

**SWMU 7
Phase III Soils
RFI QAPP ADDENDUM**

**Naval Surface Warfare Center
Crane Division
Crane, Indiana**



**Southern Division
Naval Facilities Engineering Command
Contract Number N62467-94-D-0888
Contract Task Order 0160**

October 2004

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**NAVAL SURFACE WARFARE CENTER CRANE
OLD PISTOL RANGE
FIELD MEASUREMENT AND SAMPLING FOR LEAD AND SELECT METALS
QUALITY ASSURANCE PROJECT PLAN ADDENDUM**

INTRODUCTION

Tetra Tech NUS, Inc. (TtNUS) prepared a document entitled Phase III Soils RCRA Facility Investigation for SWMU 7 [Old Rifle Range (ORR)] at Crane, IN (TtNUS, August 2002), which has been reviewed by the USEPA. As an outcome of this review, the USEPA has requested that additional investigation be conducted at the Old Pistol Range (OPR) which is located adjacent to the ORR. A telecon with the USEPA, the Navy and TtNUS was conducted on June 29, 2004 to discuss the proposed investigation. The following lists the persons present during the conference call followed by the proposed Scope of Work agreed upon.

Attendees

Navy

Bill Gates (Remedial Project Manager – Southdiv)

Tom Brent (NSWC Crane Environmental Project Manager)

USEPA

Peter Ramanauskas (Project Manager)

Mario Mangino - Toxicologist

Greg Czajkowski – Environmental Scientist

Allen Debus - Chemist

TtNUS

Roger Clark (Task Order Manager [TOM])

Mark Francis (Deputy TOM)

Leeann Sinagoga (Human Health Risk Assessor)

Aaron Bernhardt (Ecological Risk Assessor)

Scope of Work

The following Scope of Work was agreed upon for this additional investigation during a telecon with the USEPA, the Navy and TtNUS on June 29, 2004.

- The overall approach for this project including the risk assessments should be similar to what was done for the Landfarm assessments (i.e., QAPP and Report).
- For ecological risks, make any changes as necessary to benchmarks based on June 9, 2004 technical meeting with Navy, TtNUS, USEPA, and IDEM.
- The QAPP should have tables comparing screening levels to MDLs, similar to other QAPPs.
- X-Ray Fluorescence (XRF) methodology is suggested for field analysis of soils. The field screening samples will be complimented with fixed-base confirmatory lab samples. The fixed-based analysis should be done on 10 to 20 percent of the samples; a minimum of 10 samples should be analyzed by the fixed-based laboratory. The samples for fixed-based analysis should include a range of concentrations (not all biased to the high side or low side). The analytical program will include 5 metals:
 - lead
 - antimony
 - copper
 - tin
 - zinc
- TtNUS will propose the type of XRF unit and methodology for the field screening. The QAPP should define the acceptable level of correlation between XRF data and fixed-based data to determine if the screening data can be used in the risk assessment. If the correlation is good, USEPA indicated that the screening data can be used in the risk assessment. If the correlation is not good, fixed-based data will be used. All soil samples will be shipped to the laboratory so that the samples will be available for analysis, if needed.
- A short work plan addendum will be prepared specifying the scope and objectives of the soil sampling program, field screening analytical methods, fixed-base lab methods, risk-based target levels, detection limits for both field screening and fixed-base lab, and quality assurance samples.
- The QAPP should discuss in detail how the samples will be prepared (i.e., placed in plastic bag, dried, etc.). Large bullet fragments should be removed from the sample

before analysis by XRF or fixed-based lab. Any fragments removed should be noted in the field notebook.

- Samples in the berm areas will be collected from the following depths: 0 to 3 inches, 3 to 6 inches, 6 to 12 inches, and 12 to 24 inches. Samples outside the berm areas will be collected at 0 to 3 inches and 3 to 6 inches. In both cases, additional samples will be taken at depth if necessary to determine the vertical extent of contamination. Discrete samples will be collected within the berm areas. However, a grid will be established for samples collected outside the berm areas (e.g., the range floor and surrounding area). Composite samples will be collected from sub areas established by the grid (no more than 5 sub-samples will be collected to construct the composite for a sub-area of the grid). While the work plan will establish an initial grid for investigation of areas outside the berms, the grid may be expanded in the field as necessary to establish the horizontal extent of contamination. The approach will be similar to that used to collect samples for the RFI Report already submitted to EPA.
- The lower of the human health and ecological screening levels will be used to evaluate soil samples collected from 0 to 6 inches. Only human health screening levels will be used to evaluate soil samples collected from deeper than 6 inches because 6 inches is the biologically active zone for ecological receptors. Background levels will be used to evaluate the data if the screening levels are less than the base-wide background numbers.

Based on the above-listed recommendations, the following activities are proposed to address these comments.

OBJECTIVE

The objective of this investigation is to collect surface and subsurface soil samples for select metals analysis for the purposes of characterizing the vertical and horizontal extent of metals contamination at the Old Pistol Range (OPR) and to conduct a human health and ecological risk assessment.

SAMPLING RATIONALE

This section describes the sampling rationale used for the soil sampling at the OPR. The activities referred to herein will serve as an appendix to the previous site QAPP entitled SWMU 7

Phase III Soils RFI QAPP, Naval Surface Warfare Center, Crane, Indiana, October, 2000. In an attempt to expedite the fieldwork at this SWMU, similar field collection and analysis procedures that were recently conducted at this same area, including the work conducted at a companion SWMU referred to as the Old Rifle Range (ORR), will be incorporated where possible. The proposed field activities at the OPR will consist of collection and analysis of surface and shallow subsurface soil samples. The proposed work will be conducted under the same U.S. EPA-approved Quality Assurance Project Plan (QAPP) dated October 2000 for work previously conducted at this SWMU. Where possible, field procedures including sampling methodologies referenced in the ORR QAPP will be used in this Work Plan Addendum.

EVENTS LEADING TO THIS WORK PLAN

This section presents a brief history of the OPR and the chain of events leading to this Work Plan Addendum. It should be noted that SWMU 7 consists of two adjoining sites; the ORR which is the larger and historically more active firing range (also used for ammunition burning) and the OPR which is a smaller firing range that was used less frequently. Currently the ORR is maintained (grass mowing and unimproved roadway maintenance, plus occasional ammunition burning) whereas the OPR has been allowed to revegetate.

