrix interferences. Although counting statistics improve as measurement time increases, the practical limit for typical applications is 600 to 800 seconds.

The exposure time of a source is concluded with an audible signal followed by an on-screen report of the analyzed metals. Results are labeled by metal symbol and include both element concentrations and an indication of the computed standard deviations. The TN Spectrace 9000 can analyze soil samples for 26 elements with the sequential use of all three excitation sources.

After analysis of a sample is complete, it is possible to retrieve and review stored results and spectra. The stored results and spectra may be reviewed, deleted, or downloaded to a PC. Selecting the "Measure" option will immediately begin another analysis cycle.

There are several pre-operational check samples that should be analyzed prior to sample analysis. The samples include an energy calibration check, a resolution check, a blank sample check, and a target metals response check. An energy calibration should be performed after a technology is shipped and periodically during storage (approximately every 2 weeks) to ensure proper energy calibration. The energy calibration check is performed in the field daily and after an energy calibration to verify proper energy calibration.

The resolution check examines the detector's ability to resolve x-ray energies. This should be performed once at the beginning of the day. This is done by measuring a sample of iron using a minimum acquisition time of 60 seconds for the Cd^{109} source.

The blank sample check is performed to monitor the technology's zero drift in the selected application. This monitors baseline response of the technology, which affects quantitation and detection. The blank sample check should be conducted at the beginning of each day, after an energy calibration, after loading an application, and whenever the technology exhibits a persistent drift on a blank or low-level sample. The blank sample check consists of the analysis of a quartz or

Teflon blank provided with the technology using a minimum source exposure time of 60 seconds for each source.

The purpose of the target metals response check is to ensure that the technology and the selected application are working properly prior to performing sample analysis. This check should be performed at the beginning of each day. The check samples are generally standards or PE samples, such as standard reference materials (SRM), both with known concentrations for some or all of the target metals to be checked. The samples should be measured using the same source exposure times that will be used for sample analysis.

No site-specific standards are needed with the TN Spectrace 9000. The technology is calibrated at the factory using pure elements and calculates results of a soil sample using a matrix correcting Fundamental Parameters algorithm. Two types of matrix effects are inherent with x-ray fluorescence spectrometry: absorption and enhancement matrix effects. The absorption affects lower XRF data, while the enhancement affects increase the XRF data relative to true value concentrations. The Fundamental Parameters algorithm makes the appropriate matrix corrections for analysis of 25 elements in soil.

If desired, the TN Spectrace 9000 software can provide for a site-specific calibration to model a given suite of standards.

For data QA, TN Spectrace recommends that a certified reference sample be run periodically. This will provide valuable accuracy and precision data. Running a certified reference sample can also alert the operator that either the probe window is contaminated or the technology is not operating properly. The probe window can be cleaned with a towel and the condition of the detector can be checked using the Standard Operational Check, which requires running a pure iron sample and the pure Teflon sample to verify sensitivity and background, respectively.

4.1.4 Training and Maintenance

The TN Spectrace 9000 comes with a 22-minute training video which discusses the theory of XRF, operation, and general care of the technology. In cases where personalized training is requested, TN Spectrace offers a 2-day, in-house training course. A 2-day on-site training course is another option at $1,000 per day plus travel expenses.

TN Spectrace must be notified immediately of any conditions or concerns relative to the probe's structural integrity, source shielding, source switching operation, or operability. The appropriate state agency or the Nuclear Regulatory Commission must be notified immediately of any damage to the radioactive source, or any loss or theft of the device. The sources in the probe must be leak-tested every 6 months as described in the TN Spectrace 9000 Operating Instructions. The leak certificates must be kept on file, and a copy must accompany the technology at all times. If the probe window becomes damaged or punctured, it should be replaced as soon as possible to prevent dust and moisture from entering the probe. Replacement window assemblies can be ordered from TN Spectrace. General service contracts are available from TN Spectrace with the purchase of a TN Spectrace 9000.

The TN Spectrace 9000 can be cleaned with soap and water and is designed to be used in the field where conditions may be wet, dirty and rugged. Given proper care, the technology should only require the scheduled periodic maintenance of source replacement.

Due to the inherent safety design features and associated low levels of radiation and small quantities of radioactive materials, the technology is supplied under a general license for radioisotope regulatory purposes, which greatly simplifies its transportation and use.

4.1.5 Testing Time and Cost

The standard deviation for each measurement is reported with the data output. This information allows the operator to optimize the source exposure times for the task at hand, balancing the standard deviation (error) with the analysis time to meet project data quality objectives (DQO), as well as project schedules. When analyzing soils that are in areas of high contaminant concentrations at a site, the developer recommends short source exposure times of 1 or 2 minutes. As the concentration nears the action levels, the developer suggests a longer count time should be employed to increase the precision (decrease the standard deviation of a measurement) at the action level. The developer suggests that typical source exposure times for these conditions is 3 to 7 minutes. Since the measurement is automated by the TN Spectrace 9000 software, the operator can prepare the next sample or sampling area while the technology is running the previous one. An operator should be able to analyze at least 50 samples per day.

The TN Spectrace 9000 costs $55,000 to purchase. This includes all of the equipment necessary for operation of the technology. Purchased technologies are warranted for a full year with an optional extended warranty. The TN Spectrace 9000 can be rented through several rental companies for approximately $6,000 per month. Weekly rates are also available. Periodic maintenance includes replacement of the Cd^{109} source every 2 to 3 years at a cost of $3,500 to $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 so it does not need replacing.

4.2 X-MET 920

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of the X-MET 920. This technology has two detector configurations, a Si(Li) detector and a gas-filled proportional detector. Both detectors will provide different levels of data quality and for the purpose of this demonstration they will be evaluated separately.

4.2.1 Background Information

Metorex is an international supplier of advanced equipment for metal detection, materials testing, and chemical analysis. It offers a wide range of products from field portable and laboratory-grade metals and alloy analyzers to on-line systems. It has more than 20 years experience in developing x-ray detection technologies. Metorex developed the X-MET 920 to perform elemental analysis in the petroleum and petrochemical industry, the mining and minerals industry, and the environmental field. The X-MET 920 is a light-weight portable technology that can be operated in situ or intrusively. It is offered with a gas-filled proportional detector or a Si(Li) detector. The Si(Li) detector is considered the high resolution detector.

The X-MET 920 was designed as a modular system so that users can configure the technology with the precise hardware and software for their analytical needs.

4.2.2 Equipment and Accessories

The basic configuration of the X-MET 920 includes: a disk operating system-based PC, software, X-MET PC System (XPCS), and an analysis probe. The XPCS card contains a 2,048-channel MCA that is used to collect, analyze, and display the spectrum. The MCA portion of the technology is contained on a single electronic board that is plugged into one of two expansion slots of the PC.

The high resolution probe is a hand-held, compact unit that contains a Si(Li) detector. The detector achieves a manganese K-alpha x-ray resolution of 170 eV. The detector is cooled by a 0.5-liter liquid nitrogen dewar built into the probe, which allows for 8 to 12 hours of field use. A dewar is similar to a Thermos except that it is used to store super cooled liquids. It can be used as a surface probe to perform in situ analyses, or with the attachment of a sample cover, the probe can analyze soil samples intrusively from a sample cup. The probe dewar can be filled with liquid nitrogen before each measurement session or can stay connected to the "mother" dewar (30-liter capacity) and removed only for a few measurements. The "mother" dewar lasts, under normal conditions, for up to 30 days.

The other probe is also a hand-held, compact unit, but it contains a gas-filled proportional detector. The detector achieves a manganese K-alpha x-ray resolution of 750 eV. The detector operates at ambient temperatures (-13 to 140 degrees Fahrenheit, requiring no artificial cooling. It can be used as a surface probe to perform in situ analyses, or with the attachment of a sample cover, the probe can analyze soil samples intrusively from a sample cup.

Either detector will accommodate simultaneously two radioisotope sources to cover the elemental range from potassium to uranium. The developer offers the following radioisotopes: Fe^{55}, Cd^{109}, and Am^{241}. These isotopes are in the form of an 8-mm-diameter by 5-mm-thick capsule. The suggested dual source configurations are Fe^{55} and Cd^{109}, or Cd^{109} and Am^{241}. The detector is environmentally sealed by a 25-mm-diameter window of Kapton® film. The sources are driven into the measurement position with nitrogen gas, which is evolved from the liquid nitrogen to create a pressure in the dewar of 10 pounds per square inch (psi). The detector is equipped with interlock mechanisms to prevent operator exposure to the radioactive sources or instrument exposure to high voltage.

Instrument Specifications

Computer: Disk operating system-based PC with the minimum configuration:

-- Central Processing Unit 80386 DX 33 megahertz with math co-processor

-- 2 megabytes random access memory

-- 80-megabyte hard disk

-- Video graphics array (VGA) graphics

-- XPCS (One unit for each probe)

Physical Dimensions:

-- Size: 38 cm x 35 cm x 7.5 cm

-- Weight: 5.5 kg with standard battery pack

-- Environmental Protection: National Electrical Manufacturers Association (NEMA) No. 4 enclosure rating

Si(Li) Detector Physical Dimensions:

-- Size: 20 cm x 10 cm x 25 cm

-- Weight: 3.7 kg without liquid nitrogen; 4.1 kg with liquid nitrogen

Gas-Filled Proportional Detector Physical Dimensions:

-- Size: 20 cm x 10 cm x 25 cm

-- Weight: 3.7 kg

4.2.3 General Operating Procedures

The operating procedures for the two detector options are similar except for the liquid nitrogen requirements for the Si(Li) detector. The liquid nitrogen dewar in the Si(Li) detector first has to be filled. It takes approximately 15 minutes for the detector to achieve a stable operating temperature. This step is not required for the gas-filled proportional detector.

Once the technology is turned on, all the software is menu driven. The technology can be calibrated either empirically using external soil standards, or internally using instrument backscatter and fundamental parameters related to instrument backscatter. The latter of the two is a standardless calibration that uses theoretical equations to describe the functional relationship between metals concentrations and x-ray intensities. The technology uses regression analysis to establish a calibration curve for empirical calibrations. The calibration curve can contain up to six linear and nonlinear terms. Metorex points out that empirical calibration with a proper set of samples will always yield better results than the fundamental parameters-based calibrations because of particle size effects and errors in predicting the composition of the sample matrix rather than directly measuring it.

Once the technology is calibrated, the sample is placed in contact with the detector window. The measurement is initiated by pressing the start button located in the detector handle. The measurement is terminated automatically after the preset count time has expired. The detector automatically exposes either one or two excitation sources sequentially, according to its programmable calibration scheme. The operator can interrupt the measurement cycle at any time by pressing the reset button in the detector handle.

When the analysis is completed, the results are automatically displayed on the computer screen along with the standard deviation associated with each measurement result. Analysis can be based on either a single measurement or the average of multiple measurements. The X-MET 920 also can display net and raw count intensities for all measurements. The operator can store all analysis output to the hard disk by opening the log file. The x-ray emission spectrum from unknown samples also can be displayed. The horizontal axis of the spectrum is calibrated in keV and the vertical axis is the intensity of the peak measured in counts. A peak has to fall within a specific keV range to be identified as a specific element. This range is predetermined by the developer or based on real time calibration.

The primary limitation of the gas-filled proportional detector is its resolution. This detector may produce anomalous data for compounds or matrices that are affected when L-lines overlap K-lines. This can affect metals such as cobalt, nickel, and copper in the presence of rare earth elements such as erbium, thulium, ytterbium, lutecium, hafnium, and tantalium. In addition, this type of detector will only allow empirical calibration.

4.2.4 Training and Maintenance

Metorex offers a 3-day training course for X-MET 920 operators at its facility or on site. The training course covers theory, operation, calibration, and routine maintenance.

All X-MET 920 technologies are warranted against defects in materials and workmanship for a period of 1 year. Repair or replacement will be made without charge during the warranty period. The X-MET 920 is marketed as fairly maintenance free. There is an "Instrument Maintenance Options" menu in the software used in conjunction with the technology. It allows the operator to check the gain initialization, perform a gain test, perform a test measurement, test initial resolution, perform a probe and internal XPCS test, check probe parameters, and set the date, time, and colors on the computer screen. The primary hardware maintenance is replacement of the 20 mCi Cd^{109} source approximately every 1.5 to 2 years. This replacement schedule is recommended by the developer.

Since the detector contains a nuclear radiation source, it must not be opened except by authorized personnel. If the detector becomes damaged, it should be stored in a secure area and a Metorex representative should be contacted. The detector should not be stored in moist conditions because moisture can corrode the beryllium window in the detector. The X-MET 920 is sold with a general license for its radioactive sources meaning that it can be transported from state to state and used by another operator without requirements to receive a specific license.

4.2.5 Testing Time and Cost

The developer states that it is possible to analyze one soil sample in 1 to 5 minutes with the X-MET 920 equipped with the Si(Li) detector. This time includes the time required for any sample preparation, such as homogenization, drying, or grinding that may be needed. The developer states that these sample preparation tasks can be conducted by the operator while analyses are being conducted. With the daily QC procedures that are conducted, the developer states that it is possible to analyze 50 soil samples in an 8- to 10-hour working day. The developer claims that sample throughput for the use of the gas-filled proportional detector can reach 200 to 400 samples in an 8- to 10-hour working day. This is based on 10 to 100 second count times and minimal sample preparation.

The X-MET 920, equipped with a Si(Li) detector and two radioisotope sources sells for $47,470, which includes a portable computer. The computer is battery operated and contained in an industrial grade, rugged, sealed, splash-proof case. The system also includes "Automated Contaminant Evaluation" software (ACES) with the computer. The two sources in the X-MET 920 are a 20 mCi Cd^{109} and 30 mCi Am^{241} source. This price includes 3 days of training for two people at the Metorex facility. Travel and accommodation costs are not included.

The X-MET 920 can be rented from Metorex. There is a 1 month minimum rental. The cost is 15 percent of the purchase price per month, plus all shipping costs payable monthly in advance. Metorex mandates that the renters be trained on the X-Met 920. Renters have a choice of training options. The first is a 3-day training class offered at Metorex's facility at $685 per person plus travel and lodging expenses. On-site training classes also are available. Metorex must be contacted for details on the on-site training classes.

Spare batteries are available for $425 and spare battery chargers are available for $340. The developer recommends replacement of the Cd^{109} source every 1.5 to 2 years. This costs $4,500 with a $500 disposal fee for the old source.

4.3 MAP SPECTRUM ANALYZER

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of the MAP Spectrum Analyzer.

4.3.1 Background Information

The MAP Spectrum Analyzer was originally developed by Scitec to detect lead in paint. It is a lightweight, portable technology that collects in situ readings. Scitec is now marketing the MAP Spectrum Analyzer as detecting lead in soil, as well as other metals in soil.

4.3.2 Equipment and Accessories

The primary components of the MAP Spectrum Analyzer are the control console and the ambient scanner. The control console is connected to the ambient scanner with a 10-foot cable. The basic MAP system also includes a carry pack, rechargeable batteries, operator's manual, target metal standard, and a shipping case.

The control console is a 256-channel, miniature, rugged, MCA. It has a storage capacity of 1 megabyte of information or 325 spectra and analyses. It is constructed of high-impact plastic. It has a liquid crystal display (LCD) that can provide readouts of operation menus, measurement values, calibration menus, count rate, time clock, analysis identification number, number of the analyses stored in each identification area, and a graphic spectrum display. The keyboard is weatherproof and has a 14-key keypad.

<u>Control Console Specifications</u>

Size: 19.3 cm long x 20 cm wide x 7.6 cm high
Weight: 7 pounds with battery pack
Environmental: Splash proof at 100 percent humidity, operates at any angle
Operating Temperature: -6 C to 43 C
Connectors: Breech-lok connects to battery charger or sensor
Power Supply: 2 Gel-Cell type, 12-volt direct current rechargeable batteries. Each set is capable of 10 hours continuous use without recharging. Each Gel-Cell has an approximate useful life of 12 to 18 months or 150 recharges. Weighs 1.2 kg. The power supply operates at any orientation at a temperature range of -6 Centigrade (C) or higher.

The ambient scanner is an in situ detector that allows for the source to be placed in direct contact with the sample. It is shaped liked a pistol and contains the excitation source and the detector. It is capable of holding only one source.

<u>Ambient Scanner Specifications</u>

Size: 33.7 cm
Weight: 1.6 kg
Environmental: Splash proof at 100 percent humidity
Operating Temperature: -6 C to 43 C
Electronics: Solid state amplifier; custom high gain, low noise
Detector: Solid state silicon; resolution 170 keV; size 5 mm x 5 mm; active area 25 mm^2
Source Shutter: Heavy tungsten and designed to house:

(1) Co^{57} - 40 millicuries
(2) Am^{241} - 150 millicuries
(3) Cd^{109} - 80 millicuries
Safety: Removable on-off key for source shutter
Connector: Breech-lok
Grip: Rubber-cushioned pistol type
Construction: 6061 aluminum
Front Face Plate: Aluminum 0.5-mm thick
Beryllium Window: 0.5-mm thick

4.3.3 General Operating Procedures

Analysis with the MAP Spectrum Analyzer consists of placing the ambient scanner in direct contact with the sampling medium and opening a shutter with a key. The opening of the shutter exposes the sample to the radioisotope source. Emission x-rays are counted (measured) over an operator-specified period of time (source exposure time) by a counting circuit. This data is recorded by an MCA to produce a spectrum characteristic of the metals in the sample. Net intensities for each target metal are calculated by software deconvolution of the characteristic spectra and converted to concentration values by means of a calibration model. This model is derived empirically by measuring the net intensities of the target metals in a set of calibration standards, and fitting a linear function that relates net intensity to concentration by a multiple regression procedure.

The MAP Spectrum Analyzer measures an area of about 20 mm in diameter. Only the near surface (approximately 2 mm) depth is measured in samples by L-shell x-ray fluorescence, while K-shell emissions for many metals may emerge from greater depths.

Calibration of the Map Spectrum Analyzer is performed by the developer. Calibration involves measurement of known analyte concentrations (reference standards) and incorporation of data from resultant spectra into a mathematical function. This function, which is a component or proprietary software, is used to calculate concentrations of the target metals in measured field samples. The use of a wide range of matrix conditions and target metal concentrations for calibration is the method which allows accurate readings on most samples.

Two types of calibrations are performed by the developer: site-typical calibrations and site-specific calibrations. A site-typical calibration curve is based on samples similar in composition, but not necessarily matrix matched. Scitec cautions that a site-typical calibration curve should only be used in preliminary screening and characterization. Scitec states that to minimize enhancement or absorption and spectral interference errors, calibration standards should be collected from the specific site in question. The site-specific calibration (SSC) standards should closely match the matrix of the routine samples. The SSC standards are prepared as loose soils (screened through 2-mm sieve, but unpulverized) so that particle size bias of the routine samples is included in the instrument calibration. Scitec recommends that characterization of the SSC standards be done using a total digestion procedure rather than a partial extraction because x-ray fluorescence is most closely related to a total extraction or digestion type analysis.

The in situ analysis with the MAP Spectrum Analyzer does not require that a physical sample be removed from the ground. The probe is placed on the ground and the analysis mode is activated by turning on a key. Acquisition time can be preset at any desired length: "Screen," "Test," or "Confirm," are the most common. The measurement times for the three options are 15 seconds, 60 seconds, and 240 seconds, respectively. Scitec points out that the precision of the analysis will improve as the measurement time increases.

Scitec recommends that all routine samples be analyzed in triplicate and the means are the reported values. The three in situ measurements should be made in a 6- by 6- by 6-inch triangular pattern around the sample location marker. Scitec recommends that when few sample locations are to be measured, "Confirm" measurements will optimize the data precision. Large-scale, high-density sampling conducted in the "Test" mode will result in briefer measurements, but greater sampling density which may maintain optimum overall precision. Scitec recommends that one confirmatory sample be selected from each group of 25 to 40 routine samples.

QC procedures for the MAP Spectrum Analyzer include a blank check and a calibration check sample. The blank check is an instrumental blank that is a 0 milligrams per kilogram (mg/kg) sample. It is analyzed to determine if there is contamination or a malfunction of the technology. Each technology is provided with a calibration check sample. It is used to assess the accuracy of the technology. The calibration check standard should be measured by attaching the standard to the face of the excitation and detector unit with a rubber band and making measurements "air backed" (with the unit separated from the nearest surface by at least 2 feet). A calibration check should be performed every day prior to sample analysis and once each hour during the day. All values should be averaged and compared to the developer-provided value. Average values that are inconsistent with the true value should be reported to Scitec.

4.3.4 Training and Maintenance

A license or permit to possess, or operate a technology that uses ionizing radiation produced from the radioactive decay of a source is required to possess or operate the MAP Spectrum Analyzer. Each state is responsible for issuing such licenses. An operator must be trained by Scitec in the principles of radiation and in the safe operation of the MAP Spectrum Analyzer to secure a license.

Scitec provides approved training on a regular basis. The training is a 6-hour, audio-visual program that is available at Scitec's factory or at a customer's facilities.

The operator of the technology should prevent it from being exposed to dirt or dust. Any dirt or dust on the technology should be wiped off with a damp cloth or brushed off. If the rubber boot at the front of the ambient scanner becomes contaminated, it may need to be replaced. Scitec offers an annual service agreement that allows for the return of the MAP Spectrum Analyzer any time, for an unlimited number of times, for cleaning and servicing. Each 1-year contract includes one Co^{57} source replacement, hardware and software enhancements, minor repair and service work, extra parts, and a loaner system while the technology is having its source replaced.

4.3.5 Testing Time and Cost

As mentioned in Section 4.3.3, analysis times are on the order of 15 to 240 seconds. It is recommended that each sample be analyzed in triplicate. Since this is an in situ technology, there is little sample preparation required with the exception of removing any vegetation or debris from the soil surface to be measured. It is possible to analyze 50 to 100 samples in one 8- to 10-hour working day.

The standard Scitec MAP Spectrum Analyzer package sells for $15,590. The standard package includes the control console, the ambient scanner, a 40-millicuries Co^{57} isotope source, auto source decay time correction, carry pack, rechargeable batteries, spectrum display software, 256-kilobyte memory, battery charger, operator's manual, shipping case, a 10-foot cable, and a lead-check standard.

Scitec also provides other options and accessories with the technology. A lead in soil calibration costs $1,390. Upgraded memory to 768 kilobytes can be purchased for $1,175. AcuTransfer® Software, which is a data communications software utilities package that allows data to be downloaded and manipulated from the console directly to a PC, costs $495. A special shipping container with a lead shield and NIST standard reference materials can be purchased for $475 and $260, respectively.

A replacement of the Co^{57} source costs $3,695. An annual service agreement with the source replacement costs $3,895. A basic radiation safety and operator training course is offered by Scitec for $245 per person.

4.4 SEFA-P ANALYZER

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of SEFA-P Analyzer.

4.4.1 Background Information

HNU developed the SEFA-P Analyzer to be an intrusive, portable technology that could determine metals concentrations in soils and other media at hazardous waste sites or at industrial locations. The SEFA-P Analyzer has been on the market for approximately 4 years.

4.4.2 Equipment and Accessories

The basic SEFA-P Analyzer consists of one main cabinet that encloses the sample chamber, the radioactive sources, a liquid nitrogen cooled Si(Li) detector, preamplifier, spectrometer electronics, MCA, and a battery charger. It is approximately 21 inches long, 12 inches wide, 16 inches tall, and weighs less than 50 pounds. The SEFA-P Analyzer operates at relative humidities between 20 and 95 percent. The ambient temperature limits of operation are between 0 and 42 C.