Historical operations conducted at the OPR consisted of small arms firing within two discrete areas. These areas are illustrated in Figure 1. The first area identified as Hillside Range 1 consists of an open field (currently overgrown with volunteer shrubs and native trees) and an adjoining hillside. Reportedly, small arms shooters positioned themselves in the area close to the 55-gallon drum identified in Figure 1 and shot toward metal-framed targets located to the west. The backstop for the bullets was a hillside a few tens of feet west of the targets. The second shooting area referred to as Range 2 is located immediately north of Hillside Range 1. This area is also relatively flat and is currently overgrown with volunteer shrubs and native trees. The shooting area was oriented south to north. The backstop for the bullets was a manmade earthen berm located approximately 150 feet north of Hillside Range 1.

Soil sampling and analyses were conducted at SWMU 7 between 2001 and 2002. Results of this investigation were presented in a Phase III Soils RFI Report (TfNUS, August 2002). The recommendation from this report was that the Navy should conduct a Voluntary Interim Measure (VIM) for the excavation and removal of a limited amount of TNT contaminated soil at the ORR. The USEPA and the Navy agreed to this approach and the VIM was implemented. A summary report of this VIM was prepared as the Voluntary Interim Measure Letter Report for TNT Contamination Removal at Solid Waste Management Unit 7 (Old Rifle Range) Naval Surface

Warfare Center Crane (TtNUS, October 2003). The USEPA reviewed the Phase III Soils RFI Report (TtNUS, August 2002) and the VIM Report (TtNUS, October 2003). Mr. Peter Ramanauskas (USEPA Region 5 Environmental Scientist) indicated in a correspondence dated June 17, 2004 that the Phase III Soils RFI Report covering the ORR was acceptable as is although additional investigative work was required at the OPR. This was partially based on potential metals contamination in soil (primarily lead and other ammunition-related metals) as described in a previous U.S. Army Corps of Engineers report. The proposed additional investigative work described herein is in response to these requests by the USEPA.

SOIL SAMPLING LOCATIONS, RATIONALE AND ANALYTICAL PROTOCOL

The following sections describe the proposed sampling locations, rationale for the sampling analytical program, analyses to be performed, and QA samples to be collected. Details regarding the equipment and procedures for collecting, preserving, packaging, and shipping the samples are included in Section 4.0 and related SOPs in Appendix B of the QAPP for the ORR at Crane (TtNUS, October 2000).

Sampling Locations

Soil sampling locations at the OPR will be selected as follows. The OPR will be divided into two areas, the Hillside Range 1 and Range 2. Each area will be gridded off in the field using a tape measure and pin flags to aid in locating sampling points. Figures 2 and 3 illustrate the sampling grid for the Hillside Range 1 and Range 2 respectively.

The sampling rationale for the Hillside Range 1 (see Figure 2) assumes a firing lane of 200 feet followed by an impact berm (the hillside across the creek) which is roughly perpendicular to the ground surface. The impact berm is approximately 20 feet high, followed uphill by an "overspray area" of an additional 50 feet. Therefore for the Hillside Range 1, it is assumed that the total area potentially impacted by range activities was approximately 75 feet wide by 270 feet long [the impact berm (hillside) is estimated to be 20 feet high]. A grid will be manually marked in the field to aid in sample collection. The grid will be established by first marking the corners of the area. This area will then be divided lengthwise into two sub areas of 35.5 feet wide by 270 feet long. The two sub areas will then be subdivided lengthwise on 50 foot intervals (starting on either side of the impact berm area) into 10 grid cells as illustrated in Figure 2. Each grid cell will be further divided into 10 equal sub areas. Four of the sub areas will be randomly selected for sample collection. Prior to conducting the field investigation, four soil sampling locations will be identified within each grid cell by random selection using a uniform random number generator [Microsoft

Excel 97 SR-2 (h)]. This soil sampling design constitutes a stratified random design [as was used in the evaluation of SWMU 1/12 (Mustard Gas Burial Ground) during a recent NSWC Crane investigation]. Figures 2 and 3 illustrate an example random pattern of proposed sample locations. The berm area will be divided in half lengthwise and further subdivided into 5 equal sub areas for a total of 10 sampling areas. The grid of sample locations for the berm is shown on Figure 4. Sample locations will be marked in the field at the centers of each grid cell. Using this grid spacing plan, a total of 50 surface locations will be marked for sample collection (40 sample locations within the firing lanes and 10 sample locations within the berm).

For the Range 2 (see Figure 3), it is assumed that the area potentially impacted by range activities was approximately 75 feet wide by 300 feet long plus the impact berm, estimated to have a footprint of about 20 feet long x 75 feet wide. Therefore the grid will be established in the field by first marking the corners of the area. This area will then be divided lengthwise into two sub areas of 35.5 feet wide by 320 feet long. The two sub areas will then be subdivided lengthwise on 50 foot intervals (starting on either side of the impact berm area) into 12 grid cells as illustrated in Figure 3. Prior to conducting the field investigation, four soil sampling locations will be identified within each grid cell by random selection using a uniform random number generator [Microsoft.Excel 97 SR-2 (h)]. This soil sampling design constitutes a stratified random design [as was used in the evaluation of SWMU 1/12 (Mustard Gas Burial Ground) during a recent NSWC Crane investigation]. The berm area will be divided in half lengthwise and further subdivided into 5 equal sub areas for a total of 10 sampling areas. The grid of sample locations for the berm is shown on Figure 4. Sample locations will be marked in the field at the centers of each grid cell. Using this grid spacing, a total of 58 surface locations will be marked for sample collection (48 sample locations within the firing lanes and 10 sample locations within the berm).

Sampling Depths

The soil sampling depths plan for each of the two areas will use the same general format. Soil samples collected from the floors of the firing ranges will be collected from two depths; 0 to 3" and 3 to 6" below ground surface (bgs). Soil samples collected from the berms will be collected from four depths; 0 to 3", 3 to 6", 6 to 12" and 12 to 24".

Discrete samples will be collected within each grid cell of the berm areas. However, a grid will be established for samples collected outside the berm areas (e.g., the range floor and surrounding area) and composite samples will be collected from sub areas established by the grid. Four discrete samples will be collected from each randomly selected sub area and composited into one sample for analysis. As an example, at Hillside Range 1, ten (10) sub areas will be gridded

off and four (4) discrete soil samples will be collected at a specific depth within each sub area. One composite sample will be generated from the four samples collected at each sub area for a total of 10 samples to be used for analyses. This procedure will be used for each depth required.

Because of the shallow depths and unconsolidated nature of the samples to be collected, subsurface soil sampling may be performed using a hand auger or DPT, depending on site conditions. Bedrock is not anticipated to occur at shallow depths underlying the OPR, although if bedrock is shallower than the bottom of a depth interval, sampling will stop at the bedrock. Based on historical accounts of the range activities, the metals of interest should be found at the surface or shallow subsurface. Excess soil cuttings from the borings will be placed back in the borehole. Details regarding soil sampling equipment and procedures are included in the previously approved QAPP for the Old Rifle Range (ORR) at Crane (TtNUS, October 2000).

The following describes the details of the sampling plan. The XRF samples will be field analyzed using Method SW846 6200 (refer to SOP in Appendix A).

XRF and Laboratory Sample Summary Table

Hillside Range 1

Firing Lane		Hillside Berm		Totals
10 cells x 2 depths (Depths: 0-3", 3-6")	= 20 XRF samples	10 cells x 4 depths (Depths: 0-3", 3-6", 6-12", 12-24")	= 40 XRF samples	Total = 60 XRF samples. 5 of these samples will be submitted for fixed-base lab analyses + 1 duplicate (6 total).

Range 2

Firing Lane		Berm		Totals
12 cells x 2 depths (Depths: 0-3", 3-6")	= 24 XRF samples	10 cells x 4 depths (Depths: 0-3", 3-6", 6-12", 12-24")	= 40 XRF samples	Total = 64 XRF samples. 5 of these samples will be submitted for fixed-base lab analyses + 1 duplicate (6 total).

Total XRF Analyses (Field Measurements) Total = 124 samples + 5 duplicates

Fixed-Base Laboratory Analyses Total = 10 samples + 2 duplicates

Analytical Protocol

A total of 124 samples (20 composite samples from the OPR Range 1 firing lane, 40 discrete samples from the OPR Range 1 Hillside berm, 24 composite samples from the OPR Range 2 firing lane and 40 discrete samples from the OPR (Range 2 berm) will be analyzed for antimony, lead, copper, tin and zinc using field portable XRF instrumentation. This instrument is capable of analyzing the 5 metals of interest.

The analytical detection limit requirements (Table 1), analytical methods and corresponding laboratory SOPs (Table 2), quality control samples collection frequency (Table 3), matrix spike and laboratory duplicate control limits (Table 4), laboratory control sample control limits (Table 5), and bottleware, preservation, and holding time requirements (Table 6) are specified in the attached Tables 1 through 6.

Samples once collected will be placed into sandwich style sealable plastic bags for field XRF analyses and 8-ounce glass jars for fixed-base analyses and labeled with the location identity. Prior to the sample placement in the bags and glass jars, debris, rocks, and pebbles will be removed. During this activity, the sample will be homogenized and examined to insure no bullets or shot are present in the sample that could skew the results.

Prior to field analysis, the sample will be further homogenized and flattened using a rolling pin. This further permits the identification and removal of rocks, pebbles, and debris. This preparation also permits the flattening of the sample to allow full contact with the probe window of the XRF instrument.

The sample will be analyzed at three different points and the results will be averaged.

Prior to sample analysis, the instrument will be allowed to warm up for a period of time recommended by the manufacturer. The instrument will then be calibrated according to the manufacturer's specifications before sample analysis can occur. A continuing calibration verification (CCV) check standard, and continuing calibration blank (CCB), if provided by the manufacturer will be analyzed at a minimum of every 2 hours. The CCV standard should fall within +/- 20 percent of the true value. Recalibration and reanalysis will be required if this condition is not met. In addition, a sample duplicate will be performed for every 20 samples.

As shown in the XRF and Laboratory Sample Summary Table, 10 samples will be selected for confirmatory analyses at a fixed-base laboratory. (Note that all samples will be sent to the

laboratory in case analyses will be required at a later date.) Samples selected for confirmatory analyses will be selected from a range of concentrations (low, medium, high). A correlation value of 65 percent (i.e., $r=0.65$) will be considered acceptable for using the XRF data in the human health and ecological screening evaluations. The samples will be analyzed by Laucks Laboratory and will be homogenized per USEPA Region 5's Quality Assurance Guidance Document, Appendix Q (as found in Appendix B of this document).

TABLE 1

DETECTION LIMITS VERSUS RISK CRITERIA
NSWC CRANE INDIANA

Parameter	CAS NUMBER	MDL/IDL ⁽¹⁾ (mg/kg)	RL ⁽¹⁾ (mg/kg)	Human Health Screening Level ⁽²⁾ (mg/kg)	Ecological Screening Level ⁽³⁾ (mg/kg)
METALS (SW-846 Method 6020 ICP/MS)					
Antimony	7440-36-0	0.05	0.5	3.1	0.29
Copper	7440-50-8	0.05	1	310	5.4
Lead	7439-92-1	0.05	0.5	400	16
Tin	7440-31-5	0.05	5	4700	7.62
Zinc	7440-66-6	0.2	5	2300	6.62
METALS (EPA Method 6200 Field XRF)					
Antimony	7440-36-0	55	NA	3.1	0.29
Copper	7440-50-8	75	NA	310	5.4
Lead	7439-92-1	40	NA	400	16
Tin	7440-31-5	85	NA	4700	7.62
Zinc	7440-66-6	70	NA	2300	6.62

MDL = method detection limit
IDL = instrument detection limit
RL = reporting limit
mg/kg = milligrams per kilogram

Shaded cells indicate laboratory MDLs that exceed a risk-based screening level for the project.

Shaded cells indicate laboratory RLs that exceed a risk-based screening level for the project.

- 1 Laboratory IDLs and RLs as provided by Laucks Testing Laboratories, Inc. The values may change prior to the investigation as laboratory IDLs are updated. MDLs listed are the lowest of the values presented in EPA Method 6200 and will vary depending on the instrument used, sample matrix and other conditions.
- 2 Human health screening levels provided are the USEPA Region 9 PRGs divided by a factor of 10, with the exception of lead, which is not divided by 10.
- 3 Ecological screening levels provided are either USEPA Ecological Soil Screening Levels or USEPA Region 5 Ecological Screening Levels.