A mechanical interlock on the door to the sample chamber protects the operator from being accidentally exposed to radiation from any of the internal radiation sources. Access to the sample chamber involves rotating the source knob to the safety position. This allows the operator to slide the chamber door open. Each installed source is identified by a label on the source knob. The knob cannot be turned to any of the source selections while the chamber is open. When the chamber is closed, the knob can be rotated to expose the contents of the chamber to the selected radiation source.

Three excitation sources are offered with the SEFA-P Analyzer. They are Fe^{55}, Cd^{109}, and Am^{241}. The maximum activity for each of the sources is 50 millicuries, 10 millicuries, and 25 millicuries, respectively.

The SEFA-P Analyzer contains a Si(Li) detector. The detector has a manganese K-alpha line resolution of 170 eV. It is 10 mm in diameter and has an active area of 45 mm^2. The Si(Li) detector is cooled with liquid nitrogen. The internal liquid nitrogen dewar has a capacity of 0.85 liters and can last up to 24 hours.

A preamplifier in the technology collects the electronic signal from the detector, amplifies it, and sends it to the MCA. The MCA sorts the signals coming from the preamplifier by energy level and counts the number of x-rays that strike the detector. This data can be displayed on a cathode ray tube, printed, or stored on a computer disk. The internal battery can power the MCA for 8 hours. The battery charger is equipped for either 110 or 220 volt alternating current, and has a two-position setting for either battery charging or continuous operation. It is recommended that the internal battery be fully charged before operation.

The MCA has an RS232C interface that allows for external control of the SEFA-P Analyzer via a PC or laptop computer. HNU has SEFA-P software that allows the detector to be operated from a PC. All data can be downloaded and stored on the PC. The resulting spectra from the analysis of samples can be viewed on the PC screen and can be printed to obtain a hard copy. Quantitative results also are displayed on the PC screen.

Other supplies needed to operate the SEFA-P Analyzer include 30-mm-diameter polyethylene sample cups, Mylar window film to cover the cups, and a 22-liter external liquid nitrogen dewar. If sample preparation techniques are employed, the analysis also may require sieves, a mortar and pestle to grind the soil samples, plastic weigh boats, and a drying oven (either standard convection oven, toaster oven, or microwave oven). Lastly, SEFA-P Analyzer operation will require calibration standards either commercially available from such sources as NIST or site-specific calibration samples.

4.4.3 General Operating Procedures

Prior to analysis of samples, the internal liquid nitrogen dewar should be recharged from the external liquid nitrogen dewar. The SEFA-P Analyzer will not allow the operator to analyze samples until the Si(Li) detector is cool. This may require 20 to 30 minutes of cool down time after the initial charge with liquid nitrogen.

Once the SEFA-P Analyzer has been turned on, the battery voltage should be checked. If the battery voltage is low, "low battery voltage" will be indicated on the LCD of the MCA. If the battery voltage is acceptable, the amplifier gain and detector voltage can be set. The value of the amplifier gain influences the energy calibration of the MCA. The optimal gain setting is usually 1105, but should be verified periodically by analyzing a copper foil check standard. The range for the detector voltage is commonly 500 to 1,000 or more volts. Optimum operating conditions generally occur at 501 volts.

This unit can be operated from the cathode ray tube and key pad built into the unit. When operated in this mode, a mini-cassette tape is used to record numerical and spectral data. The data from approximately 10 samples can be saved on one mini-cassette tape. A PC can also be used to operate the unit. HNU markets SEFA-PC, a menu-driven software that can be used to operate the analyzer. The major SEFA-PC menus include: Acquire, Setup, Qualitative, Quantitative, and Utilities. Within the Setup menu, the acquisition setup selects which sources will be used for a selected job and which qualitative and quantitative programs will be automatically executed after data is acquired from the Acquire menu. The Report item within the Setup menu allows the operator the modify the report format, as well as create a hard copy and disk file of the report.

The Acquire menu allows the operator to enter the sample name and set the source exposure time for each sample. Up to four samples with acquisition times for up to three sources can be entered. This routine sets up the SEFA-P Analyzer, acquires and stores spectral data, prompts the user to select the appropriate sample and source, and automatically runs the programs which were selected in Acquire menu. Quantitative analysis times (source exposure times) of 300 to 500 seconds are typical for soil analysis. The operator must make sure that the proper source and sample are in the correct position in the sample chamber prior to analysis. The F2 function key is pressed on the PC to initiate the analysis. At the end of each sample analysis, the computer will beep to alert the operator that the analysis is complete. The operator can then turn the four-position sample chamber to the next sample to begin another analysis.

The Qualitative menu allows the operator to reexamine previously acquired data. This includes viewing complete sample spectra and magnifying selected portions of the spectra. This menu will provide the gross and net fluorescence intensities of each element, and concentrations based on calibration curves determined prior to sample analysis.

Prior to sample analysis, the SEFA-P Analyzer must be calibrated. Two types of calibrations can be used with this technology: empirical or Compton ratio calibration. In the case of empirical calibration, the SEFA-P Analyzer is calibrated with a minimum of three external standards. These external standards contain known concentrations of the target metals. Generally, the concentration range of the standards is 100 to 1,000 mg/kg. The other method of calibrating the SEFA-P Analyzer is the Compton ratio method. This method involves a one standard calibration. In this case, the unit is calibrated to one standard instead of generating a calibration curve for each target metal. The Compton peak is the peak created by x-ray emissions from the radioisotope source used to excite the sample. The Compton peak is present in the spectrum of every sample. The Compton peak intensity will change with differing matrices. It is possible for the internal software of the x-ray program to compute a Compton ratio by comparing the Compton peak intensity determined from the analysis of the single standard to the intensity of the Compton peak measured during the analysis of a sample. Calibration by the Compton peak can help reduce potential matrix effects between samples.

The Quantitative menu allows the operator to enter the target metals' ranges of characteristic x-ray emissions, select the correction method to be used for the empirical calibration, enter the multi- and single-standard calibration information, and calibrate the technology on both the empirical and Compton ratio, and run the analysis. The ranges of characteristic ranges of x-ray emissions is used to identify target metals and to determine gross and net metal emission peak areas for concentration quantitation.

The Utilities menu allows the operator to delete samples, display the file directory, format a disc, send a report file to a printer, display system information, display the disc space, backup or restore a job and create a new job.

QC procedures include daily source emission energy checks and calibration, with a copper foil check sample; continuing calibrations; method blanks; laboratory duplicates; and laboratory control samples (LCS). The LCSs are often SRMs produced by NIST.

4.4.4 Training and Maintenance

The SEFA-P Analyzer is sold with a general license, meaning that the operator does not have to be specifically licensed in each state that it is used in. The SEFA-P Analyzer is engineered to minimize the possibility of operator exposure to ionizing radiation. The specimen chamber cover is interlocked mechanically to prevent exposing the radiation sources. The radioisotope sources should be leak-tested every 6 months. It is necessary to replace the Cd^{109} source about every 2 years. HNU will provide a 2-day training course on XRF principles and operation of the SEFA-P Analyzer in-house or at a customer's facility.

4.4.5 Testing Time and Cost

The average time of analysis for a sample is 3 to 7 minutes. This does not include time for any sample preparation, however, sample preparation can be conducted during the analysis of a different sample. With calibration of the technology, analysis of QC samples, and sample preparation, it is possible to analyze 30 to 50 samples in one 8- to 10-hour working day.

Currently, the SEFA-P Analyzer retails for approximately $45,000 depending on the options. This does include one in-house XRF training course (not including travel expenses). A separate 2-day training course is offered for $750 per person. Other supplies needed for the operation of this instrument include an external dewar and PC (optional). These items vary in cost depending on the place of purchase. The Cd^{109} source replacement costs about $4,000.

4.5 XL SPECTRUM ANALYZER

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of XL Spectrum Analyzer.

4.5.1 Background Information

Niton was given two grants by the EPA through the Small Business Innovative Research Program to develop a lead detector that was the least expensive, most portable, safest, and easiest to use on the commercial market. Niton saw problems with other XRF technologies that used a Co^{57} source. The XL Spectrum Analyzer uses a Cd^{109} source. Niton found the advantages of the Cd^{109} source over the Co^{57} source to be lower cost, longer half life, less background interference problems, and safer to use.

Niton developed the XL Spectrum Analyzer to be a hand-held, in situ, lead-in-paint detector. However, Niton believes the capabilities of the XL Spectrum Analyzer allow it to be used to determine lead and other metals in soil. The technology can not analyze for cadmium or any other elements whose electrons cannot be discharged by the x-ray energy of the Cd^{109} source. This is because it has only a cadmium source. Niton is currently developing methodology and accessories for lead-in-soil technologies that it expects to be ready for demonstration some time in 1995.

4.5.2 Equipment and Accessories

The XL Spectrum Analyzer is a hand-held, portable, lead detector, designed to make fast, accurate, nondestructive measurements of lead concentrations. The technology is 8.25 inches long by 3 inches wide by 1.875 inches thick. It weighs slightly over 2.5 pounds with batteries. The radioactive source is Cd^{109}. The detector is a high resolution Silicon Pin-diode detector that is cooled via the thermoelectric Peltier effect. Its operating temperature is 5 to 41 C and operating humidity is 0 to 95 percent. The MCA has 1,024 channels with 100 channels displayed. The XL Spectrum Analyzer has an RS232 port for computer hook-up to transfer and print data. The internal memory is capable of storing 500 readings. The XL Spectrum Analyzer samples an area 1 cm by 2 cm. The technology comes with a waterproof, unbreakable plastic carrying case.

A battery pack can be installed on the bottom of the technology. The battery pack consists of 8 wrapped nickel metal hydride batteries. Fully charged, they will give 8 hours of use. For every minute of recharging, they will give 4 minutes of use. A 2.5-hour charge will fully charge a spent battery pack, but the 2.5-hour charge works only if the XL Spectrum Analyzer has been used recently. The batteries can be recharged from a 110-volt outlet or car cigarette lighter. The battery charger is included with the technology.

On the front of the XL Spectrum Analyzer is an LCD that shows spectra and numerical results, a three-button control panel (2 scroll keys and one clear/enter key) and a plunger to show when the technology is pressed up against the measuring surface. On the right side of the technology is a safety slide and a shutter release to allow the radioactive source window to open. The radioactive source window is in the back of the technology. At the bottom of the technology is the RS232 port for downloading data, the on/off switch, and clamp screws for the battery pack. Although the technology is currently configured to perform only in situ analysis, Niton has informed PRC that it is making adaptations to the XL Spectrum Analyzer to perform intrusive sampling.

4.5.3 General Operating Procedures

Operation of the XL Spectrum Analyzer can be summarized in 9 steps:

1. Turn on the technology.

2. Press "Clear/Enter" to begin self calibration.

3. When the XL Spectrum Analyzer beeps, calibration is complete. Press "Clear/Enter." Quickly check the logging screen.

The technology is ready for measurements. The first test will change the logging screen to measuring screen, which will remain until the XL Spectrum Analyzer is turned off.

4. Fasten the wrist strap to hold the technology.

5. Pull out the safety slide that locks the shutter release.

6. Begin the test by flicking a light pen across the template bar code. This is a software developed for lead in paint to record the locations and descriptive information for each measurement taken. This option may not be necessary for soil measurements.

7. Place the XL Spectrum Analyzer on the surface to be measured, push in the shutter release, and firmly press the XL Spectrum Analyzer flat against the surface.

8. The XL Spectrum Analyzer's timed beeps will help the operator decide when the test has reached the desired level of accuracy. For lead-in-paint analysis, results can be obtained in 15 to 30 seconds. Niton has informed PRC that it expects analysis times to be closer to 1 minute for multiple elements in soil.

9. The XL Spectrum Analyzer is lifted from the surface to end the test.

A measurement begins every time the XL Spectrum Analyzer is pressed flat against a surface, depressing the plunger fully. The test is ended when the XL Spectrum Analyzer is lifted and the plunger pops back out. The LCD screen will show a spectrum of the analysis. It also will show the quantitative lead results for the lead K-Lines and L-Lines. It is probable that the steps outlined above will be modified when using the XL Spectrum Analyzer to determine multiple metals concentrations in soil. Currently, Niton has not developed the exact procedures for conducting this type of analysis.

4.5.4 Training and Maintenance

Niton requires a 2-day radiation safety and technology training to use the XL Spectrum Analyzer. This training is performed by a company called Star Environmental Services.

All service, repair, maintenance, and source changing is handled by Niton. Niton requests that the operator not attempt any adjustments or repairs to the technology. The operator's manual provides a detailed discussion of general radiation safety and how to use the XL Spectrum Analyzer safely. Operator servicing invalidates the warranty. Niton's warranty includes 2 years standard parts and labor. The Cd^{109} source has a half life of 15 months and should be replaced every 2 years. Niton manufactures the XL Spectrum Analyzer under a specific license with the State of Rhode Island. Each operator has to be licensed to possess and operate a technology that uses ionizing radiation produced from the radioactive decay of internal sources. Generally, such a license is required in the particular state where the technology is to be operated. It is required under Niton's license that a leak test be performed every 6 months. Leak tests are performed on sealed radioisotope sources to determine if any radioactive materials are being released from the sealed source. Leak-test kits, with full instructions, are available from Suntrac. The leak-test sample should be mailed to Suntrac's laboratory.

4.5.5 Testing Time and Cost

This technology would allow for 100 measurements to be taken in a day.

The XL Spectrum Analyzer with its standard package costs $11,990. The package includes the battery pack and charger, cigarette lighter adapter, cable for RS232 downloading, waterproof carrying case, operating and safety manual, paint standards, and a basic computer software. An extra battery pack costs $300, while a wrist support costs $15. Shipping, handling, and insurance costs $80. The radiation safety and operator's training runs $350 per person. A Cd^{109} source replacement costs $2,200, which includes old source disposal, the leak test, and the certificate. Cd^{109} source replacement plus routine maintenance is another available option that costs $2,600. An expanded 15-month warranty can be purchased for $1,200. Niton now offers a "Quick View Element Scanner" software for $2,900. This program allows the operator to view the full spectrum for other elements in addition to lead. Niton hopes to offer an upgrade to the program in the future that will provide quantitative results for each element in mg/kg. Currently, the results are displayed as milligrams per square centimeter for paint analysis.

4.6 TN SPECTRACE LEAD ANALYZER

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of the TN Spectrace Lead Analyzer (Lead Analyzer).

4.6.1 Background Information

The Lead Analyzer was developed by TN Technologies for specifically analyzing lead in a variety of matrices. The Department of Housing and Urban Development, Occupational Safety and Health Administration, and EPA have developed guidelines for protecting the public from lead poisoning. The operator can use the Lead Analyzer to address each one of those guidelines by selecting the appropriate application on the analyzer. The factory installed and calibrated applications are: lead in soil, lead in paint, lead in surface dust, lead on air filters, and lead in paint chips.

The Lead Analyzer is manufactured in Austin, Texas, by TN Technologies and contains a HgI_2 detector in the analysis probe. The probe also houses one Cd^{109} radioisotope source for sample excitation. The Cd^{109} source is able to produce both lead K-shell emissions and the lead L-shell emissions from a sample. The K-shell emissions are monitored during the analysis of underlying layers of lead-based paint. The Lead Analyzer with a 30 mCi Cd^{109} source and HgI_2 detector is optimized for the analysis of lead in paint.

4.6.2 Equipment and Accessories

The Lead Analyzer comes with all of the equipment necessary for in situ and intrusive operation. A hard-shell carrying case is provided for transportation and storage.

Two main components make up the analysis system: a probe and an electronics unit. The main components are discussed in the following paragraphs. A list of all primary and secondary components follow the discussion.
The probe contains one radioisotope source, Cd^{109} (30 mCi), for efficient excitation of lead K and L shell electrons. The source is ruggedly encapsulated and housed in a metal turret with additional lead shielding inside the probe. This source is exposed to a sample through a sealed 1-inch-diameter polypropylene window in the face of the probe (probe window). The fluorescence from the sample passes back through the window and is intercepted by the HgI_2 detector. This detector quantitates the energy of each x-ray and builds a spectrum of characteristic x-ray emission peaks on a 2048-channel MCA.

Spectral data is communicated to the electronics unit through a flexible cable of 6, 12, or 20 feet in length. Metals peaks are integrated and either milligram per square centimeter (mg/cm^2), mg/kg, or percent values are calculated. The electronics unit will store and display both results and spectra from a measurement. A maximum of 600 sets of results and 100 spectra can be stored before downloading to a personal computer (PC) via an RS-232 cable.

Equipment/Optional Accessories/Instrument Specifications

Equipment

The standard Lead Analyzer system includes:

Electronics unit for data acquisition, processing, storage and display

-- Nickel cadmium battery pack (4 to 5 hours of continuous use)

Hand-held probe including:

-- HgI_2 detector
-- One excitation sources (Cd^{109})
-- Safety Cover

Uniblock allows the operator to measure sample cups, thin films and to perform the check procedure for the lead-in-paint application.

-- Sample shield
-- Positioning ring for standard 31-mm x-ray sample cups

Interconnecting probe cable (6-foot cable is standard)

Pure element check samples kit

Two blank samples for background setup and check out

Battery charger

RS-232 serial input/output interface cable

System carrying/shipping case

Operators manual, factory applications and results management software

Training video (22 minutes)

Ten 31-mm-diameter sample cups

1 roll 6.0 m Mylar XRF film (300 feet)

Spare window assembly

<u>Optional Accessories</u>

Field pack with shoulder straps ($245)

Spare battery pack, charger, and adapter ($750)

Battery eliminator for continuous use ($600)

"Applications Generator" software

NIST Soil Standard Kit (NIST No. 2579)

Micromatter Lead Thin Film Standards Kit (for lead in paint measurements)

Dust wipe kit

<u>Instrument Specifications</u>

<u>Probe Dimensions and Weight:</u> 12.7 centimeters (cm) x 7.6 cm x 21.6 cm; 1.9 kilograms (kg)

<u>Cable:</u> standard 6-foot length, optional 12- or 20-foot lengths

<u>Electronics Unit Dimensions and Weight:</u> 32 cm x 30 cm x 10 cm; 6.7 kg

<u>Power:</u> operates from a nickel cadmium battery for 4 to 5 hours of continuous use. Also can use 110 or 220 volt, 50 to 60 Hertz AC electricity.

<u>Operating Temperature:</u> 0 to 49 C (32 to 120 F)

<u>Storage Temperature:</u> -40 to 40 C (-40 to 104 F)

4.6.3 General Operating Procedures

To operate the Lead Analyzer, the nickel cadmium battery is plugged in and the probe cable is connected. The spectrometer is turned on by pressing the "On" button. A message on the screen will ask the operator for the data and time and then proceed to the MAIN MENU.

The Lead Analyzer software is menu driven. From the MAIN MENU, the operator selects a predefined "Application." The Lead Analyzer comes with the following applications installed:

1. Soils Application (measures lead, arsenic, chromium, iron, copper, zinc, and manganese in soils)

2. Lead in paint (makes in situ measurements of lead in paint, substrate independent result in (mg/cm^2)

3. Lead in Surface Dust

4. Lead in Air Filters

5. Lead in Paint Chips

Once the application is selected, the analysis is automated by the Lead Analyzer software. To begin measuring samples, the operator selects MEASURE to get to the "Ready Screen." From here the operator initiates an analysis by pressing either the probe trigger or the "Continue" button on the electronics unit. Distinct sounds signal the beginning and end of a measurement to alert the operator to take the next measurement. Results with standard deviations are displayed at the end of each measurement. If desired, results and spectra can be automatically stored on the electronics unit after each measurement. Transferring the results and spectra to a PC allows printing, archiving, spreadsheet and report generation.

No site-specific calibrations standards are needed for instrument operation. The technology is calibrated at the factory using pure elements, and calculates results of a soil sample using a matrix correcting fundamental parameters algorithm. Two types of matrix effects are inherent with X-ray fluorescence spectrometry: absorption and enhancement matrix effects. The fundamental parameters algorithm makes the appropriate matrix corrections for an accurate analysis of six elements in soil.

All applications except the lead in paint use a fundamental parameters algorithm. The lead in paint application is calibrated using NIST standards.

If desired, the Lead Analyzer software can provide for a site-specific calibration to model a given suite of standards.

For data QA, TN Technologies recommends that a certified reference sample be run periodically. This will provide valuable accuracy and precision data. Running a certified reference sample can also alert the operator that either the probe window is contaminated or the technology is not operating properly. The probe window can be cleaned with a towel and the condition of the spectrometer can be checked using the Standard Operational Check, which requires running a pure lead sample and the pure quartz sample to verify sensitivity and background, respectively.

4.6.4 Training and Maintenance

An operator can learn to use the Lead Analyzer by reading the Operators Manual. If personalized training is desired, TN Technologies offers a 2-day in-house training course. The only expense to the customer is travel. A 2-day on-site training course is also an option at $1,000 per day plus travel expenses.

The Lead Analyzer can be cleaned with soap and water and is designed to be used in the field. Given proper care, the developer claims that the technology should only require the scheduled periodic maintenance of source replacement.

Due to the inherent safety design features and associated low levels of radiation, the instrument is supplied under a general license for radioisotope regulatory purposes which greatly simplifies its transportation and use.

4.6.5 Testing Time and Cost

The standard deviation of the x-ray emission data is reported with each measurement. This information allows the operator to optimize the measurement time to meet project data quality objectives and project scheduling. When screening soils that are in areas of high concentration at the site, the developer recommends short source exposure times of 30 to 60 seconds. As the concentration nears the action level, the developer recommends a longer source exposure times of 2 to 4 minutes. This decreases the standard deviation of the measurement and thus, increases precision. Since the measurement is automated by the Lead Analyzer software, the operator can prepare the next sample or sampling site while the technology is running the previous one. The developer claims that an operator should be able to analyze at least 100 samples per day.

The Lead Analyzer costs $39,500 to purchase. This includes all of the equipment necessary for operation of the instrument. Spare parts and accessories are available as described in Section 4.6.2. Purchased technologies are warranted for a full year with an optional extended warranty. The Lead Analyzer can be rented through TN Technologies for approximately $5,000 per month or $3,000 for 2 weeks. Periodic maintenance includes replacement of the Cd^{109} source every 2 to 3 years at a cost of $3,500 to $3,800. The Cd^{109} source should also be "deshimmed" every 6 to 10 months at a cost of $1,500.

4.7 ATX-100

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of ATX-100. Much of the information below is incomplete and will be updated in the ITER.

4.7.1 Background Information

ERC conducts research and development in the area of x-ray fluorescence analysis. The company manufactures, repairs, and operates the ATX-100. This technology is not marketed for sale to the public, rather, it is marketed as an on-site x-ray fluorescence analysis service provided by ERC.

4.7.2 Equipment and Accessories

The ATX-100 is designed to make rapid, nondestructive measurements of more than 60 elements. This technology takes in situ and intrusive measurements. The technology weighs 18 pounds and is powered by eight D-size batteries. The technology is fitted with two radioactive sources: an Fe^{55} source and a Cd^{109} source. The detector records spectral data on 512 channels sorted by emission energy. The ATX-100 has an RS232 port for computer hook-up to transfer and print data. ERC has computer software that interprets the spectral data, and identifies and quantifies contaminants. Summary reports for batches of samples can be printed for up to seven target metals at a time.

4.7.3 General Operating Procedures

Operation of the ATX-100 can be summarized in five steps:

1. Cover the environmental sample or sampling location with a protective cover, such as plastic sheeting. The thickness and composition of the covering must remain constant throughout a project.

2. Place the probe window over the sample location being analyzed.

3. Open the probe window and expose the sample or location to either the Fe^{55} or Cd^{109} source. Generally, the exposure time is set between 100 and 300 seconds.