TABLE 2

SUMMARY OF ANALYTICAL PROCEDURES
SOLID SAMPLES
NSWC CRANE, CRANE, INDIANA

Analytical Parameter	Preparation Method	Analytical Method	Preparation/Analytical SOP(s) ⁽¹⁾
Fixed-Base Laboratory Analyses			
Cu, Pb and Zn	SW-846 Method 3050B (no HCl)	SW-846 Method 6020	LTL-7012 or LTL-7015/ LTL-7202
Sb and Sn	SW-846 Method 3050B (no H ₂ O ₂)	SW-846 Method 6020	LTL-7012 or LTL-7015/ LTL-7202
Field Screening Analyses			
Cu, Pb, Sb, Sn and Zn	No prep method required	EPA Method 6200	NA

1 Laboratory SOPs are attached as Appendix C to SWMU Phase III Soils RFI QAPP, Naval Surface Warfare Center, Crane Division, Crane Indiana, Volume II – Appendices Tetra Tech NUS, October 2000.

NA Not applicable.

TABLE 3

NON-CALIBRATION QC SAMPLE COLLECTION FREQUENCIES,
ACCEPTANCE LIMITS AND CORRECTIVE ACTIONS
NSWC CRANE, CRANE, INDIANA

QC Sample Type	Collection Frequency	Acceptance Limits	Corrective Action
Field Duplicate	1 per 10 investigative samples collected.	Soil = 50% RPD	Qualify data according to data validation requirements.
Equipment Rinsate Blank	1 per 10 investigative samples collected, with a minimum of one per day of sampling, per non-disposable sampling device/instrument. For pre-cleaned, dedicated, and/or disposable equipment (i.e., disposable plastic trowels, etc.), one rinsate blank will be collected and analyzed at a frequency of one per lot or "batch blank" for a specific equipment type.	< RL	Identify source of contamination, if possible. Qualify data according to validation criteria. Qualify use of data if contamination appears to have adversely affected its usability.
Laboratory Control Sample	1 per 20 environmental samples per matrix	See Table 5	Laboratory action taken per LTL-1008. TiNUS action taken per validation protocols.
Laboratory Method Blank	1 per 20 environmental samples or per preparation batch, whichever is more frequent	< RL	Laboratory action taken per LTL-1008. TiNUS action taken per validation protocols.
Matrix Spike*	1 per 20 environmental samples	See Table 4	Laboratory action taken per LTL-1008. TiNUS action taken per validation protocols.
Laboratory Duplicate*	1 per 20 environmental samples	See Table 4	Laboratory action taken per LTL-1008. TiNUS action taken per validation protocols.
Temperature Blank	One blank per sample cooler.	4 ± 2 °C	Laboratory action taken per LTL-1008. TiNUS action taken per validation protocols.

* Matrix spike and laboratory duplicates are not analyzed in the field, but additional sample material must be collected in the field to ensure that the laboratory has enough material for spiking and duplicate analysis.

TABLE 4

QUALITY CONTROL LIMITS⁽¹⁾
 MATRIX SPIKE AND LABORATORY DUPLICATE SAMPLES
 METALS ANALYSES
 NSWC CRANE, INDIANA

Chemical	Solid Matrix	
	Accuracy ⁽²⁾ (%R)	Precision ⁽³⁾ (RPD)
METALS BY SW-846 METHOD 6020		
Antimony	75-125	35
Copper	75-125	35
Lead	75-125	35
Tin	75-125	35
Zinc	75-125	35

- 1 In-house QC limits provided by Laucks Testing Laboratories, Inc.
- 2 These acceptance limits apply to spikes that augment the native sample analyte concentration by at least 25 percent.
- 3 These acceptance limits apply to original and duplicate sample concentrations >5x RL. If one or both of the results is <5x RL, the acceptance criterion is \pm RL. If one of the results is a non-detect, the reported %RPD will be 200%.

%R = Percent Recovery
 QC = Quality Control
 RL = Reporting Limit
 RPD = Relative Percent Difference

TABLE 5
QUALITY CONTROL LIMITS⁽¹⁾
LABORATORY CONTROL SAMPLES
METALS ANALYSES
NSWC CRANE, INDIANA

Chemical	Solid Matrix Accuracy (%R) ⁽²⁾
METALS BY SW-846 METHOD 6020	
Antimony	75-125
Copper	80-120
Lead	80-120
Tin	75-125
Zinc	80-120

- 1 In-house QC limits provided by Laucks Testing Laboratories, Inc.
- 2 As noted in the laboratory SOPs, the laboratory may use a purchased standard reference material (SRM) in place of a LCS. If an SRM is used, the acceptance limits provided by the supplier of the SRM may be used unless the SRM limits are wider than the acceptance limits provided in this table. If the SRM limits are wider, the laboratory must use the acceptance limits provided in this table.

%R = Percent Recovery

LCS = Laboratory Control Sample

QC = Quality Control

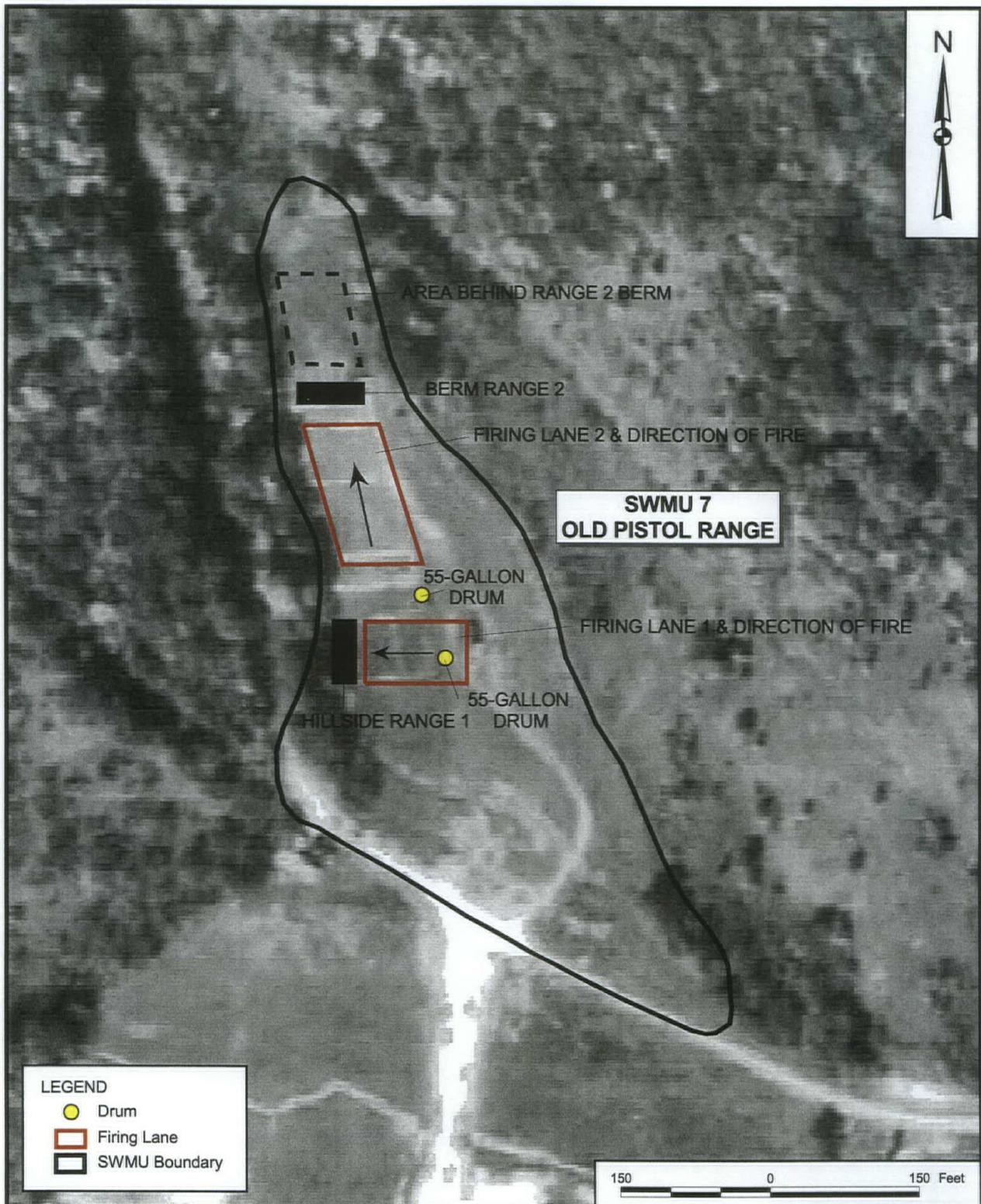
SOP = Standard Operating Procedure

TABLE 6

SUMMARY OF SAMPLE ANALYSES, CONTAINER TYPES AND VOLUMES,
PRESERVATION REQUIREMENTS, HOLDING TIMES AND ANALYTICAL LABORATORY
NSWC CRANE, CRANE, INDIANA

Parameter	Sample Container	Container Volume	Preservation	Maximum Holding Time ⁽¹⁾	Analytical Laboratory
Soil					
Metals	Wide-mouth jar, Teflon-lined plastic cap	8 ounce	Cool to 4 °C	Within 180 days	Laucks