4. Examine the resulting spectrum. Using the ERC software, identify and quantify contaminants present.

5. Clean the probe window and move to the next sample or location.

ERC provides an internal calibration for this technology. If desired, site-specific calibrations can be performed to increase the accuracy of the analysis.

When examining a sample's spectrum with the ATX-100, individual target metals are identified by marking spectral peaks with the technology's cursor and entering the appropriate commands for the software to conduct its target metal identification and quantitation routine. Cursor calibration is necessary and often associated with duplicate sample analysis. The cursor adjustment is the only field adjustment that can be made on the ATX-100. To check the cursor alignment, lead or copper foil is analyzed. Cursor adjustment is necessary when the lead or copper spectral peaks are not properly identified when the cursor marks their spectral peaks. This adjustment is made by turning the set screws on the underside of the detection head.

ERC recommends that field duplicates and replicate samples be analyzed during use of the ATX-100. The replicate sample analysis is used to monitor technology precision; the field duplicate analysis is used to monitor sample heterogeneity.

4.7.4 Training and Maintenance

ERC provides the ATX-100 as a service, and thus, it does not have a training program for non-ERC employees. In addition, ERC conducts all technology maintenance.

4.7.5 Testing Time and Cost

ERC has provided no data on sample throughput for the ATX-100.

The cost of the ATX-100 operator is billed at an hourly or daily rate, $85 or $750, respectively. The cost for using the ATX-100 is billed at a weekly or monthly rate, $1,500 or $4,500, respectively. Equipment and personnel mobilization is billed at $0.45 per mile. Per diem for the operator is billed at $75 per day. Other sample preparation equipment, such as stainless steel-sieves, mortar and pestles, sample grinders, sample cups, microwave ovens, and generators can be rented or purchased from ERC.

4.8 SEFA-Px Analyzer

This section presents information on the background, apparatus, general operating procedures, training and maintenance requirements, and cost of the SEFA-Px Analyzer.

4.8.1 Background Information

HNU developed the SEFA-Px Analyzer to provide simple and rapid in situ or intrusive analysis of lead in paint, dust, or soil. The SEFA-Px Analyzer was introduced into the market in February 1995.

4.8.2 Equipment and Accessories

The basic SEFA-Px Analyzer consists of an analysis probe for in situ and intrusive measurements, a single radioisotope sources, a liquid nitrogen cooled Si(Li) detector, preamplifier, a MCA, and a battery charger. The probe is 13 inches long, 4.5 inches wide, 10 inches tall, and weighs 7 pounds. The MCA is 10.5 inches long, 10.75 inches wide, 5 inches tall, and weighs 11 pounds. The SEFA-Px Analyzer operates at relative humidities between 10 and 95 percent. The ambient temperature limits of operation are between 0 and 40 C.

A trigger activated interlocked safety shutter on the probe and software prompts help prevent operator exposure to the radioisotope source. One excitation source is offered with the SEFA-Px Analyzer. It is low energy 10 mCi Co^{57} source.

The SEFA-Px Analyzer contains a Si(Li) detector. The detector has a manganese K-alpha line resolution of 180 eV. It is 10 mm in diameter and has an active area of 45 mm^2. The Si(Li) detector is cooled with liquid nitrogen. The internal liquid nitrogen dewar has a capacity which allows up to 8 hours of operation.

A preamplifier in the technology collects the electronic signal from the detector, amplifies it, and sends it to the MCA. The MCA sorts the signals coming from the preamplifier by energy level and counts the number of x-rays that strike the detector. This information is converted to lead concentrations based on internal or external calibration. The unit has two factory calibrations, one for NIST paint and one for NIST soil. In addition, the technology can accept user-defined calibrations for paint and soil. The MCA can store up to 325 spectra and data points. The numerical concentration data is displayed on a LCD screen on the back of the detector. The internal battery can power the MCA for 8 to 10 hours.

The MCA has a readout module that includes an LCD text display and an instrument control key pad. HNU provides software that allows the downloading of the stored data to a PC via a RS232C interface. The resulting spectra from the analysis of samples can be viewed on the PC screen and can be printed to obtain a hard copy. Quantitative results can also be displayed on the PC screen.

Other supplies needed to operate the SEFA-Px Analyzer include 30-mm-diameter polyethylene sample cups, Mylar window film to cover the cups, and an external liquid nitrogen dewar. If sample preparation techniques are employed, the analysis also may require sieves, a mortar and pestle to grind the soil samples, plastic weigh boats, and a drying oven (either standard convection oven, toaster oven, or microwave oven). Lastly, SEFA-Px Analyzer operation will require calibration standards either commercially available from such sources as NIST or site-specific calibration samples if the pre-set factory calibration is not used.

4.8.3 General Operating Procedures

Prior to analysis of samples, the internal liquid nitrogen dewar should be recharged from the external liquid nitrogen dewar. The SEFA-Px Analyzer will not allow the operator to analyze samples until the Si(Li) detector is cool. This may require 20 to 30 minutes of cool down time after the initial charge with liquid nitrogen.

Once the SEFA-Px Analyzer has been turned on, the battery voltage should be checked. If the battery voltage is low, "low battery voltage" will be indicated on the LCD of the MCA.

Once the MCA has warmed up, the operator can select either preprogrammed parameter settings for analysis or custom parameters can be imputed into the analysis program. Readings are taken by activating the trigger on the probe. This initiates and runs the analysis program which determines calibration parameters and source exposure times. Source exposure times can vary from 5 to 300 seconds. At the end of each sample analysis, the MCA will beep to alert the operator that the analysis is complete.

Prior to sample analysis, the SEFA-Px Analyzer must be calibrated. Two types of calibrations can be used with this instrument: empirical or factory set calibration. In the case of empirical calibration, the SEFA-Px Analyzer is calibrated with external lead standards. The matrix of these standards should match the matrix being analyzed. The other method of calibrating the SEFA-Px Analyzer is by using the factory pre-set calibrations for soil or paint.

QC procedures can include daily source emission energy checks, with a copper foil check sample; continuing calibrations; method blanks; laboratory duplicates; and LCSs. The LCSs are often SRMs produced by NIST.

4.8.4 Training and Maintenance

The SEFA-Px Analyzer is sold with a general license, meaning that the operator does not have to be specifically licensed in each state that it is used in. The SEFA-Px Analyzer is engineered to minimize the possibility of operator exposure to ionizing radiation. The radioisotope source is isolated by a shutter system that is interlocked mechanically to the probe trigger. The radioisotope source should be leak-tested every 6 months. It may be necessary to replace the Co^{57} source about every 1 to 2 years. HNU will provide a 2-day training course on XRF principles and operation of the SEFA-Px Analyzer in-house or at a customer's facility.

4.8.5 Testing Time and Cost

The average time of analysis for a sample is 5 to 300 seconds. This does not include time for any sample preparation, however, sample preparation can be conducted during the analysis of a different sample. With calibration of the technology, analysis of QC samples, and sample preparation, it may be possible to analyze 100 or more samples in one 8- to 10-hour working day. The retail cost of the SEFA-Px Analyzer is $25,000. The cost may include one in-house XRF training course (not including travel expenses). A separate 2-day training course is offered for $750 per person. The developer recommends the Co^{57} source be replaced annually at a cost of $2,500. Other supplies needed for the operation of this technology include an external dewar and PC (optional). These items vary in cost depending on the place of purchase.

TABLE 4-1

RADIOISOTOPE SOURCE SUMMARY

Source	Activity (mCi)	Half Life (Years)	Excitation Energy (keV)	Elemental Analysis Range	
Fe^{55}	20 - 50	2.7	5.9	Sulfur to chromium Molybdenum to barium	K Lines L Lines
Co^{57}	40	0.75	121.9 and 136	Cobalt to cerium Barium to lead	K Lines L Lines
Cd^{109}	5 - 30	1.3	22.1 and 87.9	Calcium to rhodium Tantalum to lead Barium to uranium	K Lines K Lines L Lines
Am^{241}	5 - 30	458	26.4 and 59.6	Copper to thulium Tungsten to uranium	K Lines L Lines
Cm^{244}	60 - 100	17.8	14.2	Titanium to selenium Lanthanum to lead	K Lines L Lines

TABLE 4-2

TECHNOLOGY SPECIFICATIONS

Technology	Detector	Sources
ATX-100	No information	Fe^{55}, Cd^{109}
SEFA-P Analyzer	Si(Li)	Fe^{55}, Cd^{109}, Am^{241}
SEFA-Px Analyzer	Si(Li)	Cd^{109}
X-MET 920 (Si(Li) Detector)	Si(Li)	Fe^{55}, Cd^{109}, Am^{241}
X-MET 920 (gas-filled proportional detector)	Gas Filled Proportional	Fe^{55}, Cd^{109}, Am^{241}
XL Spectrum Analyzer	Silicon Pin-Diode	Cd^{109}
MAP Spectrum Analyzer	Si(Li)	Co^{57}, Am^{241},Cd^{109}
TN Spectrace 9000	HgI_2	Fe^{55}, Cd^{109}, Am^{241}
TN Spectrace Lead Analyzer	HgI_2	Cd^{109}

XRF Chapter 5

DEMONSTRATION SITE DESCRIPTIONS

This chapter discusses the history and characteristics of the two demonstration sites.

5.1 ASARCO SITE

The Asarco site is the location of a former lead and copper smelter situated on the shore of Commencement Bay in Tacoma, Washington (Figure 5-1).

5.1.1 Site History

Prior to 1890, sawmills were operated at the location of the Asarco site. Lead smelting and refining operations began at this site in 1890 and continued until 1912. In 1905, Asarco purchased the property and continued the smelting operations. In 1912, Asarco converted the operation to a copper refining and smelting operation. Asarco further refined the by-products of the smelting operation into arsenic, sulfuric acid, liquid sulfur dioxide, and slag. All smelting-related operations were discontinued at this site in 1985.

The Asarco site is part of the Commencement Bay Nearshore/Tideflats Superfund site in Tacoma, Washington. The Commencement Bay site was placed on the NPL in September 1983. In September 1986, Asarco and EPA Region 10 entered into an Administrative Order on Consent in which Asarco agreed to conduct a remedial investigation and feasibility study. The remedial investigation was completed in 1992; the feasibility study was completed in 1994.

5.1.2 Site Characteristics

The Asarco site is located on the Point of Defiance peninsula in the municipalities of Ruston and Tacoma, Washington. The site consists of 67 acres of land adjacent to Commencement Bay. The site is marked by steep slopes leading into the bay, slag fill that was used to extend the original shoreline, a cooling water pond, and the 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.

Soil sampling has targeted four general areas of the site: the plant administration area, the former cooling pond, the 1987 demolition area, and the off-site residential areas adjacent to the smelter stack. 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. A brief summary of the confirmatory analytical data for this site is presented in Table 5-1.

The majority of the smelter site is covered with artificial fill material of varying thickness and composition. Two general types of fill are found on site: granular fill and massive slag fill. The composition of the granular fill material ranges from sand to silty, sandy gravel with demolition debris and slag debris intermixed throughout. The massive 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 in the drainage 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.

5.2 RV Hopkins Site

The RV Hopkins site is located in the west end of Davenport, Iowa, (Figure 5-2). The facility occupies approximately 6.68 acres in a heavy industrial/commercial zoned area.

5.2.1 Site History

Industrial activities in the area of the RV Hopkins property included the manufacture of railroad locomotive engines during the mid-1800s. The RV Hopkins property was a rock quarry during the late 1800s. Scott County, Iowa, acquired the property in 1921; it then passed to People's Light and Power Company in 1929; W. J. Vale and Vale, Inc. (Mr. Hopkins' uncle), in 1940; and to the Frank Berry Trust in 1957. Mr. Hopkins purchased the property in 1964 and the adjoining property, formerly Sludgemaster, Inc., in 1978.

Aerial surveys beginning in 1929 show that the rock quarry occupied the majority of the site initially, gradually decreasing until being completely filled by 1982. Mr. Vale reportedly used the site 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. After acquiring the current property in 1964, Mr. Hopkins reportedly covered the former quarry area of the site with foundry sand. RV Hopkins receives between 400 to 600 drums per day for reconditioning, accepting only drums which meet the Resource Conservation and Recovery Act (RCRA) definition of "empty" according to 40 Code of Federal Regulations (CFR) 261.7. (2). Most of the drums received at the facility come from the paint, oil, and chemical industries.

5.2.2 Site Characteristics

The area is reported to be underlain by Devonian-aged Wapsipinicon Limestone, and grey-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 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.

The most highly concentrated contaminants in the furnace area are chromium, lead, and zinc. The highest concentrations of chromium, lead, and zinc 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. In addition, polychlorinated biphenyls

(PCB) and chlordane were prevalent in the areas. Table 5-2 gives a brief summary of the predemonstration confirmatory analytical data for this site.

FIGURE 5-1 ASARCO SITE LOCATION MAP
(not available)

FIGURE 5-2 RV HOPKINS SITE LOCATION MAP
(not available)

TABLE 5-1

MAXIMUM CONCENTRATION OF CONTAMINANTS IN SURFACE SOIL SAMPLES COLLECTED DURING PREDEMONSTRATION SAMPLING ACTIVITIES

Asarco Site
Tacoma, Washington

Contaminant	Minimum Concentration of Contaminant (mg/kg)	Maximum Concentration of Contaminant (mg/kg)
Antimony	ND	2,300
Arsenic	31.8	24,800
Barium	38.1	2,630
Cadmium	ND	279
Chromium	11.0	51.9
Copper	118	44,200
Iron	9,150	41,700
Lead	27.2	15,600
Manganese	138	659
Mercury	ND	582
Nickel	ND	65.5
Silver	ND	65.4
Zinc	45.9	3,910

Notes:
Confirmatory analyses were performed by Midwest Research Institute.
ND Not detected
mg/kg Milligrams per kilogram

TABLE 5-2

MAXIMUM CONCENTRATION OF CONTAMINANTS IN SURFACE SOIL SAMPLES COLLECTED DURING PREDEMONSTRATION SAMPLING ACTIVITIES

RV Hopkins Site
Davenport, Iowa

Contaminant	Minimum Concentration of Contaminant (mg/kg)	Maximum Concentration of Contaminant (mg/kg)
Antimony	ND	68.0
Arsenic	ND	17.9
Barium	73.8	6,340
Cadmium	1.4	13.4
Chromium	24.8	1,450
Copper	21.1	155
Iron	9,100	68,500
Lead	159	10,400
Manganese	306	906
Mercury	ND	0.29
Nickel	32.8	151
Silver	ND	ND
Zinc	73.0	2,410

Notes:
Confirmatory analyses were performed by Midwest Research Institute.
ND Not detected
mg/kg Milligrams per kilogram

XRF Chapter 6

SAMPLING PLAN

The sampling plan for this demonstration specifies procedures that will be used to ensure the consistency and integrity of samples, and control within sample variation. In addition, this plan outlines the sample collection procedures necessary to meet the demonstration purpose and objectives. Careful adherence to these procedures will ensure that samples analyzed using the FPXRF technologies are comparable to samples analyzed by the confirmatory laboratory using conventional analytical methods. Figure 6-1 and Table 6-1 summarize the sampling and analysis strategy for each technology.

In addition to the standard objectives of a SITE demonstration, EPA has requested that an SW-846 method for FPXRF use be submitted to the EPA OSW for validation at the conclusion of the demonstration. To meet this objective, EPA OSW has required that a wide range of environmentally threatening metals be examined. The primary target metals discussed below are intended to meet this criteria. Also, EPA OSW has required that the performance of the FPXRF technologies be tested over a variety of soil textures. EPA OSW defined the critical soil textures as being fine grained (silts and clays), organic (loams), and coarse grained (sands).

6.1 SAMPLING AND FIELD ANALYSIS OPERATIONS

The sites for this demonstration are the RV Hopkins site and the Asarco site. These sites exist in different climatological regions of the United States; they contain surficial soils meeting the textural requirements of the demonstration; and they exhibit a wide range of concentrations for all the target metals. The differences in soil texture will allow analysis of the affects of matrix on technology performance. The RV Hopkins site is located in a humid continental climate characterized by hot summers. The Asarco site is located in a marine climate characterized by mild winters. The selection of sites in these two different climates will permit analysis of the affects of soil moisture on technology performance. The primary target metals for this demonstration are arsenic, barium, chromium, copper, lead, and zinc. Nickel, iron, cadmium, and antimony are secondary target metals. Several of these secondary target metals will allow analysis of a technology's response to metals interferences.

Approximately 100 soil samples will be collected from each of the three target soil textures: clays, loams, and sands. During the predemonstration sampling activities, PRC identified sandy and loamy textured soils at the Asarco site and silty clay soils at the RV Hopkins site. Because two of the target soil textures were found at the Asarco site and only one target soil texture at the RV Hopkins Site, it is expected that twice as many soil samples will be collected at the Asarco site.

Each type of FPXRF technology, in situ and intrusive, will involve slightly different sampling procedures. The following discusses the sampling and analysis that will take place at each soil sampling location at each site. First, an area 4 inches by 4 inches square will be cleared of all vegetation, debris, and gravel larger than 2 mm in diameter. Each of the FPXRF in situ technologies will take one measurement in the sample area. This data will represent FPXRF in situ technology measurements for unprepared soils. At 10 percent of the locations selected for this type of sampling, each FPXRF in situ technology will take 10 replicate measurements (without moving the probe) to assess instrument precision.

After all the FPXRF in situ technologies have completed their analysis of a location, the soil within the 4-inch by 4-inch square will be removed to a depth of 1 inch and homogenized in a labeled plastic bag. This will produce a soil sample of approximately 375 grams or 250 cm^3. The 1-inch-depth interval was selected as the thinnest layer of soil that could be reliably removed under normal field conditions. This interval also produces 80 to 90 percent of the signal used by the FPXRF in situ technologies to identify and quantify metals contamination.

Sample homogenization will be monitored by adding sodium fluorescein salt to the sample homogenization bag. During the predemonstration, it was determined that sodium fluorescein salts will not affect the FPXRF or confirmatory analysis. This procedure is discussed in detail in Section 6.3. The sample will be kneaded for 2 minutes. At this time, the sample preparation technician will examine the sample under ultraviolet light to assess the distribution of sodium fluorescein salt throughout the sample. The sodium fluorescein salt fluoresces when it is exposed to ultraviolet light. If the sodium fluorescein salt is not evenly distributed throughout the sample, the homogenization and checking process will be repeated until the sodium fluorescein salt is evenly distributed throughout the sample. This monitoring process assumes that even distribution of sodium fluorescein salt is indicative of good sample homogenization. Field duplicate samples will be collected to monitor the effectiveness of the homogenization procedure.

During the predemonstration sampling, field duplicates were collected and analyzed by the confirmatory laboratory to assess the demonstration's homogenization procedure. Nine duplicate samples were collected. These samples were collected from each soil texture and for each target concentration range. The mean RPD for individual metals for the field duplicates was 13.17 percent. Applying a 99 percent confidence interval around this mean yields an RPD range of 8.59 to 17.75 percent. In other words, if the same homogenization technique is used in the demonstration, 99 percent of the samples should produce RPDs from 8.59 to 17.75 percent if split analyses are run. This is below the acceptance limit of less than or equal to 20 percent RPD defined in the QAPP for pre-digestion laboratory duplicates. Based on this, PRC considers the homogenization technique adequate. In fact, it is likely that the RPD range for field duplicates will be reduced during the demonstration since sample volumes will be reduced by 100 to 150 percent relative to the predemonstration samples.

This homogenized sample will then be spread out inside a 4- by 4- by 1-inch frame. At this point, the FPXRF in situ technologies will analyze the homogenized sample material. Each FPXRF in situ technology will take one measurement from this homogenized material. This will represent prepared sample analysis for in situ technologies. Instrument precision measurements will also be collected from 10 percent of this sample material. The instrument precision data will be collected from the same soils used for unprepared soil precision measurements. This data will represent FPXRF in situ technology measurements with sample preparation.

Once the homogenized sample has been analyzed by all the FPXRF in situ technologies, the sample material will be passed through a No. 10 mesh sieve and returned to its labeled sample bag. Approximately 10 grams of this material will be placed in sample cups for analysis by the FPXRF intrusive technologies. Ten replicate measurements will be collected on 10 percent of these samples by each technology to provide a measure of instrument precision. The samples used for replicate analysis will be those collected from locations corresponding to the locations where the instrument precision measurements were taken for the FPXRF in situ technologies. Wherever possible the same sample, including the same sample cup, will be used for each of the FPXRF intrusive technologies to obtain measurements of metal concentrations. This data will represent FPXRF intrusive technology measurements on soils with no sample preparation. After a sample has been analyzed by all the FPXRF intrusive technologies, it will be returned to the labeled sample bag.

After the FPXRF intrusive technologies have completed their analysis of a sample, the material in the sample cup or cups will be placed back into their respective labeled sample bags. Aliquots of this material will be placed in two labeled polyethylene bottles. One bottle will be delivered to the confirmatory laboratory and the second bottle will be archived for QA/QC analysis by a second confirmatory laboratory, if necessary. The confirmatory laboratory requires a minimum of 20 grams of sample for extraction and analysis by SW-846 Methods 3050A and 6010A, and for QA/QC samples.

The homogenized sample in the labeled sample bag then will be dried and ground with a mortar and pestle to a uniform fine particle size. Initially the sample will be weighed to acquire a wet weight. It will then be dried in a convection oven at 150 C for 2 hours. The dried sample will be weighed to determine a dry weight. The dried material will then be ground with a mortar and pestle for 3 minutes. The ground material will then be passed through a No. 40 stainless-steel sieve (0.425 mm openings). This size sieve passes fine sands and smaller particles, as defined in the Unified Soil Classification System. Sample grinding will continue until at least 90 percent of the original sample passes the No. 40 sieve. This drying and grinding represents a standard field sample preparation to minimize variance in particle size for the FPXRF intrusive technologies. An aliquot of the ground soil will be placed in a sample cup for measurement by the FPXRF intrusive technologies. Ten percent of these samples will undergo 10 replicate measurements by each FPXRF intrusive technology to evaluate precision. These samples will be collected from locations corresponding to the locations where the precision measurements were taken for the FPXRF in situ technologies. Wherever possible, the same aliquot and sample cup will be used for all the FPXRF intrusive technologies. This data will allow an assessment of the effects of sample drying and grinding on the results from the FPXRF intrusive technologies.

Thirty percent of the samples will also be identified for extraction and analysis by SW-846 Methods 3052 and 6010A. The minimum 20 grams of sample described above should provide sufficient sample volume for this analysis also. PRC will attempt to evenly distribute these samples over the target soil textures and concentration ranges. PRC will note the additional analytical procedures on sample labels and field sheets. This analysis will be used to produce confirmatory data based on total digestion, more closely related to the type of measurement made by FPXRF technologies. The standard method for metals analysis (SW-846 Methods 3050A and 6010A) does not use a total sample digestion extraction.

Ten percent of the sample material also will be split and further dried by microwaving on high for 5 minutes. PRC will attempt to evenly distribute these samples across the target soil textures and concentration ranges. The microwave dried samples will be submitted to the confirmatory laboratory for analysis by SW-846 Methods 3050A and 6010A. In addition, matching aliquots (same sample location) of unprepared samples, packaged at the beginning of the FPXRF intrusive technology analysis, will be submitted for confirmatory analysis. This data will assess the potential loss of metals due to volatization from either convection oven drying or microwave drying. PRC does not anticipate the loss of any metals other than mercury (not a target metal for this demonstration) during the convection oven drying process. Arsenic is the most volatile target metal, sublimating at 188 C.