1 All holding times are from date of collection.



LEGEND	
	Drum
	Firing Lane
	SWMU Boundary

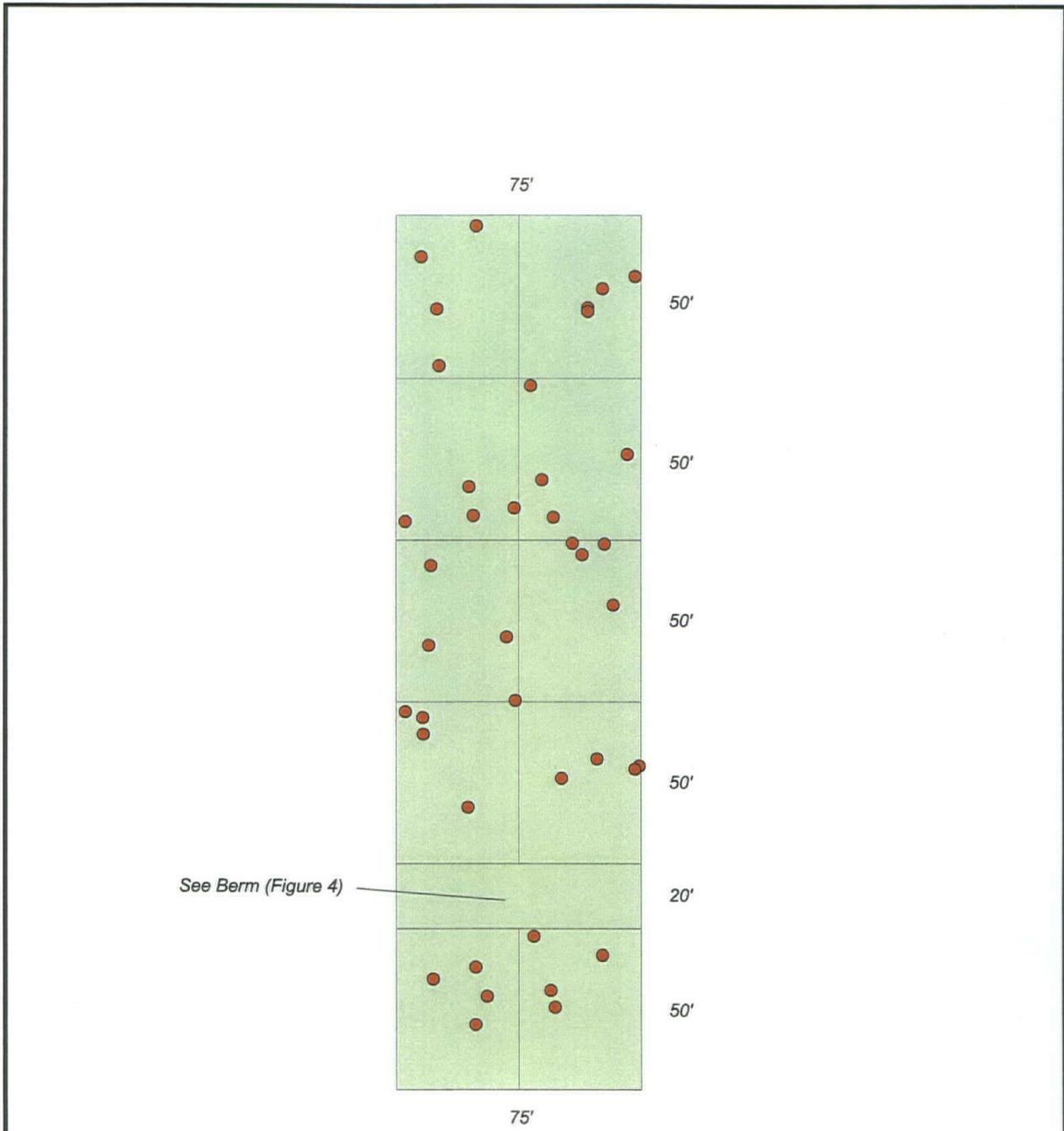


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CHECKED BY R. CLARK	DATE 9/03/04
COST/SCHEDULE-AREA	
SCALE AS NOTED	



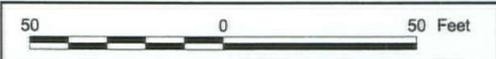
GENERALIZED LAYOUT OF HISTORICAL OPERATIONS
 SWMU 7 - OLD PISTOL RANGE
 NAVAL SURFACE WARFARE CENTER
 CRANE, INDIANA

CONTRACT NUMBER 3961 CTO 160	
APPROVED BY M. FRANCIS	DATE 9/03/04
APPROVED BY R. CLARK	DATE 9/03/04
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LEGEND

- Proposed Sample Location
- Sample Area

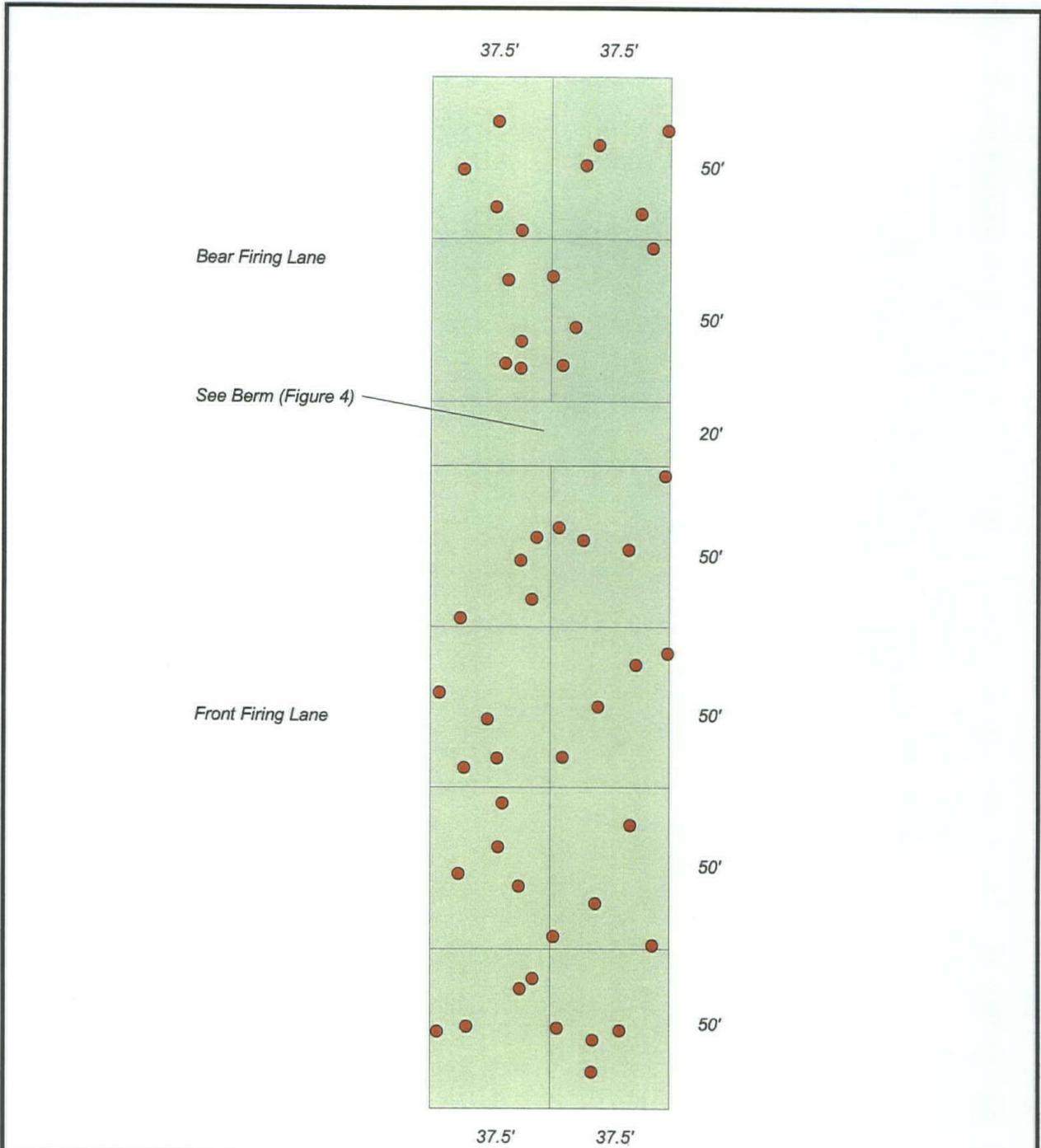


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<small>COST/SCHEDULE-AREA</small>	
<small>SCALE</small> AS NOTED	



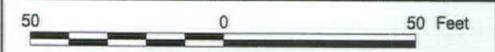
HILLSIDE RANGE 1
 SWMU 7 - OLD PISTOL RANGE
 NAVAL SURFACE WARFARE CENTER
 CRANE, INDIANA

<small>CONTRACT NUMBER</small> 3961 CTO 160	
<small>APPROVED BY</small> M. FRANCIS	<small>DATE</small> 9/03/04
<small>APPROVED BY</small> R. CLARK	<small>DATE</small> 9/03/04
<small>DRAWING NO.</small> FIGURE 2	<small>REV</small> 1



LEGEND

- Proposed Sample Location
- Sample Area

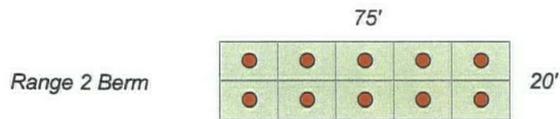
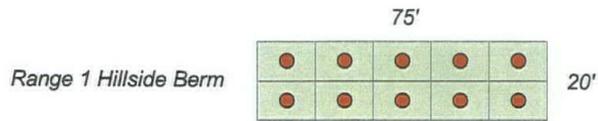


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<small>COST/SCHEDULE-AREA</small>	
<small>SCALE</small> AS NOTED	



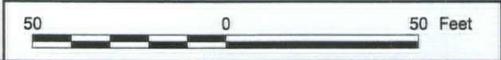
RANGE 2
SWMU 7 - OLD PISTOL RANGE
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA

<small>CONTRACT NUMBER</small> 3961 CTO 160	
<small>APPROVED BY</small> M. FRANCIS	<small>DATE</small> 9/03/04
<small>APPROVED BY</small> R. CLARK	<small>DATE</small> 9/03/04
<small>DRAWING NO.</small> FIGURE 3	<small>REV</small> 1



LEGEND

-  Proposed Sample Location
-  Sample Area



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CHECKED BY	DATE
R. CLARK	9/08/04
COST/SCHEDULE-AREA	
SCALE AS NOTED	



RANGES 1 & 2 BERMS
 SWMU 7 - OLD PISTOL RANGE
 NAVAL SURFACE WARFARE CENTER
 CRANE, INDIANA

CONTRACT NUMBER 3961 CTO 160	
APPROVED BY	DATE
M. FRANCIS	9/03/04
APPROVED BY	DATE
R. CLARK	9/03/04
DRAWING NO.	REV
FIGURE 4	1

APPENDIX A

STANDARD OPERATING PROCEDURE USEPA METHOD SW 846 6200

METHOD 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed in Table 1 for soil and sediment samples. Some common elements are not listed in Table 1 because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). They are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed in Table 1 are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF.

1.2 Detection limits depend on several factors, the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. General instrument detection limits for analytes of interest in environmental applications are shown in Table 1. These detection limits apply to a clean matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (600-second) count times. These detection limits are given for guidance only and will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of field performance-based detection limits is presented in Section 13.4 of this method. The clean matrix and field performance-based detection limits should be used for general planning purposes, and a third detection limit discussed, based on the standard deviation around single measurements, should be used in assessing data quality. This detection limit is discussed in Sections 9.7 and 11.3.

1.3 Use of this method is restricted to personnel either trained and knowledgeable in the operation of an XRF instrument or under the supervision of a trained and knowledgeable individual. This method is a screening method to be used with confirmatory analysis using EPA-approved methods. This method's main strength is as a rapid field screening procedure. The method detection limits (MDL) of FPXRF are above the toxicity characteristic regulatory level for most RCRA analytes. If the precision, accuracy, and detection limits of FPXRF meet the data quality objectives (DQOs) of your project, then XRF is a fast, powerful, cost effective technology for site characterization.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use sealed radioisotope sources to irradiate samples with x-rays. X-ray tubes are used to irradiate samples in the laboratory and are beginning to be incorporated into field portable instruments. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This later process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons

results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples: the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α) or beta (β), which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a K_α line is produced by a vacancy in the K shell filled by an L shell electron, whereas a K_β line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is on average 6 to 7 times more probable than the K_β transition; therefore, the K_α line is approximately 7 times more intense than the K_β line for a given element, making the K_α line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines (L_α and L_β) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.7 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments: in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

3.0 DEFINITIONS

3.1 FPXRF: Field portable x-ray fluorescence.

3.2 MCA: Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS: Site specific calibration standard.

3.4 FP: Fundamental parameter.

3.5 ROI: Region of interest.

3.6 SRM: Standard reference material. A standard containing certified amounts of metals in soil or sediment.

3.7 eV: Electron Volt. A unit of energy equivalent to the amount of energy gained by an electron passing through a potential difference of one volt.

3.8 Refer to Chapter One and Chapter Three for additional definitions.

4.0 INTERFERENCES

4.1 The total method error for FPXRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup, the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.3 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by drying the samples in a convection or toaster oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between FPXRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.4 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.5 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. As examples of absorption and enhancement effects; iron (Fe) tends to absorb copper (Cu) x-rays, reducing the intensity of the Cu measured by the detector, while chromium (Cr) will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients. The effects also can be compensated for using SSCS, which contain all the elements present on site that can interfere with one another.

4.6 When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks.

The most common spectrum overlaps involve the K_{β} line of element Z-1 with the K_{α} line of element Z. This is called the K_{α}/K_{β} interference. Because the $K_{\alpha}:K_{\beta}$ intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V K_{α} and K_{β} energies are 4.95

and 5.43 keV, respectively, and the Cr K_{α} energy is 5.41 keV. The Fe K_{α} and K_{β} energies are 6.40 and 7.06 keV, respectively, and the Co K_{α} energy is 6.92 keV. The difference between the V K_{β} and Cr K_{α} energies is 20 eV, and the difference between the Fe K_{β} and the Co K_{α} energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively. The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) K_{α} /lead (Pb) L_{α} and sulfur (S) K_{α} /Pb M_{α} . In the As/Pb case, Pb can be measured from the Pb L_{β} line, and As can be measured from either the As K_{α} or the As K_{β} line; in this way the interference can be corrected. If the As K_{β} line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As K_{α} line. If the As K_{α} line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in no As being reported regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis by an EPA-approved method.

4.8 If SSCS are used to calibrate an FPXRF instrument, the samples collected must be representative of the site under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentrations of the contaminants of concern at a given time and location. Analytical results for representative samples reflect variations in the presence and concentration ranges of contaminants throughout a site. Variables affecting sample representativeness include differences in soil type, contaminant concentration variability, sample collection and preparation variability, and analytical variability, all of which should be minimized as much as possible.