Figure 6-1 presents a sample collection, packaging, and analysis flow chart for this demonstration.

Instrument drift and potential temperature effects will be monitored during this demonstration. At each site, each technology will analyze the same PE sample at 2-hour intervals during at least one day of field operation. Whenever these measurements are collected, the ambient air temperature will be recorded.

Sampling will be conducted in areas of each site that, based on data from the predemonstration sampling, exhibit wide ranges of metal concentrations. This will allow the FPXRF technologies to be evaluated on their effectiveness in analyzing a broad range of metal concentrations. Sampling personnel will collect samples using the equipment and procedures described in Section 6.2.

6.2 COMMUNICATIONS, DOCUMENTATION, AND EQUIPMENT

PRC will communicate regularly with the demonstration participants to coordinate all field activities associated with this demonstration and to resolve any logistical, technical, or QA issues that may arise as the demonstration progresses. The successful implementation of the demonstration will require detailed coordination and constant communication between all demonstration participants.

All PRC field activities will be thoroughly documented. Field documentation will include field logbooks, photographs, field data sheets, and chain-of-custody forms. FPXRF data reporting forms and sample packaging forms are discussed and presented in Chapter 8. The PRC field team leader will be responsible for maintaining all field documentation. Field notes will be kept in a bound logbook. Each page will be sequentially numbered and labeled with the project name and number. Completed pages will be signed and dated by the individual responsible for the entries. Errors will have one line drawn through them and this line will be initialed and dated.

All photographs will be logged in the field logbook. These entries will include the time, date, direction, subject of the photograph, and the identity of the photographer. Specific notes about each sample collected will be written on sample field sheets, as well as in the field logbook. Any deviations from the approved final demonstration plan will be thoroughly documented in the field logbook and communicated to the EPA TPM and other parties that may be affected by the change.

Original field sheets and chain-of-custody forms will accompany all samples that are shipped to the confirmatory laboratory. Copies of field sheets and chain-of-custody forms for all samples will be maintained in the project file.

PRC will obtain all equipment needed for field work associated with this demonstration. A list of field equipment expected to be used for this demonstration is provided in Table 6-2.

6.3 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

A key issue in ensuring the effectiveness of this demonstration is ensuring that environmental samples analyzed by the confirmatory laboratory and by each of the FPXRF technologies are subsamples from a homogeneous sample. To address this issue, sampling personnel will exercise particular care throughout the field work to ensure that samples are thoroughly homogenized before they are split into replicate samples. Homogenization will be conducted by kneading the soil in a plastic bag for a minimum of 2 minutes. If after this time the samples do not appear to be well homogenized, they will be kneaded for an additional 2 minutes. This will continue until the samples appear to be well homogenized. In the case of the FPXRF in situ technologies, this is not as critical because these technologies will analyze the entire sample and produce a concentration based on the mean concentration throughout the sample. For the FPXRF intrusive technologies, however, only a small aliquot of the homogenized sample will be used, therefore, homogenization is critical.

PRC will use sodium fluorescein as an indicator of thorough homogenization. If the samples are dry, past experience has shown that sodium fluorescence will not work as an indicator of thorough homogenization. If the samples are moist, approximately one-quarter teaspoon of dry sodium fluorescein powder will be added to the sample prior to homogenization. The sample will be homogenized for the specified time. After homogenization is completed, the sample will be examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly dispersed in the sample, homogenization will be considered complete. If the dye is not evenly distributed throughout the sample, the homogenization mixing will be continued and repeatedly checked until the dye is evenly distributed throughout the sample. PRC anticipates that the homogenization process should take approximately 2 to 4 minutes per sample.

Field duplicates will be collected during the demonstration and submitted for confirmatory analysis. These samples will be submitted for analysis at a rate of at least one duplicate for every 10 samples submitted. These samples will be collected by splitting a single homogenized sample in the field. Duplicate samples will be submitted for analysis to the confirmatory laboratory and to each of the FPXRF technologies. These samples will be used to evaluate the precision (reproducibility) of sample collection, homogenization, processing, and analysis. Multiple duplicate samples from each concentration range will be collected.

Additional QA/QC information, including procedures for analytical work associated with this demonstration, is provided in the QAPP in Chapter 8. All field activities for this demonstration will be conducted according to the requirements of the sampling plan and the QAPP.

6.4 HEALTH AND SAFETY PROCEDURES

Health and safety procedures that will be used during demonstration field work are detailed in the HASP in Chapter 10.

6.5 SAMPLE COLLECTION PROCEDURES

Sampling personnel will collect and homogenize samples using the procedures described below. All field activities will conform with requirements of the HASP and with all requirements in this demonstration plan.

Sampling personnel will maintain communication with the EPA TPM and the EPA regional site contacts during field activities. If unanticipated or unusual situations are encountered that may alter the sampling design, sampling location, or data quality, the situation will be discussed with the EPA TPM and the EPA regional site contacts before changes to the approved demonstration plan are made. Any deviations from the approved demonstration plan will be thoroughly documented as discussed in Section 6.2.

6.5.1 Sampling Locations

Soil samples will be collected from areas at the sites known to exhibit metal concentrations ranging from less than 100 milligrams per kilogram (mg/kg) to concentrations greater than 1,000 mg/kg (based on the target metals listed in Section 6.1). PRC is anticipating that the detection limit for most metals using the FPXRF technologies will be in the range of 50 to 100 mg/kg.

Approximately 25 soil samples will be collected from the less than 100 mg/kg concentration range for each of the three target soil textures. These samples will be used to evaluate the low detection limits of each FPXRF technology. Approximately 50 soil samples will be collected from areas with metal concentrations ranging from 100 to 1,000 mg/kg, for all three target soil textures. There are more soil samples in this range because action levels for metals in soil, such as lead and chromium, are often in this concentration range, and PRC believes that this is within the linear range of these technologies. The additional sampling is required to increase the statistical power of this range of evaluation. Evaluating the performance of each FPXRF technology near action levels also will determine their potential usefulness for site screening to determine the action or no action status of sites. The remaining 25 soil samples will be collected from areas containing metals at concentrations greater than 1,000 mg/kg, for each target soil texture. The results from the high concentration soil samples will be used to evaluate data trends, such as linearity, at high concentrations.

Every effort will be made to collect the samples necessary to evaluate the FPXRF technologies over the three concentration ranges, relative to all the target metals. If the some of the primary target metals do not provide sufficient distribution to allow evaluation over these concentration ranges, the data evaluation concerning these metals will be less thorough, however, PRC anticipates no problem in obtaining the desired sample distribution in the 100 to 1,000 mg/kg range. This range contains most of the FPXRF technology detection levels and environmental action levels for the target metals. If secondary target metals are not present at the desired concentrations or distributions, then these compounds may not be assessed.

Exact sample locations for the demonstration will be determined by the PRC field team leader in the field. These locations will not be permanently marked or recorded. Locations will be selected based on data and sampling maps obtained from previously written reports for both sites and from predemonstration sampling data. The PRC field team leader will ensure that the appropriate number of samples from each concentration range are collected. Since the confirmatory data will not be available to guide the sampling, the field team leader will use the FPXRF technology data to track the progress of sampling and the approximate concentration of the samples.

6.5.2 Soil Sampling Procedures

PRC will place plastic or fiberboard 4-inch by 4-inch squares at each sampling point at each site. These squares will be numbered and secured to the ground surface with wire anchors. Each square will also have an area for FPXRF operator sign-off to indicate that an operator's measurements have been completed at a given square. The ground surface within each square will be cleared of all living and dead organic matter and all rocks. The soil surface will then be smoothed to a level plane using a metal masonry trowel. At this point, the square sample location will be ready for the initial FPXRF in situ technology measurements. Once these measurements are complete at a sampling point, PRC will remove surface soil samples in the square areas to a 1-inch depth. The surface soil samples will be removed and collected by using a hand trowel or putty knife to scrape the soil surface. Sampling personnel will comply with all health and safety requirements in the HASP (Chapter 10). All soil sampling will be conducted according to the soil sampling procedures discussed in PRC SOP No. 5 "Soil Sampling at Hazardous Waste Sites." This material will be placed into a numbered plastic zip-lock bag. Before soils are homogenized, rocks, pebbles, sticks, organic matter, and foreign debris will be removed from the sample bag. Once the sample is placed in the sample bag, it will be handled as described in Section 6.1.

6.5.3 Sample Storage, Packaging, and Shipping

After collection and until analysis, all samples will be stored in coolers. Custody of samples will be maintained as discussed in Section 6.2 and according to the requirements of applicable sections of PRC SOP No. 18 "Sample Custody."

Samples to be shipped to the confirmatory laboratory will be packaged and shipped according to the sample packaging and shipment requirements of PRC SOP No. 19 "Packaging and Shipping Samples." Technical requirements for holding times for soil samples being analyzed for metals according to SW-846 methods have not been established. The recommended holding time prior to extraction and analysis is 6 months. For the purpose of this demonstration, the samples will be extracted and analyzed within 30 days of their receipt by the confirmatory laboratory. Analyzed samples will be stored for 90 days pending data reduction. If any samples are identified as outliers, those samples will be reanalyzed by a second confirmatory laboratory (QA laboratory). Outliers will be identified by statistical analysis (Chapter 7) or by failure to meet QA/QC requirements (Chapter 8.) The QA laboratory will be different from the original confirmatory laboratory, and it will be identified prior to the implementation of this demonstration plan. Analytical data produced by the QA laboratory will replace original confirmatory laboratory results if the QA laboratory meets all the QA/QC conditions specified in the QAPP.

6.5.4 Decontamination

Disposable clothing or sampling equipment coming into contact with grossly contaminated material will be double-bagged and handled as investigation-derived waste (IDW). IDW will be properly disposed of according to the requirements in the EPA "IDW Management Guidance Manual - Second Draft" (1990). EPA will be considered the generator of any IDW produced during this demonstration.

Only material that has come into contact with grossly contaminated material will be treated as IDW. Contamination avoidance practices will be used whenever possible to minimize the volume of IDW generated. Waste not coming into contact with grossly contaminated material will be disposed of in a local sanitary landfill.

Health and safety monitoring equipment will be bagged to prevent instrument contamination. The only open areas on the monitoring equipment will be at sample entry points.

Nondisposable sampling equipment will be decontaminated by scrubbing with an Alconox solution and water with a final water rinse. The sieves will undergo a dry brushing prior to the wet wash. Sieves will be oven dried before they are used again. If the wet decontamination method is not adequate to remove soil particles, a high-pressure hot water cleaning unit may be used for decontamination. All decontamination water will be contained in 30-gallon steel drums pending confirmatory analysis. Depending on the concentration of metals in the decontamination water, the water will either be disposed of at a local publicly owned treatment works or by a licensed hazardous waste disposal contractor.

6.5.5 Schedule

Demonstration activities are scheduled to start at the Asarco site on April 2, 1995. Demonstration activities will begin on April 17, 1995, at the RV Hopkins site. This demonstration should require 7 to 12 field days at each site.

TABLE 6-1

SAMPLE COLLECTION AND ANALYSIS STRATEGY

Step	Sample Preparation	FPXRF Analysis
1.	Mark a 4-inch by 4-inch square area with a plastic or fiberboard square. Clear loose rocks and organic matter from the soil surface. Conduct 10 replicate measurements at 10 percent of these areas.[a]	Conduct measurements over the entire square with the FPXRF in situ technologies. The data generated by each technology will be averaged to produce one measurement representative of the entire square.
2.	Remove the upper 1 inch of the soil within the square. Homogenize this material and verify degree of homogenization with fluorescein dye. Evenly distribute this material onto a 1-inch-deep, 4- by 4-inch square frame lined with wax paper. Conduct 10 replicate measures on the homogenized materials corresponding to the areas where replicate measurements were collected in Step 1.[a]	Conduct measurements over the entire square with the FPXRF in situ technologies. The data generated by each technology will be averaged to produce one measurement representative of the entire square.
3.	Place approximately 10 grams of the material described in Step 2 into a plastic analysis cup. Collect a sample aliquot for moisture content determination. Package approximately 20 grams of this material in a labeled polyethylene sample bottle.[b] Store this material until the microwave drying in Step 4. Conduct 10 replicate measures on the homogenized materials corresponding to the areas where replicate measurements were collected in Step 1 above.[a]	Analyze this material with each FPXRF intrusive technology. Attempt to use the same sample cup for each analysis.
4.	Dry the sample in a convection oven at 150 C for 2 hours. Then grind this material until 90 percent passes through a No. 40 sieve. Conduct 10 replicate measures on the homogenized materials corresponding to the areas where replicate	Analyze this material with each FPXRF intrusive technology. Attempt to use the same sample cup for each analysis. Submit approximately 20 grams of every sample to the confirmatory laboratory for extraction and analysis by SW-846 Methods 3050A and 6010A. Twenty

	measurements were collected in Step 1 above.[a] Collect field duplicates at a 1:10 ratio.[c] Dry splits from 10 percent of the sample material in a microwave oven on high for 5 minutes.[b] Analyze 10 to 12 PE samples for method accuracy check.	percent of these samples also will be extracted and analyzed by SW-846 Methods 3052 and 6010A. The field duplicates also will be submitted for these confirmatory analysis.[c] Submit the microwave dried samples for confirmatory analysis by SW-846 Methods 3050A and 6010A. Submit samples (unprepared) from the same locations already packaged in Step 2 above.[b] Submit all PE samples, double blind, for confirmatory analysis by SW-846 Methods 3050A and 6010A, and 3052 and 6010A. Archive approximately 20 grams of every sample for potential submittal to the QA laboratory.
5.	Analyze PE samples.[d]	Analyze these samples every 2 hours during at least one day with all the technologies. Record the ambient air temperature when these samples are analyzed.[d]

Notes:
[a] Precision determination data.
[b] Metals volatization check
[c] Homogenization check data.
[d] Calibration check and drift monitoring data.

TABLE 6-2

LIST OF FIELD EQUIPMENT NEEDED

Equipment

NIST SRMs
PE Samples
Stainless-steel garden trowels
Stainless-steel spoons
Polyethylene sample bottles (2 ounce)
Field forms
Clipboard
ASTM Type II water
Stainless-steel sprayers
Plastic bins
Disposable aluminum pans
Plastic sheeting
Aluminum foil
Tap water
Alconox

Plastic bags (Ziploc bags)
Permanent markers
Kimwipes
Field logbook
Sample labels
Wash tubs
Brushes
Sieves
Mortars and pestles
Microwave ovens
Wax Paper
Plastic frames
Fluorescein dye
Black light
No. 40 Stainless-Steel Sieve
Sieve Decontamination Station
Convection Oven

Shipping Equipment

Cooler chests
Tape (duct, packing, and Teflon)
Shipping forms
Shipping labels
Bubble wrap

Health and Safety Equipment

Disposable latex gloves
Disposable nitrile gloves
Tyvek coveralls
Cloth coveralls
Hard hats
Air-purifying respirators
AEP3 HEPA combination cartridge filters
Safety glasses
Steel-toe shoes
First aid kit
Disposable overboots
Miniram Model PDM-3

Photographic Equipment

35-mm camera
Film

Miscellaneous

Barricade tape (yellow, caution)
Paper towels
Garbage bags

XRF Chapter 7

EXPERIMENTAL DESIGN

7.0 EXPERIMENTAL DESIGN

This section discusses the objectives of the demonstration, the factors that must be considered to meet the performance objectives, and the statistical and other means that SNL will use to evaluate the results of the demonstration.

The primary objectives of this demonstration are to evaluate developer claims for the use of field transportable GC/MS technologies for use in the analysis of VOCs.

The following areas will be evaluated:

- Their performance relative to conventional analytical methods (e.g., confirmatory laboratory) accuracy and precision
- The logistical and economic resources necessary to operate these technologies in a field environment
- To obtain verified performance data on the GC/MS technologies that may be provided to potential technology users
- Verify performance claims

Secondary objectives for this demonstration are evaluating:

- Data quality
- Field portable GC/MS technologies for their reliability
- Ruggedness
- Cost
- Range of usefulness
- Ease of operation

7.1 Vendor Claims

7.1.1 Bruker-Franzen Analytical

1. <u>Air and water samples</u>--analysis time 8-10 minutes per sample; throughput time of 6 samples per hour

- Accuracy--35% of the confirmatory laboratory value
- Precision--30% RPD (Relative Percent Differences)
- Completeness--96%

2. <u>Soil samples</u>--analysis time 7-9 minutes headspace; throughput time of 7-8 samples per hour

- Accuracy--35% of the confirmatory laboratory value
- Precision--35% RPD
- Completeness--96%

3. Set-up time of instrument 60 minutes.

4. Shut-down time of instrument 5 minutes

5. Data presented after each sample run

7.1.2 Teledyne Electronic Technologies

1. Compact, lightweight, and easily transportable mass spectrometer. Low power consumption (will operate under battery power). No cooling water or other utilities required for field use.

2. Set up time for Ion Trap mass spectrometer system 30 min. or less.

3. Direct sampling inlet system is time and cost effective by elimination the need for extensive sample handling and pretreatment, the use of trapping sorbents, and expensive, bulky, gas chromatographic equipment.

4. Samples analyzed by Direct Sampling techniques at the rate of 1 sample every 10 min. or less.

5. MS Windows PC based data acquisition and storage system will produce stored sample data within 1 min. after sample run and quantitative results within 5 min. after sample run.

7.1.3 Viking Instruments Corporation

1. Precision--RPD < 25%

2. Accuracy--within 30% of confirmatory laboratory value

3. Completeness--95% of known target compounds detected.

4. Sample--throughput which depends on methodology. Samples requiring concentration may run for 30 minutes apiece. Direct injections average 10-15 min. apiece. Direct membrane analyses can be performed several times per minute.

5. Calibration--the instrument will be initially calibrated before arriving at the demonstration site and daily calibration samples will be analyzed.

6. Data--quantitative results will be submitted at the end of the demonstration. The data analysis software is also capable of full, detailed reports which include ion chromatograms, spectra, library searches, and calibration reports. Detailed data may be submitted when time permits.

7. Deployment--the Viking SpectraTrak can be set up and ready to run within 30 minutes.

7.2 Objectives

The primary objectives of this demonstration are to evaluate GC/MS technology in the following areas: (1) how well it performs relative to conventional analytical methods, (2) verify each developer's performance claims, and (3) the logistical and economic resources necessary to operate the technology. Secondary objectives for this demonstration are to evaluate GC/MS technology for its: (1) reliability, ruggedness, cost, and range of usefulness, and (2) data quality, and ease of operation. The performance will be compared to the performance of conventional analytical methods used in performing site characterization activities.

7.3 Factors to Be Considered

This section discusses factors that were considered in the design and implementation of the demonstration. These factors include comparability, precision, portability, ease of operation, ruggedness and instrument reliability, health and safety issues, sample throughput, and sample matrix effects. The importance of these factors and ways of measuring their effects are discussed when warranted.

7.3.1 Qualitative Factors

Some factors, while important, are difficult or impossible to quantify. These are considered qualitative factors. Important factors that cannot easily be quantified are the portability of a technology and the logistical requirements necessary for using it. The weight and size of each technology will be documented per developer's specifications. An evaluation of the logistical requirements will include an assessment of the technology's power source, operator's level of training, routine instrument maintenance, and the need for other equipment or supplies, such as a computer to operate the technology. Each operator will record notes in a field logbook on the logistical requirements for the technology.

Demonstration procedures will simulate routine field conditions as much as possible. For the purpose of this demonstration, vendors will supply their own personnel to set up and operate the field equipment. Operators will have prior experience with the GC/MS technologies they will use in the demonstrations.

7.3.2 Quantitative Factors

Many factors in this demonstration can be quantified by various means. These are quantitative factors. Some can be measured while others, such as the presence of interferants, cannot be controlled. These quantitative factors are discussed below.

One quantitative factor is instrument reliability or susceptibility to environmental conditions. One environmental factor is change in temperature. Temperature change effects will be monitored by conducting repeated measures of one or more media over the course of each day at the demonstration site. Air temperature will be recorded hourly during operation. SNL will use PE samples for this demonstration. This will produce data that can be used to identify trends in the effect of changing temperature on technology drift.

The cost of using GC/MS technology is another important factor. Cost includes expendable supplies such as helium, non-expendable equipment, labor, licensing agreements, operator training costs, and waste disposal costs. These costs will be tracked during the demonstration. The cost per sample will then be computed. Sample throughout will also be documented and will have an effect on cost per sample.

Technology performance relative to the confirmatory laboratory and the associated secondary sample quantitation objectives are the most important quantitative factors. These factors will be statistically evaluated. Instrument performance near detection limits and action levels is of great interest to potential users. To evaluate performance, all samples collected for the demonstration will be split between the GC/MS technologies and the confirmatory laboratory for analysis. Results from the confirmatory laboratory will be considered the reference values of the analytes in each sample. Where the duplicate samples exist, the concentrations for the duplicates will be averaged unless the QA/QC indicates a problem with one of the samples. The average concentration will represent the true value for the sample pair. If one or both samples in a pair exhibit a nondetect for a particular compound, that pair of data will not be used in the statistical evaluation of that compound.

Many analytical methods can have significant "operator effects" in which individual differences in operator technique have a significant effect on the numerical result. For the GC/MS technologies being demonstrated, the primary anticipated operator effect will be the variation in sample presentation to the developers and sample introduction which is instrument dependent. The potential also exists for this type of operator effect to occur in the confirmatory laboratory. To reduce the potential impact of measurement technique variation, SNL will use site specific personnel to conduct the sampling. Each technology will be operated by developer personnel.

The results from the technologies will be dependent on the quality of the data generated. Many factors could affect the quality of the data generated. The following factors will be used in determining GC/MS technologies' data qualities.
Method blanks will be used to evaluate technologies-induced contamination. An example of this

contamination is residual build-up of VOCs in the capillary column, or detector saturation from highly contaminated samples. Method blanks to be analyzed each day will consist of 99.9% nitrogen, soil blanks, and water blanks. Method blank results will be tabulated and discussed in the TER.

Calibration check samples will be analyzed to assess instrument drift. Accuracy will be assessed by analyzing two PE samples per media that contain known concentrations of VOCs. The PE samples for these samples are PE samples generated for the EPA Superfund Analytical Program. The soil gas samples will be NIST certified VOC standards. These samples will be analyzed by GEL at SRS and TA at WAFB using GC/MS SW-846 Method 8260. The data generated by the laboratory or established acceptance windows will be used to define mean concentrations and 95% confidence intervals for use in evaluating the accuracy of the GC/MS technology.

7.4 Sampling Design

As described in the sampling plan (Section 6), the basis for the experimental design of the demonstration is to validate/verify the performance of field transportable GC/MS technology. Two demonstration sites were chosen to accurately assess the GC/MS technology. Descriptions and site geology is described in Section 4.

The number of samples to be analyzed were determined using the following criteria:

- Number of samples needed to make a meaningful decision regarding the validity of the performance claims
- Cost for confirmatory laboratory analysis
- Time frame to conduct demonstration
- Through-put time needed per sample
- Personnel available to conduct demonstration

Number of samples to be analyzed at SRS is found in Table 3-1. Number of samples and concentration levels for WAFB is in Table 3-2.

7.5 Statistical Analysis

Guidance for Data Quality Assessment EPA QA/G-9 will be used. A specific protocol of statistical techniques to be used in the analysis of the demonstration data (Protocol II) is under development.

Statistical analysis will be performed on the data generated from the demonstrations. Basic statistical approaches to be used in this demonstration are comparison tests, variability, comparability, accuracy, and precision. Statistical calculations to be used for data analysis are found in Section 8.6.

XRF Chapter 8

QUALITY ASSURANCE PROJECT PLAN

The QAPP for this demonstration specifies procedures that will be used to ensure data quality and integrity. Careful adherence to these procedures will ensure that data generated from the confirmatory laboratory will meet the desired DQOs and will provide sound analytical results that can be used for a comparison with the data from the FPXRF technologies.

8.1 PURPOSE AND SCOPE

The primary purpose of this QAPP is to outline steps that will be taken by the confirmatory laboratory and by operators of the FPXRF technologies to ensure that data resulting from this demonstration is of known quality and that a sufficient number of critical measurements are taken. This QAPP also details the QA/QC criteria that will be used to validate the confirmatory laboratory results. According to the EPA EMSL statement of work for this demonstration, the demonstration is classified as a Category II project. This chapter of the demonstration plan addresses the key elements that are required for Category II projects prepared according to guidelines in the EPA guidance documents "Preparing Perfect Project Plans" (1989) and the "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans" (Stanley and Verner 1983).

The scope of the QAPP includes a comparison of FPXRF technology results to results generated by a confirmatory laboratory using EPA-approved methods. Each FPXRF operator will use a method specified by the developer. These methods may include written instructions and verbal directions. The confirmatory laboratory will use EPA SW-846 Method 6010A "Inductively Coupled Plasma-Atomic Emission Spectroscopy" for sample analysis. All samples will be extracted by EPA SW-846 Method 3050A "Acid Digestion of Sediments, Sludges, and Soils" prior to analysis by SW-846 Method 6010A. Thirty percent of the samples also will be extracted by SW-846 draft Method 3052 "Microwave Assisted Acid Digestion of Ash and Solid Waste."

Data generated by each FPXRF technology will be evaluated to determine the level of data quality it is capable of generating. Each FPXRF technology is expected to produce Level 1 or Level 2 data quality, which is expected to generally parallel, if not match, the results from SW-846 Method 6010A. Extraction methods SW-846 Method 3050A, draft Method 3052, and Method 6010A, can provide Level 3 data quality. Adherence to the QA/QC requirements of this QAPP will ensure that definitive level data quality is generated by the confirmatory laboratory.

8.2 QUALITY ASSURANCE RESPONSIBILITIES

The PRC project manager is responsible for coordinating the preparation of a QAPP for this demonstration and its approval by the EPA TPM and the developers. The PRC project manager will ensure that the QAPP is implemented during all demonstration activities. The PRC analytical QA manager for the demonstration will review and approve the QAPP and will provide independent QA oversight of all demonstration activities.

Samples will be collected and analyzed on site by the FPXRF technologies and off site by the confirmatory laboratory using EPA-approved methods. Many individuals will be responsible for sampling and analysis QA/QC throughout the demonstration. Primary responsibility for ensuring that sampling activities comply with the requirements of the sampling plan (Chapter 6) will rest with the PRC field team leader.

FPXRF operators will be responsible for following written and verbal directions given by the developer, for supplying information required for the preparation of the draft SW-846 method, recording observations in logbooks, and recording FPXRF data on the forms exhibited on Figures 8-1 to 8-4. QA/QC activities for each FPXRF technology will at least follow the recommendations of the developers. If PRC adds QA/QC measurements not required by the developers, PRC will document these measurements and the rationale for their addition. At this time, PRC anticipates adding additional QA/QC measurements, such as matrix blanks, precision determination measurements, and PE sample measurements, all of which are generally not included in a developer's instructions. The purpose for each of these additions is discussed in Chapters 6 and 7.

QA/QC activities for the confirmatory laboratory analysis of samples will be the responsibility of the confirmatory laboratory analysts, supervisors, and manager. If problems arise or any data appear unusual, they will be thoroughly documented and corrective actions will be implemented as specified in the confirmatory laboratory's QAPP and this demonstration QAPP. Many of the QA/QC measurements made by the confirmatory laboratory are dictated by the analytical methods being used. This QAPP includes additional QA/QC guidance which must be followed during the analysis of FPXRF demonstration samples.

8.3 DATA QUALITY PARAMETERS

The data obtained during the demonstration must be of sound quality for conclusions to be drawn on the FPXRF technologies, and to support the submission of a draft SW-846 method for FPXRF technologies. For all measurement and monitoring activities conducted for EPA, the agency requires that data quality parameters be established based on the proposed end uses of the data. Data quality parameters include five indicators of data quality referred to as the PARCC parameters: precision, accuracy, representativeness, completeness, and comparability.

High quality, well documented confirmatory laboratory results are essential for meeting the purpose and objectives of this demonstration. Therefore, the PARCC parameters, which will be used as indicators of data quality, will be closely evaluated to determine the quality of data generated by the confirmatory laboratory. In addition, the PARCC parameters will be utilized to evaluate the quality of data generated by each of the FPXRF technologies.

The following subsections detail each of the PARCC parameters and include specific QA/QC samples which will be used to evaluate the quality of data generated by the confirmatory laboratory and each FPXRF technology.

8.3.1 Precision

Precision refers to the degree of mutual agreement among individual measurements and provides an estimate of random error. Precision for this demonstration will be expressed in terms of the percent RSD between replicate sample measurements and the RPD of laboratory and field duplicate samples.

Precision for each FPXRF technology will be assessed with field duplicate samples and the analysis of replicate sample measurements, and through the use of PE samples. The field duplicate samples will provide precision data for the sample collection, field preparation, handling, and transportation procedures, as well as the FPXRF analysis precision. Replicate sample measurements will provide data for FPXRF analysis precision.

PE samples also will be used to determine FPXRF technology precision through the use of means, standard deviations, and RSDs for percent recoveries of each target metal in the PE samples. It is expected that between 10 to 12 PE samples will be submitted for analysis for each FPXRF technology during the course of the demonstration.

Precision for SW-846 Method 6010A will be assessed through field duplicate and laboratory duplicate samples. Laboratory duplicate samples will include pre- and post-digestion sample duplicate analyses. Pre-digestion laboratory duplicate samples will provide precision data for sample extraction and analysis activities. Post-digestion laboratory duplicate samples will provide precision data for analysis activities.

Method precision for each FPXRF technology and SW-846 Method 6010A will be evaluated. Instrumental precision data for each FPXRF technology will be evaluated through a RSD calculation for replicate sample measurements. Instrumental precision for SW-846 Method 6010A will be evaluated through post-digestion laboratory duplicate samples. Extraction and analysis precision of SW-846 Method 6010A will be evaluated through pre-digestion laboratory duplicate samples.

A comparison of the FPXRF precision to the SW-846 Method 6010A precision will be performed through the evaluation of field duplicate samples. Field duplicate sample RPDs will be statistically evaluated through determination of the RPD mean and through a one-sided student's T-test using the 95 percent confidence interval. The student's T-test will provide an upper control limit for RPD of demonstration field duplicate samples and will identify any outlier duplicate sample results. The field duplicate RPD upper control limit for each FPXRF technology can be compared to the field duplicate RPD upper control limit of the confirmatory laboratory for a comparison of precision. An additional statistical comparison of the FPXRF to the confirmatory laboratory precision can be performed through the use of a matched pair student's T-test, which compares the mean RPDs of the FPXRF field duplicate samples to SW-846 Method 6010A field duplicate samples. This statistical comparison can determine if there is a significant difference between the two means. If a significant difference does exist, an inference can be made which is that the lower mean value provides better precision.

PE samples also will be used to determine SW-846 Method 6010A precision through the use of means, standard deviations, and RSDs for percent recoveries of each target metal in the PE samples. It is expected that between 10 to 12 PE samples will be submitted for analysis using both SW-846 Methods 3050A and 3052 extraction procedures for SW-846 Method 6010A analysis during the course of the demonstration.

8.3.2 Accuracy

Accuracy refers to the difference between a sample result and the reference or true value for the sample. Bias, a measure of the departure from the complete accuracy, can be caused by such processes as errors in standard preparations, technology calibrations, incomplete extraction of the target analyte, loss of target analyte in the extraction process, interferences, and systematic or carryover contamination from one sample to the next.

Accuracy and bias will be assessed for the FPXRF technologies using data on method blank results and PE samples. Data quality parameters for accuracy of the FPXRF technologies in this demonstration will be method blank results which contain no target compounds above the method detection limits. Accuracy will also be evaluated through the use of PE samples. PE samples used during this demonstration will provide the best estimate of accuracy because they will represent the best estimate of target analyte concentrations in any of the samples analyzed during the demonstration. Accuracy for the PE sample results will be evaluated through the comparison of percent recoveries for each target analyte.

Accuracy and bias will be assessed for SW-846 Method 6010A using data on method blanks, instrument check standards, pre- and post-digestion matrix spike samples, and PE samples. Data quality parameters for accuracy in this demonstration will be method blank results which contain no target compounds above the method reporting limits, instrument check standard results which are within 10 percent of the expected recoveries, pre- and post-digestion spike recoveries which fall within accepted limits listed in SW-846 Method 6010A, and PE sample results which fall within acceptance limits as published in SW-846 Method 6010A or those generated through inter-laboratory analyses which have been published by EPA or by PE sample suppliers.

8.3.3 Representativeness

Representativeness refers to the degree to which the data accurately and precisely represents the conditions or characteristics of the parameter represented by the data. In this demonstration, representativeness will be ensured by executing consistent sample collection procedures, including sample locations, sampling procedures, sample storage, sample packaging, sample shipping, sample equipment decontamination, and proper laboratory subsampling (Chapter 6). Representativeness also will be ensured by using each method at its optimum capability to provide results that represent the most accurate and precise measurement it is capable of achieving. QC samples which will be used to evaluate representativeness during this demonstration include method blank samples, field duplicate samples and PE samples. These QC samples will be used for both the FPXRF technologies and SW-846 Method 6010A.

8.3.4 Completeness

Completeness refers to the amount of data collected from a measurement process compared to the amount that was expected to be obtained. For this demonstration, completeness refers to the proportion of valid, acceptable data generated using each method. The completeness objective for data generated during this demonstration is 95 percent.

8.3.5 Comparability

Comparability refers to the confidence with which one data set can be compared to another. A primary objective of this demonstration is to evaluate how well the FPXRF technologies perform in comparison to conventional analytical methods used by a confirmatory laboratory based on the experimental design discussed in Chapter 7. Additional QC for comparability will be achieved by analyzing QC samples and method blanks as discussed in Chapter 6 and by adhering to methods and SOPs for sample preparation and instrument operation. This will be performed through a Wilcoxon signed rank test of each FPXRF technology result to the SW-846 Method 6010A result. An evaluation of the detection limit achieved for the target metals by each FPXRF technology will be compared to the lower reporting limits (LRL) achieved by SW-846 Method 6010A for an additional check of comparability. Expected SW-846 Method 6010A LRLs for target metals identified during the demonstration activities is presented in Table 8-1.

Soil sample drying and homogenization will be performed prior to FPXRF technology and SW-846 Method 6010A analysis. Samples will be reported on an "as received" basis by both the FPXRF technology and SW-846 Method 6010A.

8.4 CALIBRATION PROCEDURES, QUALITY CONTROL CHECKS, AND CORRECTIVE ACTION

Calibration procedures, method-specific QC requirements, and corrective action associated with non-conformance QC for the FPXRF technologies and the SW-846 Method 6010A are described in the following subsections. Table 8-2 lists calibration procedures, method-specific QC requirements, and corrective action for SW-846 Method 6010A.

QC criteria for FPXRF technologies will be specified by each developer and are not available for tabulation, but will be noted by each technology operator and included in the TER, ITER, and the draft SW-846 method for FPXRF technologies. Primary target metals that will be determined using the FPXRF technologies and SW-846 Method 6010A include: arsenic, barium, chromium, copper, lead, and zinc. Secondary target metals for SW-846 Method 6010A include: nickel, cadmium, antimony, and iron. Other metals may also be reported by both the FPXRF technologies and SW-846 Method 6010A.

Some of the metals which may be reported by SW-846 Method 6010A can be affected by the extraction and analysis methods used. Antimony (a secondary target metal) and silver form insoluble precipitants when mixed with the hydrochloric acid used for the SW-846 Methods 3050A and 3052 extraction techniques. Mercury may also form insoluble precipitants when mixed with hydrochloric acid, and due to its volatility may be lost during sample extraction procedures. Antimony, silver, and mercury results provided by SW-846 Method 6010A using extraction Methods 3050A and 3052 may not meet all QA/QC criteria and can be coded and reported as estimated values.

QC requirements listed in Table 8-2 for initial and continuing calibrations, calibration verification standards, calibration blank standards, method blank samples, and LCSs must be met by the confirmatory laboratory. Corrective actions required for these QC requirements are listed in Table 8-2. Other QC requirements included in Table 8-2 pertain only to the primary target metals. These include pre- and post-digestion spike samples and pre- and post-laboratory duplicate samples. Corrective action required by the confirmatory laboratory when pre- and post-digestion spike and duplicate samples fall outside of the control limits for the primary target metals include: (1) reanalysis of the QC sample, (2) re-extraction and reanalysis of the QC sample, and if the re-extraction and reanalysis of the QC sample produces results which fall within the control limits, then (3) re-extraction and reanalysis of the QC sample and the batch of samples associated with the QC sample.

When re-extraction and reanalysis of the QC sample produces results which fall outside control limits, the QC sample and the batch of samples associated with the QC sample will be set aside and options for corrective action will be discussed and balanced with project needs, after all samples have been initially analyzed. When this occurs, the confirmatory laboratory QC manager must contact the PRC project manager. The PRC project manager will advise the EPA TPM of the situation and will coordinate with the EPA TPM and the confirmatory laboratory QC manager to determine specific options which may be employed to correct the problem.

The control limits for secondary target metals can be relaxed to those listed in SW-846 Method 6010A. If the QC control limits are exceeded for secondary target metals, corrective action must be taken one time. If this does not resolve the problem, the data from the two runs will be averaged for the secondary target metals in question and reported with data qualifiers identifying the data as estimated values.

It is expected that QC samples will be designated by PRC. Instructions for samples which require pre- and post-digestion spike samples and pre- and post-digestion laboratory duplicate samples will be included on sample chain-of-custody forms submitted to the confirmatory laboratory along with the samples. Pre- and post-digestion spike samples and pre- and post-digestion laboratory duplicate samples will all be performed on the same sample.

All QC samples and control limits listed in Table 8-2 and detailed in the following subsections will be used for all samples extracted with SW-846 Method 3050A and 3052.

8.4.1 Initial Calibration Procedures

Initial calibration for each FPXRF technology will be performed according to the developer's recommendation. The types of standards used and the acceptance criteria for the initial calibration or calibration curve also will be those recommended by the developer. These recommendations will be thoroughly documented by each observer and included in the TER, ITER, and the draft SW-846 method prepared for the FPXRF technologies.

The initial calibration for SW-846 Method 6010A consists of the analysis of three concentration levels of each target metal and a calibration blank. The low-level calibration standard will be at a concentration which defines the LRLs of the method. The remaining calibration standard levels will be used to define the linear range of the instrument. The initial calibration is used to establish calibration curves for each target analyte.

Accuracy of the initial calibration are verified through the use of a calibration blank, an initial calibration verification (ICV) standard, the reanalysis of the high level calibration standard, and the analysis of an interference check standard (ICS).

A calibration blank is used to establish technology responses to the reagents used for standard and sample preparation. An analysis of the calibration blank must show that no target metals are present at concentrations above the low-level standard, or above the result of multiplying the low-level standard by the ratio of the final volume of the sample extractant divided by the mass of the soil sample extracted. This blank also must show that interfering spectral lines are not present in the analytical system that may interfere with the quantitation of any target analyte in the standards or samples. Corrective action, which can be taken if the above criteria can not be met includes: (1) cleaning the analytical system according to developer's recommendations, (2) reanalyzing the calibration blank and calibration standards, and (3) re-preparation of calibration standards until the above criteria is met.

The validity of the initial calibration used for SW-846 Method 6010A is verified through the use of the ICV standards. The ICV is performed with each initial calibration performed. The ICV standard is obtained from a different source than the initial calibration standards, and is prepared at a concentration near the mid-level concentration of the initial calibration. The results of the ICV standard must be within 10 percent of the expected value. When results are greater than 10 percent of the expected value, the analysis must be halted and the source of the problem must be identified and corrected. Corrective action which must be taken if the above criteria cannot be met includes: (1) reanalysis of the initial calibration, (2) reanalysis of the ICV standard, and (3) re-preparation of the initial calibration and ICV standards.

Before sample analysis begins the high-level standard is again analyzed. Concentration values for this standard should not deviate by more than 5 percent of the expected value as determined from the initial calibration. If the deviation is greater than 5 percent, corrective action is required to find the source of the problem and to correct it. Corrective action which must be taken if the above criteria cannot be met includes: (1) reanalysis of the high-level calibration standard, (2) reanalysis of the initial calibration standards, and (3) follow manufacturer's recommendations for correction of the problem. A new initial calibration must then be analyzed along with the high-level standard check to ensure response deviations of less than 5 percent.

An ICS is analyzed to verify the accuracy of background correction used for spectral interferences. The ICS is analyzed along with each initial calibration and is used to evaluate appropriate correction factors used by SW-846 Method 6010A. The ICS includes known concentrations of interfering elements along with target compounds. QC criteria of the ICS is 80 percent recovery of each target compound in the ICS. Corrective action which must if the above criteria cannot be met includes: (1) reanalysis of the ICS, (2) reanalysis of the initial calibration, (3) re-preparation of the calibration standards.

8.4.2 Continuing Calibration Procedures

Continuing calibration checks for each FPXRF technology will be performed according to the developer's recommendation. The standard levels used and the acceptance criteria for continuing calibrations also will be those recommended by the developer. These recommendations will be thoroughly documented by each observer and included in the TER, ITER, and the draft SW-846 method prepared for the FPXRF technologies.

The validity of the initial calibration used for SW-846 Method 6010A is verified after the analysis of every 10 samples through a continuing calibration. The continuing calibration is performed with a calibration blank and a continuing calibration standard (CCS), which is the mid-level initial calibration standard. Requirements for the continuing calibration blank are the same as those of the initial calibration blank sample. The results of the CCS must be within 10 percent of the expected value. When results are greater than 10 percent of the expected value, the analysis must be halted and the source of the problem found and corrected. Corrective action which must be taken if the above criteria cannot be met includes: (1) reanalysis of the CCS, (2) reanalysis of the initial calibration standards, and (3) reanalysis of the ten samples analyzed prior to the CCS.

An ICS sample is analyzed after the analysis of 20 samples and is an ongoing check of instrumental interference. QC requirements of this ICS are the same as those listed in the initial calibration ICS.

8.4.3 Method Blanks

The analysis of method blanks by the FPXRF technologies will be performed as directed by the developers. If a developer does not require method blanks, PRC will add method blanks analysis to the field use of the technology. If PRC adds method blanks analysis to an FPXRF technology's operating procedure, the resulting data will not be used for corrective action, rather it will be used in the TER and ITER to explain strengths or weaknesses of a particular FPXRF technology.

Method blanks will be analyzed for SW-846 Method 6010A. Method blanks monitor laboratory-induced contaminants or interferences. Method blanks are analyzed with each batch of samples analyzed. A batch is defined as up to 20 samples of a similar matrix extracted and analyzed together. To be acceptable, a method blank must not contain any target compound above the LRLs. Corrective action that must be taken if the above criteria cannot be met includes: (1) reanalysis of the method blank sample, (2) re-preparation of the method blank and all associated samples extracted with the method blank, and (3) reanalysis of the method blank and all associated samples.

8.4.4 Laboratory Control Samples

LCSs will not be used for the FPXRF technologies unless their use is recommended by the developer. However, if the developer does recommend LCSs, their use will be performed following the developer's recommendations.

LCSs will be used for SW-846 Method 6010A. LCSs are a clean soil matrix to which a known concentration of target metals is added. The source of the target metals used for spiking must be from a different source than those used for calibration standards. LCSs are be prepared and analyzed in exactly the same manner as all other samples, and are prepared with each batch of up to 20 samples and are used to evaluate the precision of the analytical method. Control limits for LCSs are from 80 to 120 percent recovery. Corrective action that must be taken if the above criteria cannot be met include: (1) reanalysis of the LCS, (2) re-preparation of the LCS and all samples extracted along with the LCS, and (3) reanalysis of the LCS and all associated samples.

8.4.5 Matrix Spike Samples

Matrix spike samples will not be used for the FPXRF technologies unless their use is recommended by the developer. However, if the developer does recommend matrix samples, their use will be performed following the developer's recommendations.

Matrix spike samples will be performed for SW-846 Method 6010A and will be performed through the use of pre- and post-digestion spike samples. Pre- and post-digestion spike samples will be analyzed to assess the accuracy of SW-846 Method 6010A and to evaluate matrix effects of samples. Pre-digestion spike samples are samples to which a known concentration of target analytes are added prior to sample extraction. The pre-digestion spike sample are prepared and analyzed in exactly the same manner as all other samples, and can be used to evaluate the accuracy of the extraction and analysis process of the method. Post-digestion spike samples are samples which have been extracted in the same manner as other samples, but to which a known amount of target analytes have been added to the sample extractant. These samples are analyzed in the same manner as other samples and are used to evaluate the accuracy of the method without the losses incurred through the extraction process. Control limits for both pre- and post-digestion spike samples are from 80 to 120 percent recovery. Corrective action that must be taken if the above criteria cannot be met include: (1) reanalysis of the spiked sample, (2) re-extraction and reanalysis of the spiked sample, and if the re-extraction and reanalysis of the spiked sample produces results which fall within the control limits, then (3) re-extraction and reanalysis of the spiked sample and the batch of samples associated with the spiked sample. However, when re-extraction and reanalysis of the spiked sample produces results which fall outside of the control limits, the spiked sample and the batch of samples associated with the spiked sample will be set aside. The PRC project manager will then be contacted and advised of the situation. Final decisions on corrective action regarding samples outside the QA/QC control limits due to matrix efforts will be delayed until all samples have undergone initial analysis. These decisions will be based on project needs.

8.4.6 Performance Evaluation Samples

Between 10 and 12 PE samples will be purchased and submitted for analysis by both the FPXRF technologies and by SW-846 Method 6010A. These samples are very important to the demonstration because they will provide the only absolute check of method accuracy during the demonstration. PE samples which will be used during the demonstration will be SRMs supplied by NIST, the U.S. Geological Survey, or the Canadian Geological Survey. The PE samples are generally supplied with true value results and a statistical error range. PE samples will be submitted as double blind samples for both FPXRF technologies and for SW-846 Method 6010A. This means that the operator will not know that the sample is a PE sample and will not know the concentrations of target analytes in the samples.

FPXRF results of the PE samples will be compared to the published true value for each PE sample. The accuracy of each FPXRF technology will be assessed through a determination of the percent recovery for each target metal in each of the PE samples. Statistical evaluations of mean recoveries, standard deviations, and relative standard deviations will be utilized for each target metal to assess FPXRF accuracy.

SW-846 Method 6010A will be expected to provide percent recoveries of all target metals within the range of 80 to 120 percent recovery. Accuracy for SW-846 Method 6010A will be assessed through a determination of the percent recovery for each target metal in each of the PE samples. Statistical evaluations of mean recoveries, standard deviations, and relative standard deviations will be utilized for each target metal to assess SW-846 Method 6010A accuracy and precision. PE samples for SW-846 Method 6010A will be prepared for both extraction methods, SW-846 Methods 3050A and 3052. This will provide an absolute accuracy assessment of both extraction methods.

Because PE samples will be submitted as double blind samples, the corrective actions will not be initiated by the confirmatory laboratory. When confirmatory laboratory results are received for the PE samples, PRC will compare the results to the true values and acceptance ranges of each PE sample. When the SW-846 Method 6010A results fall outside of the acceptance ranges, PRC will request that the confirmatory laboratory re-extract and reanalyze the PE samples. This will be the only corrective action required.

8.4.7 Duplicate Samples

Two types of duplicate samples will be used during this demonstration to provide an evaluation of precision: field duplicate samples and laboratory duplicate samples. Field duplicate samples are the same sample which are collected in the field, but are submitted for analysis in separate sample containers. Field duplicate samples are used to provide an evaluation for the precision of sample collection, handling, transportation, as well as laboratory precision. One field duplicate samples will be submitted with each set of ten samples submitted for analysis. Laboratory duplicate samples are the duplicate analysis of the same sample. Laboratory duplicate samples are used to provide an evaluation of laboratory precision. One laboratory duplicate sample will be prepared and analyzed with each set of 20 samples submitted for analysis.

Field duplicate samples will be used by the FPXRF technologies to assess precision. Precision for field duplicate samples will be assessed through an RPD calculation of the original sample result compared to the field duplicate samples result. An additional precision measurement will be performed for each FPXRF technology through the use of replicate measurements. One replicate measurement will be performed for each ten samples submitted for analysis. A replicate measurement will be performed ten times on the same sample, and the mean, standard deviation, and relative standard deviation will be calculated. The replicate measurements will provide data on instrumental precision for each FPXRF technology.

Duplicate samples which will be used by the SW-846 Method 6010A to assess precision include field and laboratory duplicate samples. Precision for field duplicate samples will be assessed through an RPD calculation of the original sample result compared to the field duplicate samples result. Field duplicate samples will be used to measure total precision and will also be used to evaluate the adequacy of soil sample homogenization. The data generated from the analysis of field duplicate samples will be used to determine total precision and will be used to generate precision control limits for total precision.

Two types of laboratory duplicate analyses will be performed by SW-846 Method 6010A: pre- and post-digestion laboratory duplicate samples. Pre-digestion laboratory duplicate samples are two samples from the same sample jar that are extracted and analyzed, separately. Post-digestion laboratory duplicate samples are two analyses performed on the same sample extractant. Both, pre- and post-digestion laboratory duplicate samples will be evaluated through an RPD calculation. Control limits for both pre- and post-digestion laboratory duplicate samples will only be enforceable when both original and laboratory duplicate results are greater than or equal to 5 times the LRLs for each primary target metal. If matrix interferences make this control limit impractical, PRC may raise the lower level control limit to 10 times the LRLs. Control limits for RPD of pre-digestion laboratory duplicate samples are RPD values less than or equal to 20 percent. Control limits for RPD of post-digestion laboratory duplicate samples are less than or equal to 10 percent. Corrective action which must be taken when these control limits are not met include: (1) reanalysis of the duplicate sample, (2) re-extraction and reanalysis of the laboratory duplicate sample, and if the re-extraction and reanalysis of the laboratory duplicate produces results which fall within the control limits, then (3) re-extraction and reanalysis of the laboratory duplicate sample and the batch of samples associated with the laboratory duplicate sample. However, when re-extraction and reanalysis of the laboratory duplicate sample produces results which fall outside of the control limits, the laboratory duplicate sample and the batch of samples associated with the laboratory duplicate sample will be set aside. The PRC project manager will then be contacted and advised of the situation. Decisions regarding corrective action for these samples will be delayed until all samples have undergone initial analysis. Final decisions on corrective action for these samples will be based on project needs.

8.5 DATA REDUCTION, VALIDATION, AND REPORTING

To maintain good data quality, specific procedures will be followed during data reduction, validation, and reporting. These procedures are detailed below. These procedures will be implemented for FPXRF technology and confirmatory laboratory data.

8.5.1 Data Reduction

Data reduction will be performed by the operator performing the analyses. The FPXRF technologies and the confirmatory laboratory will produce data in field logbooks, hard copy spectrograms and reports, hard copy spreadsheet reports, and floppy disks or computer cassettes containing both spectroscopic data and spreadsheet data. This data will be reduced to produce a report detailing the analytical results. Data reduction will be performed following the formats and requirements of pertinent SOPs or the laboratory QA plan. This will include qualifying data that failed one or more of the QC checks and providing definitions for each code used.

The FPXRF technologies will produce results for individual target metals based on internal or external calibrations. The developers' procedures for calibration will be used during this demonstration. After calibration, the FPXRF technologies will produce direct readouts of analyte concentrations. No data conversions are necessary.

SW-846 Method 6010A will provide results for individual target metals. The results will be reported in units of milligrams per liter as determined from the calibration curve and any dilution factor employed. A general calculation to convert the solution concentration to the sample concentration for each target metal is shown below.

Concentration (as received) (mg/kg) = (C x V)/W (8-1)
where
C = concentration from regression equation based on initial calibration (mg/L)
V = final volume after sample preparation (L)
W = weight of sample as received (Kg)

This equation allows the final data to be reported in units of mg/kg (as received).

8.5.2 Data Validation

The operator will verify the completion of the appropriate data forms and the completeness and correctness of data acquisition and reduction. The confirmatory laboratory or field team leader will review calculations and inspect laboratory logbooks and data sheets to verify accuracy, completeness, and adherence to the specific analytical method protocols. Calibration and QC data will be examined by the technology operators and the confirmatory laboratory supervisor. Laboratory project managers and QA managers will verify that all instrument systems are in control and that QA objectives for accuracy, precision, completeness, and method detection limits on LRLs have been met.

Analytical outlier data are defined as those QC data lying outside a specific QC objective window for precision and accuracy for a given analytical method. Should QC data be outside of control limits, the confirmatory laboratory or field team leader will investigate the cause of the problem. If the problem involves an analytical problem, the sample will be reanalyzed. If the problem can be attributed to the sample matrix, the result will be flagged with a data qualifier. This data qualifier will be included and explained in the final analytical report submitted by the confirmatory laboratory.

8.5.3 Data Reporting

SW-846 Method 6010A analytical data will be reported using the confirmatory laboratory's standard data report forms. At a minimum, the forms will list the results for each sample and include detection limits, reporting units, sample numbers, results, and data qualifiers.

PRC also will request that all QC forms and raw analytical data be included in the final analytical report submitted by the confirmatory laboratory. This data will enable PRC to evaluate and determine the margin of error associated with SW-846 Method 6010A analytical data to obtain a fair comparison to the data produced by each FPXRF technology. The FPXRF technology data will be recorded on the appropriate forms shown on Figures 8-1 to 8-4. The preparation and packaging of samples will be logged on the forms shown on Figures 8-5 and 8-6.

8.6 CALCULATION OF DATA QUALITY INDICATORS

The following calculation will be used by all methods for determining precision for the confirmatory laboratory. This calculation is used to determine the precision between sample results and duplicate sample results.

RPD = [(A - B) / {(A + B)/2}] x 100 (8-2)
where
RPD = absolute relative percent difference
A = sample result
B = duplicate sample result

In the case of the FPXRF technologies, an RSD will be calculated to assess precision. The following equation is used to calculate an RSD.

RSD = (SD / mean concentration) x 100 (8-3)
where
RSD = relative standard deviation
SD = standard deviation
Mean concentration = average concentration of analyte in replicate sample measurements

Standard deviation is determined through the following calculation.

$SD = [\{ (x_i - \text{avg } x)^2\} / (n-1)]$ (8-4)
where
SD = standard deviation
= sum of
x_i = concentration of analyte in specific replicate sample
avg x = average concentration of analyte in all replicate samples
n = total number of replicate sample measurements

The following calculation is used to determine percent recovery which can be used to assess the accuracy of the analytical method. This calculation can be used to calculate post digestion spike recovery.

% Rec = [(amt. found in Sp - amt. found in sample) / amt. spiked] x 100 (8-5)
where
% Rec = percent recovery
amt. found in Sp = amount of analyte found in the spiked sample
amt. found in sample = amount of analyte found in the original sample
amt. spiked = amount of analyte added to the spiked sample

The following calculation is used to determine the LCS and PE recovery, which can be used to assess the accuracy of the analytical method.

% Rec = (conc. found / true value) x 100 (8-6)
where
% Rec = percent recovery
conc. found = concentration found in sample
true value = the true certified value as provided in the LCS documentation

8.7 PERFORMANCE AND SYSTEM AUDITS

The following audits will be performed during this demonstration. These audits will determine if this demonstration plan is being implemented as intended.

8.7.1 Performance Audit

A performance audit will be performed during this demonstration. PE samples will be ordered from a QC sample supplier and will be submitted to the confirmatory laboratory and to the FPXRF technologies for analysis. The control limits for the PE samples will be used to evaluate the FPXRF technology and confirmatory laboratory's method performance.

PE samples come with statistics about each sample, which have been derived from the analysis of the sample by a number of laboratories using EPA-approved methods. These statistics include a true value of the PE sample, a mean of the laboratory results obtained from the analysis of the PE sample, and an acceptance range for sample values. The confirmatory laboratory is expected to provide results from the analysis of the PE sample that fall within the QC sample supplier-generated acceptance limits. However, if the PE sample does not have acceptance ranges, then the acceptance ranges will be 80 to 120 percent of the true value concentration for each target analyte.

The FPXRF technologies will analyze the PE samples periodically during the demonstration. These samples will act as technology accuracy check samples. If the replicate measures on the check samples vary by more than recommended by the developer, the technologies will be recalibrated and the samples analyzed between the recalibrations will be reanalyzed.

8.7.2 On-Site System Audits

On-site system audits for sampling activities, field operations, and laboratories will be conducted as requested by the EPA TPM. These audits will be scheduled through the EPA TPM and separate audit reports will be completed by PRC after the audits.

8.7.3 Secondary QC Laboratory

This demonstration may use a secondary laboratory to check confirmatory laboratory results, only for SW-846 Methods 3050A and 6010A analyses that deviate significantly from results obtained with the FPXRF technologies. The secondary QC laboratory will analyze samples from the demonstration when all of the FPXRF technologies' results vary from the confirmatory laboratory's results by more than a factor of 10.

The secondary QC laboratory will use SW-846 Methods 3050A and 6010A for sample analysis. The samples sent to the secondary QC laboratory will be split samples collected concurrently with the initial confirmatory sample, and archived by PRC. The analytical result obtained from the secondary QC laboratory will be compared to the confirmatory laboratory result through an RPD calculation. It is expected that the confirmatory laboratory and the secondary QC laboratory results will not vary by more than a factor of 2, or an RPD value of 67 percent. When this occurs, the confirmatory laboratory result will be used for comparison to the FPXRF technology. When the confirmatory laboratory and the secondary QC laboratory results vary by more than 67 percent RPD, the secondary QC laboratory results will be used for comparison to the FPXRF technologies.

The secondary QC laboratory also will be required to analyze PE samples to establish its accuracy and will analyze field and laboratory duplicate samples to establish its precision. The secondary laboratory is required to comply with all QC parameters listed in Section 8.4.

8.8 QUALITY ASSURANCE REPORTS TO MANAGEMENT

QA reports provide management with the necessary information to monitor data quality effectively. It is anticipated that the following types of QA reports will be prepared as part of this demonstration project.

8.8.1 Monthly Reports

The PRC project manager will prepare monthly reports for the EPA TPM. These reports will discuss project progress, problems and associated corrective actions, and future scheduled activities associated with the demonstration. When problems occur, the PRC project manager will discuss them with the EPA TPM, estimate the type and degree of impact, and describe the corrective actions taken to mitigate the impact and to prevent a recurrence of the problems.

8.8.2 Audit Reports

Any QA audits or inspections that take place in the field or at the confirmatory laboratory while the demonstration is being conducted will be formally reported by the auditors to the PRC analytical QC manager and the PRC project manager who will forward them to the EPA TPM.

FIGURE 8-1

SAMPLE ANALYSIS RECORDING FORM FOR FPXRF IN SITU TECHNOLOGIES

Technology Name:
Circle One: Unprepared or Prepared

Sample Number	Analyte Concentration (mg/kg)									
	Antimony	Arsenic	Barium	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Zinc

FIGURE 8-2

SAMPLE ANALYSIS RECORDING FORM FOR PRECISION FPXRF IN SITU TECHNOLOGIES

Technology Name:
Circle One: Unprepared or Prepared

Sample Number	Analyte Concentration (mg/kg)									
	Antimony	Arsenic	Barium	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Zinc

FIGURE 8-3

SAMPLE ANALYSIS RECORDING FORM FOR FPXRF INTRUSIVE TECHNOLOGIES

Technology Name:
Circle One: Unprepared or Prepared

Sample Number	Analyte Concentration (mg/kg)									
	Antimony	Arsenic	Barium	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Zinc

FIGURE 8-4

SAMPLE ANALYSIS RECORDING FORM FOR PRECISION FPXRF INTRUSIVE TECHNOLOGIES

Technology Name:
Circle One: Unprepared or Prepared

Sample Number	**Analyte Concentration (mg/kg)**									
	Antimony	**Arsenic**	**Barium**	**Cadmium**	**Chromium**	**Copper**	**Iron**	**Lead**	**Nickel**	**Zinc**
Reading 1										
Reading 2										
Reading 3										
Reading 4										
Reading 5										
Reading 6										
Reading 7										
Reading 8										
Reading 9										
Reading 10										
Mean										
Std. Deviation										

FIGURE 8-5

SAMPLE PREPARATION TRACKING FORM

Sample No.	Grid Sample	Homog. All Samples	Field Duplicate 20 %	In Situ Analysis for All Samples	Intrusive Analysis for All Samples	Package 20 grams of All Samples for C.L.	Det. Water Content for All Samples	Microwave 10% of Samples	Convect. Oven Drying of All Samples	Det. Water Content for All Samples	Grind and Sieve All Samples

Notes:
Homog. Homogenized
C.L. Confirmatory Laboratory
Det. Determination

FIGURE 8-6

CONFIRMATORY LABORATORY SAMPLE PACKAGING TRACKING FORM

Sample Number	Date Packaged					
	10% of the Homogenized Sample[a]	All of the Prepared Sample	Field Duplicate Sample[b]	10% of the Microwave Dried	30% Labeled for Both SW-846 Methods 3050A and 3052	Other Samples (e.g., PE Samples)

Notes:
[a] These 10 percent must be from the same original sample.
[b] These samples must be collected at the rate of 1:10 and they must be evenly divided among soil texture and concentration ranges.

TABLE 8-1

SW-846 METHOD 6010A SOIL SAMPLE DETECTION LIMITS

Primary and Secondary Target Metals	Lower Reporting Limit[a] (mg/kg)
Antimony	6.4
Arsenic*	10.6
Barium*	5.0
Cadmium	0.80
Chromium*	2.0
Copper*	1.2
Iron	600
Lead*	8.4
Nickel	3.0
Zinc*	2.0

Notes:
[a] Lower reporting limit for extraction Methods 3050A and 3052 are expected to be similar.
* Primary target metal

TABLE 8-2

SW-846 METHOD 6010A CALIBRATION PROCEDURES, METHOD-SPECIFIC QC REQUIREMENTS, AND CORRECTIVE ACTION

QC Parameter	Frequency	Control Limits	Corrective Action
Initial Calibration Verification (ICV) Standard	With each initial calibration	10 percent of expected value	1. Reanalyze initial calibration 2. Re-prepare ICV standards 3. Re-prepare initial calibration standards
Continuing Calibration Standard (CCS)	After analysis of every 10 samples and at the end of analytical run	10 percent of expected value	1. Reanalyze CCS 2. Reanalyze initial calibration standards 3. Re-prepare initial calibration standards
Calibration Blank	With each continuing calibration, after analysis of every 10 samples, and at the end of analytical run	No target analytes above method detection limit	1. Reanalyze calibration blank 2. Reanalyze calibration standards 3. Re-prepare initial calibration standards and calibration blank
Interference Check Standards (ICS)	With every initial calibration and after analysis of 20 samples	80 percent recovery	1. Reanalyze ICS 2. Reanalyze initial calibration and ICS 3. Evaluate instrument for possible problems
High Level Calibration Check Standard	With every initial calibration	5 percent expected value	1. Reanalyze high level standard 2. Reanalyze initial calibration 3. Follow technology developers recommendations for correction
Method Blanks	With each batch of samples of a similar matrix	No target analytes above method detection limit	1. Reanalyze method blank 2. Re-prepare method blank 3. Re-prepare all associated samples

Laboratory Control Samples (LCS)	With each batch of samples of a similar matrix	80 to 120 percent recovery[a]	1. Reanalyze LCS 2. Re-prepare LCS and all associated samples 3. Perform new initial calibration
Pre-Digestion Matrix Spike Samples	With each batch of samples of a similar matrix	80 to 120 percent recovery[a]	1. Reanalyze pre-digestion matrix spike sample sample 3. Re-prepare all associated samples
Post-Digestion Matrix Spike Samples	With each batch of samples of a similar matrix	80 to 120 percent recovery[a]	1. Reanalyze post-digestion matrix spike sample 2. Re-prepare post-digestion matrix spike sample 3. Re-prepare all associated samples
Performance Evaluation (PE) Samples	As submitted during demonstration	80 to 120 percent recovery[a]	1. Re-prepare and reanalyze PE sample
Pre-Digestion Laboratory Duplicate Samples	With each batch of samples of a similar matrix	20 percent relative percent difference (RPD)[b]	1. Reanalyze sample and duplicate 2. Re-prepare sample and duplicate 3. Re-prepare all associated samples
Post-Digestion Laboratory Duplicate Samples	With each batch of samples of a similar matrix	10 percent relative percent difference (RPD)[b]	1. Reanalyze sample and duplicate 2. Re-prepare sample and duplicate 3. Re-prepare all associated samples

Notes:

[a] Stated control limits pertain only to primary target metals. Control limits for secondary target metals identified and quantified in SW-846 Method 6010A should fall within published control limits listed in SW-846 Method 6010A. If these control limits are not met, qualification of the data for these analytes may be performed.

[b] RPD control limits only pertain to original and laboratory duplicate sample results which are greater than or equal to 5 times the LRL.

XRF Chapter 9

DATA MANAGEMENT AND ANALYSIS

As part of this demonstration, PRC will establish a data management system that will include computerized data files and hard copy documentation, such as field and laboratory sheets and hardbound logbooks. This data management system will be used to store analytical data obtained from each technology and the confirmatory laboratory. This data management system will be used to conduct statistical analyses of the data as described in Chapter 7 and to verify that the data meets the data quality parameters established in Chapter 8.

This chapter describes the procedures that will be used for obtaining and entering data into this system and for analyzing the data after it has been entered.

9.1 LABORATORY DATA MANAGEMENT ACTIVITIES

All soil samples will be collected and documented as described in Chapter 6. Each sample will be labeled with a unique sample number assigned in the field. The sample number will include a three-digit, alpha-numeric code that will identify the sample number, as well as the site from which it was collected. Each sample will be submitted for analysis accompanied by a field sheet containing additional information about the sample. Once a sample has been submitted for analysis, data associated with the sample will be managed as described below.

9.1.1 Moisture Content Data Management

Samples collected for soil moisture analysis will be analyzed on site. A project-specific logbook will be used to document sample receipt for each sample submitted for analysis. Laboratory tracking will be performed by the operator responsible for sample analysis. Samples will be analyzed and the data obtained will be reduced, validated, and reported as described in Chapter 8. Sample result tables will then be transferred from the report forms generated by the operators to the computerized data management system by computer file transfer or by data entry transcription. In either case, all data transferred to the data management system will be checked for transcription errors before the actual statistical evaluation is performed.

9.1.2 Qualitative and Quantitative Analyses and Evaluations

Samples submitted for chemical analysis will be analyzed by a confirmatory laboratory. Each shipment of samples sent to the laboratory will be accompanied by a chain-of-custody form, which will be completed by the laboratory's sample custodian and returned to the PRC project manager. Samples will be entered into the laboratory's Laboratory Information Management System. This system tracks the progress of sample analysis within the laboratory and provides a reporting format for sample results. After samples are analyzed, the data will be reduced, validated, and reported as described in Chapter 8.

Validated sample results will be sent to PRC for entry into its data management system. In addition to sample results, PRC will request QA/QC summary forms for the confirmatory analysis. These forms will enable PRC to verify the quality of data generated by these methods. PRC will then transfer this data into its data management system. All data transcribed will be double-checked for accuracy in PRC's data management system.

9.1.3 Technology Data Management

The sample analysis methods for each technology differ from those used by the confirmatory laboratory.

The PRC operator assigned to each technology will record the technology sample number and corresponding confirmatory sample numbers. The PRC operators will be responsible for obtaining, reducing, interpreting, validating, and reporting data associated with their technology's performance. Each operator will be required to provide the PRC field team supervisor with copies of the results obtained from each sampling point, as well as any graphical data used for the delineation of site contamination. PRC will compare this data to the data generated by the confirmatory analysis.

The PRC operators also will be responsible for obtaining information about the assigned technology. This information will include a general description of the technology and how it is used in the field. Each PRC observer will take notes on specific aspects of the technology. These notes will be based on a checklist created for each technology before the demonstration activities begin. The checklist will provide information that will be used in the TER and ITER. In general, the checklists will contain the following items:

- Description of equipment used
- Logistical considerations including size and weight of technologies, power requirements, and other accessories needed, but not provided by the developer
- Historical uses and applications of the technology
- Estimated cost of the equipment or the cost of using the equipment
- Number of people required to operate equipment
- Qualifications of technology operator
- Training required for technology operator
- Description of data each technology can produce and a description of the operational mode required for producing this data
- Analytes which the technology can detect
- Approximate detection levels of each analyte
- Initial calibration criteria
- Calibration check criteria
- Corrective action used for unacceptable calibrations
- Specific QC procedures followed
- QC samples used
- Corrective action for QC samples
- Description of the number of samples that can be analyzed in one work day
- Description of the amount of time required for data interpretation
- Description of the reports and graphics that each technology will produce
- Specific problems or breakdowns occurring during the demonstration
- Matrix interferences found during the demonstration

The PRC operators will be responsible for reading the approved demonstration plan, as well as any other information submitted to PRC by the developers. A copy of the completed checklists will be included in the TER. Notes taken by each PRC operator will be documented in a hardbound logbook and will be used as a reference when preparing the TER and ITER.

XRF CHAPTER 10

HEALTH AND SAFETY PLAN

This chapter describes specific health and safety procedures PRC will use during the field work to be performed at the demonstration sites. The demonstration sites include the RV Hopkins site and the Asarco site.

The purpose of the HASP is to define the requirements and designate the protocols to be followed during the field work specified under Occupational Health and Safety Administration (OSHA) 29 CFR 1910.120(b) Final Rule. All PRC personnel, subcontractors, and visitors on site must be informed of site emergency response procedures and any potential fire, explosion, health, or safety hazards related to demonstration activities. A copy of the HASP will be provided to all PRC personnel, subcontractors, and site visitors who may be exposed to dangerous conditions during the demonstration.

This HASP must be reviewed and approved by the PRC health and safety director (HSD), the PRC project manager, and the EPA TPM. A HASP compliance agreement form must be signed by all field personnel before they enter site. Any revisions to this plan must be approved by the EPA TPM and the PRC HSD.

10.1 HEALTH AND SAFETY PLAN ENFORCEMENT

The PRC project manager, field site supervisor, HSD, and site health and safety officer (SHSO) will be responsible for implementing and enforcing the health and safety provisions of this HASP. Their duties are described in the following subsections.

10.1.1 Project Manager and Field Site Supervisor

The PRC project manager will ultimately be responsible for ensuring that all demonstration participants abide by the requirements of this HASP. The PRC field site supervisor will oversee and direct field activities, including subcontractor activities, and also is responsible for ensuring compliance with this HASP.

10.1.2 Health and Safety Director

The PRC HSD will be responsible for coordinating the technical aspects of the health and safety program. The HSD will act in an advisory capacity to the PRC SHSO and will report to the PRC project manager. Liaison with EPA representatives on matters relating to health and safety will be handled by the HSD or SHSO. The HSD will be responsible for maintaining up-to-date records of HASP-related documentation and HASP participants. HASP-related documentation will be maintained at PRC's Chicago office. This documentation will include the following:

- Documentation of the physician's examination of each employee (Section 10.10, Medical Surveillance)
- The training record for each employee who has completed the training necessary to perform his or her job
- Documentation of a fit test for each employee required to wear respiratory protection equipment meeting the requirements of OSHA 29 CFR 1910.134 and American National Standards Institute Z88.2-1980
- Task-specific air monitoring information (regarding drilling, drumming of waste, and other activities)
- Any employee who does not meet HASP requirements will not be allowed to conduct field work.

10.1.3 Site Health and Safety Officer

The PRC SHSO will be responsible for implementing and enforcing the requirements of this HASP in the field. The SHSO will have advanced field work experience and will be familiar with health and safety requirements specific to the demonstration. The SHSO will ensure that a Safety Meeting Sign-off Sheet is signed by all employees who are to perform field work, and that each employee complete a Daily Site Log before leaving the site.

10.2 VISITORS

All visitors to PRC operations at the site will be required to read the HASP and sign a compliance agreement form. Visitors will be expected to comply with relevant OSHA requirements. Visitors will also be expected to provide their own personal protection equipment (PPE) as required by the HASP.

Any visitors who do not adhere to the provisions of the HASP will be ordered to leave the work area. Visitors who have not met OSHA training and medical surveillance requirements will not be permitted to enter areas where exposure to hazardous materials is possible. Exceptions will be strongly discouraged, but they can be made on a case-by-case basis under the following conditions: (1) respirators are not required, (2) visitors' time on site is limited, (3) visitors are given a pre-entry briefing, (4) visitors are accompanied by trained personnel at all times, and (5) PRC SHSO approval is obtained.

10.3 DEMONSTRATION-SPECIFIC HAZARD EVALUATION

The hazards associated with this demonstration include worker exposure to heavy metals, exposure to weather extremes, physical hazards associated with work on active or abandoned industrial facilities, and exposure to x-rays associated with the FPXRF in situ technologies.

The hazardous materials expected to be present at the sites and a work task hazard analysis are provided in Tables 10-1 and 10-2. These elements are heavy metal contaminants in the surface soils. Therefore, the primary exposure pathway will be inhalation of contaminated dusts.

This demonstration will occur in early spring; therefore, the possibility for cold weather exists, particularly at the RV Hopkins site. In addition to cold exposure, it is possible that the demonstration team will be working during precipitation events. This coupled with the cold temperatures of the season present the possibility of workers experiencing hypothermia.

General hazards associated with active or abandoned industrial facilities include trip and fall hazards, surficial debris, unmaintained structures, and manufacturing processes themselves.

The primary hazard associated with the use of FPXRF technologies involves exposure to ionizing radiation. The FPXRF intrusive technologies have shielded radioactive sources; those sources remain shielded during sample analysis. This virtually eliminates the potential for operator exposure to ionizing radiation. The FPXRF in situ technologies have sources that are shielded until measurements are taken. During the measurement process, ionizing radiation is directed through the probe and into the matrix being analyzed. If an operator's body comes between the detector and the sample matrix during measurement, the operator will be exposed to ionizing radiation. This also will occur if the sample matrix is too thin to absorb all the ionizing radiation, and a portion of the radiation passes through the opposite side of a sample matrix. This is most likely to occur if the technologies are used on vertical surfaces, such as walls. In this case, an operator on the other side of the sample matrix has the potential for exposure to ionizing radiation. To eliminate this exposure potential, all measurements will be on horizontal surfaces. If the horizontal surface is above the ground surface, physical barriers will put in place to prevent operator contact with any ionizing radiation passing through the sample matrix.

10.4 EXPOSURE PATHWAYS

Exposure to heavy metal contaminants during field activities may occur through inhalation or ingestion of airborne contaminated dust, or dermal contact. Descriptions of these exposure pathways are provided below.

10.4.1 Inhalation

One possible exposure pathway for heavy metals contaminants during this demonstration will be through inhalation of airborne dust.

PRC personnel will monitor the concentrations of airborne dust in real-time with a dust monitoring instrument, such as a Miniram Model PDM-3.

Level D personal protection will generally be used, but when the monitoring instruments indicate potential problems, personal protection will be upgraded to Level C.

10.4.2 Dermal Contact

Dermal contact with contaminated soil may occur at both sites during demonstration activities. Dermal contact will be prevented with the use of PPE, such as inner and outer gloves. Safe personal protection procedures are described in Section 10.9.

10.4.3 Ingestion

Ingestion of heavy metals, although unlikely, may occur if personnel demonstrate a lack of proper hygiene or decontamination. Section 10.14.2 discusses safe work practices that may prevent ingestion of contaminated material.

10.5 HEALTH EFFECTS

This section describes the possible health effects of exposure to heavy metals. Health effect information has been determined by the National Institute for Occupational Safety and Health (NIOSH). Low, medium, or high levels of heavy metals may be encountered during sampling activities at the demonstration sites.

Acute symptoms of exposure to the heavy metals detected at the demonstration sites are listed in Table 10-1. Chronic symptoms of exposure to heavy metals such as lead, chromium, and cadmium include: histologic fibrosis of lungs, pulmonary edema, diarrhea, emphysema, anemia, and cancer.

Exposure to heavy metals in soil will be controlled through proper use of PPE and real-time air monitoring for airborne particles. The need for respiratory protection (air purifying respirators) will be based on real-time air monitoring results. If the concentration of airborne particles exceeds 0.3 milligrams per cubic meter (mg/m^3) as measured with a dust-monitoring instrument, the level of protection will be upgraded from Level D to Level C.

The OSHA permissible exposure limit for lead, the most toxic of the heavy metal constituents potentially present, is 0.03 mg/m^3. Given a worst-case scenario of 3 percent (30,000 mg/kg) lead in soil, the permissible exposure limit could be increased to 1 mg/m^3. Adding a safety factor of 2, PRC's action level for upgrading to Level C personal protection is 0.5 mg/m^3 total dust.

10.6 PHYSICAL HAZARDS

Physical hazards associated with sampling and other field activities present a potential threat to on-site personnel. Dangers are posed by utility and power lines, unseen obstacles, noise, cold, and poor illumination.

Injuries may result from the following:

- Accidents due to slipping, tripping, or falling
- Improper lifting techniques
- Moving or rotating equipment
- Equipment mobilization and operation (for example, electrocution from contact with overhead or underground power lines)
- Improperly maintained equipment

Injuries resulting from physical hazards can be avoided by adopting safe work practices and by using caution when working with machinery. Safe work practices to be used during all field activities are described in Section 10.14.2. To ensure a safe work place, the PRC SHSO will conduct and document regular safety meetings to make sure that all personnel are informed of any potential physical hazards related to the site.

10.7 TRAINING REQUIREMENTS

All PRC personnel, subcontractors, and site visitors who may be exposed to hazardous on-site conditions at the demonstration sites will be required to meet the training requirements outlined in OSHA 29 CFR 1910.120, which covers hazardous waste operations and emergency response. All PRC personnel, subcontractors, and visitors entering the site will be required to read this HASP and sign the compliance agreement form. All site workers will be required to sign a Safety Meeting Sign-off Sheet as well.

Before field activities begin, a briefing will be presented by the SHSO for all personnel who will participate in field activities. The following topics will be addressed during the briefing:

- Names of the PRC SHSO and the designated alternate
- Site history
- Hazardous chemicals that may be encountered during on-site activities
- Physical hazards that may be encountered on site
- Training requirements
- Levels of protection to be used for specific work tasks
- Work tasks
- Environmental surveillance equipment use and maintenance
- Action levels (Section 10.11.3, Monitoring Parameters) and identification of situations requiring an upgrade or downgrade in levels of protection
- Site control measures, including site control zones, communications, and safe work practices (Section 10.14)
- Emergency communication signals and codes
- Decontamination procedures
- Environmental accident emergency procedures (in case contamination spreads outside the exclusion zone)
- Personnel exposure and accident emergency procedures (in case of exposure to hazardous substances, falls, and other hazardous situations)
- Fire and explosion emergency procedures
- Emergency telephone numbers
- Emergency routes

Any other health- and safety-related topics that may arise before field activities begin also will be discussed at the briefing.

Issues that arise during implementation of field activities will be addressed during "tailgate" safety meetings to be held daily before the shift begins. Any changes in procedures or site-specific health- and safety-related matters will be addressed during these meetings.

10.8 PERSONAL PROTECTION REQUIREMENTS

PPE will be worn to protect personnel from known or suspected physical hazards, and air and soil contamination. The levels of personal protection to be used for work tasks have been selected based on known or anticipated physical hazards and concentrations of contaminants that may be encountered on site, and their chemical properties, toxicity, exposure routes, and contaminant matrices. The following sections describe levels of protection, protective equipment and clothing, limitations of protective clothing, duration of work tasks, and respirator selection, use, and maintenance.

10.8.1 Levels of Protection

Personnel will wear protective equipment when field activities involve known or suspected atmospheric contamination, when dust particles may be generated by field activities, or when direct contact with skin-affecting substances may occur. Full-face respirators will protect lungs, the gastrointestinal tract, and eyes against airborne contaminants. Chemical-resistant clothing will protect the skin from contact with skin-destructive and absorbable chemicals.

For this demonstration, the levels of protection and necessary components for each are classified under two categories according to the degrees of protection afforded:

- Level D: This level provides minimal protection against chemical hazards. Worn only as a work uniform; not to be worn in areas posing respiratory or skin hazards.
- Level C: Worn when the criteria described for Level C protection in Section 10.11.3 for using air-purifying respirators are met, and a lesser level of skin protection is needed.

Field activities for this demonstration will be conducted in Level D. The demonstration team will monitor the ambient air for airborne particles. If the concentration of airborne particles exceeds 0.3 mg/m^3, personnel will upgrade their level of protection to Level C.

10.8.2 Protective Equipment and Clothing

The following general levels of protection and the associated PPE ensembles have been selected for use by personnel during sampling and field screening activities (see Table 10-2, Work Task Hazard Analysis). Because the anticipated hazard level is low, field work will be performed using Level D protection. If site conditions or the results of air monitoring performed during field activities warrant Level C protection, all personnel will upgrade to Level C protection. Descriptions of equipment and clothing required for Levels D and C protection are provided below.

Level D

- Coveralls or work clothes, if applicable
- Steel-toed boots with shanks
- Hard hat (face shield optional)
- Disposable outer gloves (polyvinyl chloride or nitrile), if applicable
- Safety glasses or goggles
- Chemical-resistant clothing (Tyvek® or Saranex®), if applicable
- Disposable boot covers (when entering wet or muddy areas with known elevated contamination levels, such as previously excavated waste areas)
- Hearing protection (for areas with a noise level exceeding 85 decibels on the A-weighted scale)

Level C

- Coveralls or work clothes, if applicable
- Chemical-resistant clothing (Tyvek® or Saranex®)
- Outer gloves (neoprene or nitrile)

- Inner gloves (nitrile or polyvinyl chloride)
- Steel-toed boots with shanks
- Disposable boot covers or chemical-resistant outer boots
- Full- or half-face, air-purifying respirator with NIOSH- or OSHA-approved cartridges to protect against organic vapors, dust, fumes, and mists (cartridges will be changed at the end of each shift or at breakthrough, whichever occurs first)
- Safety glasses or goggles (with half-face respirator only)
- Hard hat (face shield optional)
- Hearing protection (for areas with a noise level exceeding 85 decibels on the A-weighted scale)

10.8.3 Limitations of Protective Clothing

PPE clothing ensembles designated for use during field activities have been selected to provide protection against contaminants at known or anticipated concentrations in soil. However, no protective garment, glove, or boot is entirely chemical-resistant, nor does any protective clothing provide protection against all types of chemicals. Permeation of a given chemical through PPE depends on contaminant concentrations, environmental conditions, the physical condition of the protective garment, and the resistance of the garment to the specific contaminant. Chemical permeation may continue even after the source of contamination has been removed from the garment.

To obtain optimum use from PPE, the following procedures will be followed by all personnel:

- When using Tyvek® or Saranex® coveralls, don a new, clean garment after each rest break or at the beginning of each shift.
- Inspect all clothing, gloves, and boots both before and during use for the following:
  - -- Imperfect seams
  - -- Nonuniform coatings
  - -- Tears
  - -- Poorly functioning closures
- Inspect reusable garments, boots, and gloves both before and during use for visible signs of chemical permeation such as the following:
  - -- Swelling
  - -- Discoloration
  - -- Stiffness
  - -- Brittleness
  - -- Cracks
  - -- Any sign of puncture
  - -- Any sign of abrasion

Reusable gloves, boots, or coveralls exhibiting any of the characteristics listed above must be discarded. PPE clothing used in areas with known or suspected elevated concentrations of contaminants should not be reused. Reusable PPE will be decontaminated according to the procedures described in Section 10.15 and will be neatly stored in the support zone away from work zones.

10.8.4 Duration of Work Tasks

The duration of field activities involving use of PPE will be established by the PRC SHSO or a designee and will be based on ambient temperature and weather conditions, the capacity of personnel to work in the designated level of PPE (taking into account such conditions as hypothermia), and the limitations of the PPE. All rest breaks will be taken in the support zone after decontamination and removal of PPE.

10.8.5 Respirator Selection, Use, and Maintenance

All PRC personnel and subcontractors taking part in field activities must fulfill worker provisions outlined in OSHA 29 CFR 1910.120. PRC and subcontractor personnel will be informed of the proper use, maintenance, and limitations of air-purifying respirators during the daily safety briefing, if applicable. All personnel must complete a qualitative fit test for the respirator to be used on site.

Respirator use is not anticipated at the demonstration sites. However, if respirator use becomes necessary, a full-face air-purifying respirator equipped with NIOSH- or OSHA-approved cartridges will be selected for use to protect against dust. Respirators will be selected by the PRC SHSO based on knowledge of the substances that may be present at the sites and the concentrations of compounds previously encountered at the sites. Air-purifying respirators will be used only when they can provide protection against the substances encountered at the sites.

Respirators will be inspected daily and any necessary repairs will be made during the time of inspection. Damaged respirators will be properly disposed of. Respirators issued to personnel will be cleaned and disinfected in the support zone at least weekly. When a respirator is used by more than one person, the respirator will be cleaned and disinfected after each use. After being cleaned, respirators will be placed in clean plastic bags and stored in the support zone. The following respirator inspection and cleaning procedures will be followed whenever respirator protection is used:

- Daily inspection and checkout procedures:
    -- Visually inspect the entire unit for obvious damage and deteriorated rubber.
    -- Inspect the face-piece harness for damage.
    -- Inspect the lens for damage and make sure the face piece has the proper seal.
    -- Pull the plastic cover off the exhalation valve and check the valve for debris and tears in the neoprene that could cause leakage.
    -- Unscrew the cartridges of both inhalation valves and visually inspect the neoprene valves for tears.
- Make sure the inhalation valves and cartridge receptacle gaskets are in place.
    -- Make sure a protective cover is attached to the lens.
    -- Make sure the speaking diaphragm retainer ring is hand-tight.
    -- Don the respirator, and perform a negative pressure test.
- Weekly cleaning procedures:
    -- Disassemble the respirator in the support zone by removing the cartridges, damaging them to prevent accidental reuse, and discarding them. To clean the respirator thoroughly, remove the inhalation and exhalation valves, speaking diaphragm, and any hoses.
    -- To clean the respirator, dissolve cleaning and disinfecting solution (usually provided by the manufacturer) in warm water in an appropriate tub. With gloved hands, swirl the respirator in the tub for at least 1 minute. A soft brush may be used to facilitate cleaning.
    -- Rinse the cleaned and disinfected respirator thoroughly with potable water to remove all traces of detergent and disinfectant. This step is very important in preventing dermatitis.
    -- Air dry the respirator on a clean surface. The respirator may also be hung upside down, but care must be taken not to damage or distort the face piece.
    -- Reassemble the clean, dry, respirator and inspect it in an area separate from the disassembly area to avoid contamination. Inspect the respirator carefully for detergent or soap residue left by inadequate rinsing. Residue appears most often under the seat of the exhalation valve and can cause valve leakage or sticking.
- Procedures to follow after routine use in the exclusion zone:
    -- Wash and rinse the respirator in the support zone with soap and warm water.
    -- At a minimum, wipe the respirator with disinfectant wipes that have been soaked in benzoalkaloid or isopropyl alcohol. Allow the respirator to air dry in the support zone.

The effectiveness of the respiratory protection program will be continuously monitored by the PRC SHSO or designee. Monitoring of worker stress levels during activities that require respiratory protection will also be performed by the SHSO or designee.

10.9 MEDICAL SURVEILLANCE

The following sections describe PRC's medical surveillance program, including health monitoring, documentation and record keeping, and medical support and follow-up requirements. This program will be followed for all field activities during this demonstration.

10.9.1 Health Monitoring Requirements

All PRC and subcontractor personnel involved in field activities at the demonstration sites must participate in a health monitoring program, as required by OSHA 29 CFR 1910.120(f). PRC has established a health monitoring program with Environmental Medicine Resources, Inc., of Atlanta, Georgia. Under this program, PRC personnel receive annual or biennial physical examinations consisting of the following:

- A baseline medical examination that includes the following:
  - Completion of a personal, family, and environmental history questionnaire
  - Physical examination
  - Vision screening
  - Laboratory tests
  - Audiometric screening
  - Pulmonary function test
  - Resting electrocardiogram
  - Chest x-ray (required once every 3 years)
- A complete blood count that includes the following:
  - White blood count
  - Red blood count
  - Hemoglobin test
  - Hematocrit test
  - Liver function test
  - Kidney function test
  - Lipid metabolism test
  - Carbohydrate metabolism test
- A urinalysis that includes the following:
  - Sugar content test
  - Albumin content test
  - Specific gravity test
- Laboratory chemistries for the following:
  - Cholinesterase
  - Coproporphyrin and uroporphyrin
  - Arsenic
  - Cadmium
  - Iron

PRC receives a copy of the examining physician's written opinion after post-examination laboratory tests have been completed. PRC employees also receive a copy of the written opinion. This written opinion includes the following information (according to 29 CFR 1910.120(f)(7)):

- The results of the medical examination and tests.
- The physician's opinion on whether or not the employee has any medical conditions that might place the employee at an increased risk of health impairment from work in hazardous waste operations or during an emergency response.
- The physician's recommended limitations, if any, on the employee's assigned work. Special emphasis is placed on fitness for duty, including the ability to wear any required PPE under conditions expected on site (for example, temperature extremes).
- A statement that the employee has been informed by the physician of the medical examination results and of any medical conditions that require further examination or treatment.

10.9.2 Documentation and Record keeping Requirements

PRC's Chicago office will maintain medical surveillance records for each PRC employee performing hazardous waste site activities. These records will be in compliance with OSHA 29 CFR 1910.120(f). The records also will be maintained at Environmental Medicine Resources in Atlanta, Georgia. Any visitor or observer at the site will be required to provide records in compliance with OSHA 29 CFR 1910.120(f) before entering the site. PRC will be responsible for recording and reporting accidents, illnesses, and injuries involving PRC employees in accordance with OSHA 29 CFR 1910 and 1926 and EPA requirements. A copy of this information will be added to PRC's medical surveillance records in the event of a reportable accident, illness, or injury.

10.9.3 Medical Support and Follow-up Requirements

PRC personnel will be required to seek medical attention and physical testing in the event of injury or possible exposure above established exposure limits. Depending on the type of injury or exposure, follow-up testing, if required, must be performed within 24 to 48 hours of this incident. The type of test to be performed to monitor exposure effects will be based on the circumstances involved and will be selected by a qualified health professional from Environmental Medicine Resources.

10.10 ENVIRONMENTAL SURVEILLANCE

Air monitoring will be performed during designated sampling and other field activities to protect personnel against exposure to airborne hazardous substances and to determine appropriate levels of PPE for work tasks. The following sections discuss initial air monitoring, periodic air monitoring, monitoring parameters, use and maintenance of survey equipment, and cold stress monitoring.

10.10.1 Initial Air Monitoring

Initial air monitoring of the work area will be performed before beginning site activities. This monitoring will be performed using real-time field survey instrumentation, such as a Miniram Model PDM-3, to determine the concentrations of airborne dust particles. Airborne dust concentrations also will be monitored at the beginning of each work day to identify background contaminant concentrations and to detect any potentially hazardous situation that might have developed during off-shift periods.

10.10.2 Periodic Air Monitoring

Periodic air monitoring will be performed during all site activities. This type of monitoring will be performed as a minimum requirement when the following situations arise:

- Work begins on a different portion of the site
- Workers experience physical difficulties

Required survey instrumentation, sampling procedures, and monitoring procedures are specified in Section 10.11.3. Sampling methods will be subject to review by the PRC SHSO.

10.10.3 Monitoring Parameters

Air monitoring for dust particles will be performed at shoulder height (in the breathing zone) on personnel most likely to be exposed to potentially hazardous concentrations of contaminants. The following instrument and monitoring frequency may be used to monitor for dust particles during site activities:

Instrument: Miniram Model PDM-3

Activity: Direct Real-Time Air Monitoring

Monitoring Frequency: Monitoring will occur continuously during field activities. Miniram readings will initially be recorded in the field logbook every hour. If continued monitoring does not indicate the presence of dust at or above 5 mg/m^3, readings may be recorded every 2 hours or longer based on the PRC SHSO's review of the monitoring data collected.

The OSHA permissible exposure limit for lead is 0.03 mg/m^3. Given a worst-case scenario of 3 percent (30,000 mg/kg) lead in the airborne particulates, the permissible exposure limit could be increased to 1 mg/m^3. Adding a protection factor of 2, the action level drops to 0.5 mg/m^3 total dust.

General action levels
-- **Situation**: Concentration of dust below 0.5 mg/m^3
Action: Continue investigation at Level D without respiratory protection and continue monitoring
-- **Situation**: Concentration of dust at or above 0.5 mg/m^3
Action: Notify PRC SHSO; upgrade to Level C protection and continue work unless otherwise specified

10.11 USE AND MAINTENANCE OF SURVEY EQUIPMENT

All personnel using field survey equipment will be briefed on its operation, limitations, and maintenance by the PRC SHSO. Maintenance and calibration will be performed according to manufacturer guidelines by a designated individual familiar with the devices. Repairs, maintenance, and routine calibration of this equipment will be recorded in an equipment maintenance logbook that will be signed by the trained service technician. The equipment maintenance logbook for each piece of equipment will be kept in the carrying case for that equipment.

Air monitoring equipment, such as the Miniram, will be calibrated before work begins. Only routine maintenance (such as changing batteries and cleaning the optical chamber) will be performed by field personnel. Any additional maintenance will be performed by a trained service technician.

10.12 COLD STRESS MONITORING

Cold stress may be of particular concern when a wind chill-adjusted temperature of 10 F or less is expected. The following guidelines describe different forms of cold stress, conditions under which cold stress may occur, and preventative measures:

Personnel working outdoors in temperatures at or below freezing may be frostbitten. Working in extreme cold even for a short time may cause severe injury to the surface of the body or may result in profound generalized cooling, causing hypothermia and possibly death. Areas of the body that have a high surface area-to-volume ratio, such as ears, fingers, and toes are most susceptible to frostbite.

Local injury from cold is included in the generic term "frostbite." Frostbite symptoms can be categorized according to the following degrees of severity:

-- Frostbite nip or initial frostbite is characterized by sudden blanching or whitening of the skin.
-- Superficial frostbite causes the skin to have a waxy appearance and to be firm to the touch while the tissue underneath is resilient.
-- Deep frostbite causes tissues to be cold, pale, and solid. This degree of frostbite is extremely serious.

Systemic hypothermia manifests itself in five stages of symptoms: (1) shivering; (2) apathy, listlessness, sleepiness, and sometimes rapid cooling of the body to less than 95 F; (3) unconsciousness, glassy eyes, and slow respiration and pulse; (4) freezing of the extremities; and (5) death.

Trench foot or immersion foot occurs when feet are kept cold and wet for an extended period of time. Feet become pale, cold, and possibly pulse less. During recovery, feet become red, hot, and swollen from excessive blood flow.

Ambient temperatures and wind velocity influence the development of a cold injury. Wind chill (the chilling effect of moving air) should be taken into consideration along with the air temperature when determining whether or not outdoor work is safe.

When chemical-resistant equipment is removed and the clothing underneath is perspiration-soaked, the body cools very rapidly. Workers should therefore avoid removing equipment until they are in a warm area.

Thermal socks, long cotton or thermal underwear, hard-hat liners, and other cold-weather gear can help prevent hypothermia.

Blankets, warm drinks (other than captivated coffee), and warm rest areas are essential.

The following chart contains general guidelines that can be used to monitor cold weather field work:

Cooling Power of Wind on Exposed Flesh Expressed as Equivalent Temperature
Estimated Wind Speed (in miles per hour [mph])
Actual Temperature Reading (F)

calm	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60
5	48	37	27	16	6	-5	-15	-26	-36	-47	-57	-68
10	40	28	16	4	-9	-24	-33	-46	-58	-70	-83	-95
15	36	22	9	-5	-18	-32	-45	-58	-72	-85	-99	-112
20	32	18	4	-10	-25	-39	-53	-67	-82	-96	-110	-121
25	30	16	0	-15	-29	-44	-59	-74	-88	-104	-118	-133
30	28	13	-2	-18	-33	-48	-63	-79	-94	-109	-125	-140
35	27	11	-4	-20	-35	-51	-67	-82	-98	-113	-129	-145
40	26	10	-6	-21	-37	-53	-69	-85	-100	-116	-132	-148

(Wind speeds greater than 40 mph have little additional effect.)

LITTLE DANGER in less than 1 hour with dry skin; maximum danger from false sense of security
INCREASING DANGER from freezing of exposed flesh within 1 minute
GREAT DANGER that flesh may freeze within 30 seconds
Trench foot may occur at any point on this chart.

SOURCE: MODIFIED FROM AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS 1993-1994.

In addition to cold stress preventative measures, personnel will be briefed on the dangers of cold stress and frostbite. Personnel will be monitored by the PRC SHSO during all rest periods and site activities for signs of hypothermia or frostbite. Self-monitoring and peer monitoring will be encouraged.

10.13 SITE CONTROL

Work areas on or near the demonstration sites will, depending on results of environmental monitoring, be divided into three zones: an exclusion zone, a contamination reduction zone (CRZ), also known as decontamination zone, and a support zone. Generally, the exclusion zone will be designated by barricade tape or traffic cones. Access to a contaminated exclusion zone will be through the CRZ, and it will be restricted to authorized personnel. The support zone will be the area where supplies are staged and samples are packaged. A daily roster with the date of each person's entrance into the contaminated zone; the person's name, signature, and organization; the time of entry; and the time of exit will be kept for all personnel working in such an area. Any visitors to the area must present proper identification and be authorized to be on site. Visitors must comply with all provisions of this HASP. The PRC SHSO will identify work areas that visitors or personnel are authorized to enter and will enforce site control measures. The following subsections discuss site control zones, safe work practices, HASP enforcement, and complaints.

10.13.1 Site Control Zones

The PRC SHSO will establish site control zones after initial monitoring of site conditions. Should the conditions change during field activities, the SHSO will reevaluate the current site control zones and establish new zones, if necessary.

10.13.2 Safe Work Practices

Safe work practice requirements for field activities will include the following:

All personnel will enter a designated exclusion zone only through the contamination reduction corridor. All personnel leaving an exclusion zone must exit through the contamination reduction corridor and undergo the CRZ decontamination procedure.

Only equipment necessary to complete sampling will be permitted within an exclusion zone. All nonessential equipment will remain within the support zone.

All personnel will avoid contact with potentially contaminated substances. Walking through puddles or mud and kneeling on the ground will be avoided whenever possible.

Equipment will not be placed on potentially contaminated surfaces.

Food and beverages will not be permitted in the exclusion zone or CRZ. Possession or use of tobacco products and application of cosmetics also are prohibited in these areas.

Matches and lighters will not be permitted in the exclusion or CRZ zones.

During rest periods, all personnel will be required to observe each other for signs of toxic exposure and heat stress. Indications of adverse effects include, but are not limited to, the following:

-- Changes in complexion and skin discoloration
-- Changes in coordination
-- Changes in demeanor
-- Excessive salivation and pupillary response
-- Changes in speech patterns

Personnel will inform each other of nonvisual effects of illness, such as the following:

-- Headache
-- Dizziness
-- Nausea
-- Blurred vision
-- Cramps
-- Irritation of eyes, skin, or the respiratory tract

The following paragraphs describe safe work practices regarding avoidance of trip and fall hazards, performance of activities near utility and power lines, avoidance of excessive noise exposure, illumination, sanitation, working near bodies of water, and site housekeeping.

Avoidance of Trip and Fall Hazards

Personnel will be informed of any potential trip and fall hazards during regular health and safety meetings. Whenever possible, trip and fall hazards will be eliminated or clearly identified with yellow caution tape.

Field Activities Near Utility and Power Lines

Field activities will proceed with caution in any area where historical data or instrument surveys indicate the presence of utility lines (such as gas, telephone, water, and other lines). All field activity locations will be coordinated by the PRC project manager.

The demonstration sites have overhead power lines in certain areas of the sites. The PRC project manager and PRC SHSO will be responsible for ensuring that field activities, especially drilling or probing, will not place equipment or personnel near power lines. However, if site activities near power lines are required, necessary arrangements to turn off the power will be coordinated by the PRC project supervisor.

Illumination

Outdoor work will not be performed after sunset or when a lack of natural illumination makes outdoor work difficult.

Sanitation

Potable water, drinking cups, nonpotable water, toilet facilities, washing facilities, and other sanitation requirements will be provided in compliance with specifications of OSHA 29 CFR 1910.120(n).

Site Housekeeping

Potentially hazardous wastes generated during field activities will be drummed, if necessary, and handled in accordance with RCRA requirements. Nonhazardous waste and debris will be disposed of as standard municipal waste.

10.13.3 Health and Safety Plan Enforcement

The PRC SHSO will be responsible for enforcement of the HASP during field sampling activities. Personnel who fail to follow HASP procedures will face disciplinary action that may, at a maximum, include dismissal from the site.

At least one copy of this HASP will be available to all personnel at all times. Any necessary changes in HASP procedures will be made at the beginning of each work day by the SHSO.

10.13.4 Complaints

Personnel will be encouraged to report to the PRC SHSO any conditions or practices that they consider detrimental to their health or safety or that they believe are in violation of applicable health and safety standards. Such complaints may be made orally or in writing. Personnel who believe that an imminent danger threatens human health or the environment will be encouraged to bring the matter to the immediate attention of the SHSO for resolution.

10.14 DECONTAMINATION

Decontamination is the process of removing or neutralizing contaminants from personnel or equipment. When properly conducted, decontamination procedures protect personnel from contaminants that may have accumulated on PPE, tools, and other equipment. Proper decontamination also prevents transport of potentially harmful materials to unaffected areas. Personnel and equipment decontamination procedures are described in the following subsections.

10.14.1 Personnel Decontamination

Minimal personnel decontamination is anticipated at the demonstration sites because disposable PPE will be used. If necessary, personnel decontamination will be completed according to the guidance given in the "Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities" (Department of Health and Human Services 1985). Personnel and PPE will be decontaminated with potable water or a mixture of detergent and water. Liquid and solid wastes produced during decontamination will be collected and drummed.

The following decontamination procedures will be conducted if personnel decontamination is required:

Wash neoprene boots (or disposable booties) with a Liquinox® or Alconox® solution, and rinse them with water. Remove and retain neoprene boots for reuse, if possible. Place disposable booties in plastic bags for disposal.

Wash outer gloves in a Liquinox® or Alconox® solution and rinse them in water. Remove outer gloves and place them in a plastic bag for disposal.

Remove the Tyvek® or Saranex® suit and place it in a plastic bag for disposal.
Remove the air-purifying respirator, if used, and place the spent filter in a plastic bag for disposal. The filter may be changed daily or at longer intervals, depending on the use and application. Clean and disinfect the respirator with towelettes or a non-phosphate cleaning solution. Place it in a plastic bag for storage.

Remove inner gloves and place them in a plastic bag for disposal.

Thoroughly wash hands and face with water and soap.

Used, disposable PPE will be collected in plastic bags and placed in fiberboard drums and disposed of as municipal waste, unless otherwise specified. Further personnel decontamination procedures may be established as needed.

10.14.2 Equipment Decontamination

Decontamination of all nondisposable sampling and field monitoring equipment used during field activities will be required. The equipment decontamination procedures described in the following paragraphs are based on guidelines appropriate for low-level contamination. When appropriate, Liquinox® or Alconox® cleaning solutions and deionized water rinses will be used to decontaminate equipment. Wastewater from equipment decontamination activities will be placed in a 55-gallon drum. A representative sample will be collected from the wastewater and analyzed for contaminants of concern before a decision regarding its disposal is made.

Sampling Equipment

Sampling equipment, such as stainless-steel spades, spoons, and stainless-steel or aluminum pans, will be decontaminated before and after each use. Potable water will be used for the following sampling equipment decontamination procedures:

Scrub the equipment with a brush in a bucket containing Liquinox®, or Alconox® solution and potable water.

Triple-rinse the equipment with water, and allow it to air dry.

Reassemble the equipment and place it in a clean area on plastic.

Field Monitoring Equipment

A Miniram Model PDM-3 will be used for monitoring concentrations of dust in the atmosphere. This equipment will be cleaned daily by wiping it with isopropyl alcohol. Also, the equipment will be kept in a bag to minimize the exposure to the dust.

10.15 EMERGENCY CONTINGENCY PLANNING

The PRC SHSO will be notified of any on-site emergencies and will be responsible for ensuring that appropriate emergency procedures are followed. Standard emergency procedures to be used by personnel are described in the following subsections. All subcontractors, developers, and visitors will be informed about emergency procedures and the location of the nearest hospital. A copy of this HASP will be available to all personnel before field work begins.

10.15.1 Injury in the Exclusion or Contamination Reduction Zones

In the event of an injury in the exclusion or CRZ zones, all personnel will exit the exclusion zone and assemble at the decontamination line, and the PRC SHSO will be immediately notified if necessary. The SHSO will contact the PRC HSD, and together they will evaluate the nature and extent of the injury. The affected person will be decontaminated to the extent practical before being moved to the support zone. Appropriate first aid procedures will be performed, an immediate request for an ambulance will be made (if necessary), and the designated medical facility will be notified (if necessary). Emergency numbers for each site are provided in Section 10.16.5. No personnel will re-enter the exclusion zone until the cause of injury or illness is determined and re-entry is considered safe. In case of severe injury, the PRC SHSO will implement procedures to minimize the possibility of further injury. If the need to transport the patient to a medical facility supersedes the need to decontaminate the patient, the medical facility will be notified that the patient has not been decontaminated before the patient arrives. Documentation requirements are outlined in Section 10.10.2.

10.15.2 Injury in the Support Zone

If an injury occurs in the support zone, the PRC SHSO will be notified immediately. Appropriate first aid will be administered and, if necessary, the injured individual will be transported to the designated medical facility. If the injury does not affect the safety or performance of site personnel, operations will continue. Documentation requirements are outlined in Section 10.10.2.

10.15.3 Fire or Explosion

In the event of a fire or explosion at the site, the local fire department will be contacted as soon as possible, and an evacuation of the site will begin immediately.

10.15.4 Protective Equipment Failure

If personnel in the exclusion zone experience a failure of protective equipment that affects his or her personal protection, all personnel will immediately leave the exclusion zone. Re-entry to the exclusion zone will not be permitted until the protective equipment has been repaired or replaced and the cause of equipment failure has been determined and is no longer considered a threat.

10.15.5 Emergency Information Telephone Numbers

PRC will have a cellular telephone on site that can be used for any emergency situations. Emergency telephone numbers for each of the demonstration sites are listed below. Emergency telephone numbers not presented below can be obtained, during working hours, by calling Ms. Kathy Schuessler of PRC at (312) 856-8700.

RV Hopkins Site

Emergency Service	Telephone Number
Local Police Department	911
Local Fire Department	911
Local Hospital (Mercy Hospital)	(319) 383-1100
Local Ambulance Service	911

Asarco Site

Emergency Service	Telephone Number
Local Police Department	911
Local Fire Department	911
Local Hospital (St. Joseph Hospital)	911
Local Ambulance Service	911

The following emergency contacts are applicable to all demonstration sites:
Poison Control Center: 1 (800) 822-3232

National Response Center: 1 (800) 424-8802

CHEMTREC Chemical Transportation
Emergency Center: 1 (800) 424-9300

PRC (Kansas City office): (913) 281-2277

Eric Hess, PRC Project Manager: (913) 573-1822

Kurt Sorensen, PRC HSD: (312) 856-8763

Steve Billets, EPA PM and TPM: (702) 798-2232

The following numbers can be used to contact the demonstration team at the sites on PRC's mobile telephone. To access the mobile telephone, dial the first number, wait for a tone, and then dial the second number:

RV Hopkins Site: (319) 349-ROAM, (816) 536-0944
Asarco Site: (206) 972-ROAM, (816) 536-0944

10.15.6 Hospital Route Directions

Before performing any field activities, PRC personnel will conduct a pre-emergency hospital run from each site to the hospital. Maps showing the hospital routes from each site are provided in Figures 10-1 and 10-2.

FIGURE 10-1 RV HOPKINS SITE HOSPITAL ROUTE MAP
(not available)

FIGURE 10-2 ASARCO SITE HOSPITAL ROUTE MAP
(not available)

TABLE 10-1

HAZARDOUS MATERIALS POTENTIALLY PRESENT AT THE DEMONSTRATION SITES

Chemicals Present at the Site	**Highest Observed Concentration in Soil (mg/kg)**	Airborne Exposure **Limits**	IDLH	Symptoms and Effects of Acute Exposure
Antimony and compounds (as Sb)	No Data	0.5 mg/m^3	80 mg/m^3	Irritated nose, throat, mouth; cough; dizziness; headache; nausea, vomiting, diarrhea; cramps; insomnia; anorexia; irritated skin; unable to smell; cardiac
Barium soluble compounds (as Ba)	2,640	0.5 mg/m^3	250 mg/m^3	Upper respiratory irritation; gastrointestinal; muscle spasms; slow pulse, extrasystoles; hypokalemia; irritated eyes; skin burns
Beryllium and compounds (as Be)	No Data	2.0 g/m^3	Ca	Respiratory symptoms; weakness, fatigue; weight loss; carcinogen
Cadmium dust (as Cd)	500	0.2 mg/m^3	Ca	Pulmonary edema, dyspnea, cough, tight chest, substernal pain; headache; chills, muscle aches; nausea, diarrhea; anosmia, emphysema; proteinuria; anemia; carcinogen
Calcium arsenate (as As)	403,100	10 g/m^3	Ca	Weakness; gastrointestinal; peripheral neuropathy; hyperpigmentation, palmar planter hyperkeratoses; dermatitis; carcinogen
Chromic acid and chromates (as $Cr0_3$)	22,100	0.1 mg/m^3	30 mg/m^3	Respiratory, nasal septum irritation; leukocytosis, leukopenia, monocytosis, eosinophilia; eye injury, conjunctivitis; skin ulcer,

				sensitization dermatitis
Chromium metal and insoluble salts (as Cr)	22,100	1 mg/m^3	500 mg/m^3	Histologic fibrosis of lungs; Chromium (VI): carcinogen
Cobalt metal, fume, and dust (as Co)	No Data	0.1 mg/m^3	20 mg/m^3	Cough, dyspnea, decreased pulmonary function; weight loss; dermatitis; diffuse nodular fibrosis, respiratory hypersensitivity
Copper dust and mist (as Cu)	341,000	1 mg/m^3	NA	Irritated mucus membrane, pharynx; nasal perforation; eye irritation; metal taste; dermatitis
Lead Inorganic fumes and dusts (as Pb)	33,750	0.03 mg/m^3	NA	Lassitude; insomnia; pallor, eye grounds; anorexia, weight loss, malnutrition; constipation, abdominal pain, colic; hypotenuse; anemia; gingival lead line; trembling, paralyzed wrist
Manganese and compounds (as Mn)	22,000	5 mg/m^3	10,000 mg/m^3	Parkinson's disease; asthenia, insomnia, mental; metal fume fever; dry throat, cough, tight chest, dyspnea, rales; low back pain; vomiting, malnutrition; fatigue
Mercury and inorganic compounds (as Hg)	700	0.1 mg/m^3	28 mg/m^3	Cough, dyspnea, bronchial pneumonia; tremor, insomnia; irritability, indecision; headache; fatigue, weakness; stomatitis; salivation; gastrointenstinal, anorexia, loss of weight; proteinuria; irritated eyes, skin
Molybdenum insoluble compounds	No Data	15 mg/m^3	NA	In animals: irritated eyes, nose, throat; weight loss

(as Mo)				
Nickel metal and soluble compounds (as Ni)	519	1 mg/m^3	Ca	Sensitization dermatitis; allergic asthma; nasal cavities; pneumonitis; carcinogen
Selenium compounds (as Se)	No Data	0.2 mg/m^3	100 mg/m^3	Irritated eyes, nose, throat; disturbed vision; headache; chills, fever; dyspnea, bronchitis; metal taste, garlic breath; gastrointestinal; dermatitis; blurry eyes; skin
Silica (crystalline)	No Data	10 mg/m^3	NA	Cough, dyspnea, wheeze; impaired pulmonary functions; progressive symptoms
Thallium soluble compounds (as Tl)	1,080	0.1 mg/m^3	20 mg/m^3	Nausea, diarrhea, abdominal pain; ptosis, strabismus; peripheral neuritis tremors; paresthesia legs, retster chest pain, pulmonary edema; seizure chorea psychialopecia
Tin inorganic compounds except oxides (as Sn)	No Data	2 mg/m^3	400 mg/m^3	Irritated eyes, skin

Notes:
NA Not applicable
Ca Carcinogen

TABLE 10-2

WORK TASK HAZARD ANALYSIS

Task	Potential Hazard	Anticipated Level of Protection	Upgraded Level of Protection
Task 1 Sampling	Chemical Physical	Level D	Level C
Task 2 Field Screening	Chemical Radiological	Level D	Level C

Note:
Levels of protection are discussed in detail in Section 10.9.2.

XRF CHAPTER 11

DELIVERABLES

Several documents and reports will be produced as part of this demonstration. Anticipated deliverables include a work plan, a demonstration plan, a TER, an ITER, and technology briefs. Other reports may be submitted as requested by the EPA TPM. Each of these reports is discussed below.

11.1 DEMONSTRATION WORK PLAN

The work plan was submitted to EPA EMSL on September 29, 1994. The work plan described the tasks PRC will complete for this demonstration. Tasks listed in the work plan include: work plan preparation and project coordination, technical support, predemonstration sampling and analysis, preparation of a demonstration plan, field method development, demonstration activities, and preparation of draft and final TERs, ITERs, and technology briefs. The work plan describes each of these tasks and discusses the steps PRC will take to complete each task.

11.2 DEMONSTRATION PLAN

This demonstration plan has been prepared to provide a detailed description of all activities that will take place as part of this demonstration. This plan includes the following elements:

<u>Test Plan</u>. The test plan includes an overview of the demonstration process (Chapter 1), a description of the roles and responsibilities of involved parties (Chapter 2), a discussion of the sampling protocols (Chapter 6), a discussion of the experimental design for the demonstration (Chapter 7), and an explanation of the methodology for evaluating the performances of the technologies (Chapter 7).

<u>QAPP</u>. This document was prepared according to EPA guidelines listed in the statement of work. The QAPP includes a project description, delineation of QA/QC responsibilities, QA objectives for critical measurements, sampling and analytical procedures, data reduction, validation, and reporting procedures, plans for system and performance audits, and descriptions of internal QC checks, calculation of data quality indicators, plans for corrective actions, and QC reports to management. The QAPP is provided in Chapter 8.

<u>HASP</u>. The HASP identifies the key personnel who will be involved with demonstration activities and the minimum training requirements for field personnel, evaluates anticipated hazards associated with field work, and discusses site entry, personal protection equipment, communication, and decontamination procedures to be followed during field work. The HASP is provided in Chapter 10.

<u>Sampling Plan</u>. The sampling plan describes the objectives of the sampling proposed for the demonstration and identifies specific sampling methods and analytical procedures to be followed. The sampling plan is provided in Chapter 6. Analytical procedures for the confirmatory laboratory are outlined in Chapter 8.

11.3 TECHNOLOGY EVALUATION REPORT

The main product of a completed demonstration under the SITE Program is a TER. This report documents the results of the demonstration and reports on the performances of the technologies. The TER will include descriptions of analytical and instrument procedures, data collection and management procedures, and associated QA/QC requirements.

The report for this demonstration project will include the following specific elements:

- A demonstration summary prepared according to directions from the EPA TPM
- A description of the technologies that were demonstrated including diagrams, operating instructions, and a brief discussion of the theoretical concepts under which the technologies operate
- One generic method for using FPXRF technologies in a format comparable to EPA SW-846 methods
- A description of any deviations in the experimental design for the demonstration including method protocols, sampling and analysis procedures and methods, QA/QC procedures and records, descriptions of the demonstration sites, and any other pertinent information about the demonstration
- An interpretation and assessment of the technologies comparing their analytical results to those obtained using conventional analytical methods
- Analytical performance data and data interpretation for each technology including an evaluation of data quality parameters (precision, accuracy, comparability, completeness, representativeness), and a description of the methods used to assess this data
- Conclusions about the advantages and limitations of each technology on its own merit compared to conventional EPA sample analysis
- Recommendations for the potential use of the technologies for site characterization and regulatory activities, as well as recommendations for improvements or further testing, if appropriate

11.4 INNOVATIVE TECHNOLOGY EVALUATION REPORT

The vehicle used to publish the results of a completed demonstration under the SITE Program is an ITER. This report condenses the data presented in a TER, focusing primarily on application-related data and observations. This report will be similar to the TER except all appendices will be eliminated and detailed data analysis discussions will be eliminated.

11.5 TECHNOLOGY BRIEFS

The technology briefs are one-page summaries of the gross findings presented in the ITER. A technology brief will be produced for each technology demonstrated. These documents are intended to be technology transfer fact sheets.

11.6 OTHER REPORTS

PRC will prepare other reports or documents as directed by the EPA TPM. Examples of other reports which may be required include memorandum trip reports following field activities or visits to developer facilities. In addition, the EPA TPM may require development of technology transfer documents including technology mailers, bulletins, journal articles, or other publications.

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