4.9 Soil physical and chemical effects may be corrected using SSCS that have been analyzed by inductively coupled plasma (ICP) or atomic absorption (AA) methods. However, a major source of error can be introduced if these samples are not representative of the site or if the analytical error is large. Another concern is the type of digestion procedure used to prepare the soil samples for the reference analysis. Analytical results for the confirmatory method will vary depending on whether a partial digestion procedure, such as SW-846 Method 3050, or a total digestion procedure, such as Method 3052 is used. It is known that depending on the nature of the soil or sediment, Method 3050 will achieve differing extraction efficiencies for different analytes of interest. The confirmatory method should meet the project data quality objectives.

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method, the confirmatory method used was Method 3050, and the FPXRF data

compared very well with regression correlation coefficients (r^2 often exceeding 0.95, except for barium and chromium. See Table 9 in Section 17.0). The critical factor is that the digestion procedure and analytical reference method used should meet the data quality objectives (DQOs) of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Section 9.2.

If the operator is instructed by the manufacturer to manually conduct a gain check because of increasing or decreasing ambient temperature, it is standard to perform a gain check after every 10 to 20 sample measurements or once an hour whichever is more frequent. It is also suggested that a gain check be performed if the temperature fluctuates more than 10 to 20°F. The operator should follow the manufacturer's recommendations for gain check frequency.

5.0 SAFETY

5.1 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operators manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. Licenses for radioactive materials are of two types; (1) general license which is usually provided by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) specific license which is issued to named persons for the operation of radioactive instruments as required by local state agencies. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals. A copy of the radioactive material licenses and leak tests should be present with the instrument at all times and available to local and national authorities upon request. X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. Finally, an additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply. The danger of electric shock is as substantial as the danger from radiation but is often overlooked because of its familiarity.

5.2 Radiation monitoring equipment should be used with the handling of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs should be worn in the area of most frequent exposure. The maximum permissible whole-body dose from occupational exposure is 5

Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

5.3 Refer to Chapter Three for guidance on some proper safety protocols.

6.0 EQUIPMENT AND SUPPLIES

6.1 FPXRF Spectrometer: An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

6.1.1 Excitation Sources: Most FPXRF instruments use sealed radioisotope sources to produce x-rays in order to irradiate samples. The FPXRF instrument may contain between one and three radioisotope sources. Common radioisotope sources used for analysis for metals in soils are iron (Fe)-55, cadmium (Cd)-109, americium (Am)-241, and curium (Cm)-244. These sources may be contained in a probe along with a window and the detector; the probe is connected to a data reduction and handling system by means of a flexible cable. Alternatively, the sources, window, and detector may be included in the same unit as the data reduction and handling system.

The relative strength of the radioisotope sources is measured in units of millicuries (mCi). All other components of the FPXRF system being equal, the stronger the source, the greater the sensitivity and precision of a given instrument. Radioisotope sources undergo constant decay. In fact, it is this decay process that emits the primary x-rays used to excite samples for FPXRF 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 the radioisotopes strength or activity by half. Developers of FPXRF technologies recommend source replacement at regular intervals based on the source's half-life. The characteristic x-rays emitted from each of the different sources have energies capable of exciting a certain range of analytes in a sample. Table 2 summarizes the characteristics of four common radioisotope sources.

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum required for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic

x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of accelerating voltage is governed by the anode material, since the electrons must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

6.1.2 Sample Presentation Device: FPXRF instruments can be operated in two modes: in situ and intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. For most FPXRF instruments operated in the intrusive mode, the probe is rotated so that the window faces upward. A protective sample cover is placed over the window, and the sample cup is placed on top of the window inside the protective sample cover for analysis.

6.1.3 Detectors: The detectors in the FPXRF instruments can be either solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include mercuric iodide (HgI_2), silicon pin diode and lithium-drifted silicon $\text{Si}(\text{Li})$. The HgI_2 detector is operated at a moderately subambient temperature controlled by a low power thermoelectric cooler. The silicon pin diode detector also is cooled via the thermoelectric Peltier effect. The $\text{Si}(\text{Li})$ detector must be cooled to at least -90°C either with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Instruments with a $\text{Si}(\text{Li})$ detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 liter. Proportional counter detectors are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter detector is not as good as that of a solid-state detector. The energy resolution of a detector for characteristic x-rays is usually expressed in terms of full width at half-maximum (FWHM) height of the manganese K_α peak at 5.89 keV. The typical resolutions of the above mentioned detectors are as follows: HgI_2 -270 eV; silicon pin diode-250 eV; $\text{Si}(\text{Li})$ -170 eV; and gas-filled, proportional counter-750 eV.

During operation of a solid-state detector, an x-ray photon strikes a biased, solid-state crystal and loses energy in the crystal by producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the x-ray photon absorbed by the crystal of the detector. A gas-filled, proportional counter detector is an ionization chamber filled with a mixture of noble and other gases. An x-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the x-ray photon absorbed by the gas in the detector.

6.1.4 Data Processing Units: The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (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. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in parts per million on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 100 to 500 sets of numerical analytical results. Most FPXRF

instruments are menu-driven from software built into the units or from PCs. Once the data-storage memory of an FPXRF unit is full, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery chargers.

6.3 Polyethylene sample cups: 31 millimeters (mm) to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

6.4 X-ray window film: Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 micrometers (μm) thick.

6.5 Mortar and pestle: glass, agate, or aluminum oxide; for grinding soil and sediment samples.

6.6 Containers: glass or plastic to store samples.

6.7 Sieves: 60-mesh (0.25 mm), stainless-steel, Nylon, or equivalent for preparing soil and sediment samples.

6.8 Trowels: for smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags: used for collection and homogenization of soil samples.

6.10 Drying oven: standard convection or toaster oven, for soil and sediment samples that require drying.

7.0 REAGENTS AND STANDARDS

7.1 Pure Element Standards: Each pure, single-element standard is intended to produce strong characteristic x-ray peaks of the element of interest only. Other elements present must not contribute to the fluorescence spectrum. A set of pure element standards for commonly sought analytes is supplied by the instrument manufacturer, if required for the instrument; not all instruments require the pure element standards. The standards are used to set the region of interest (ROI) for each element. They also can be used as energy calibration and resolution check samples.

7.2 Site-specific Calibration Standards: Instruments that employ fundamental parameters (FP) or similar mathematical models in minimizing matrix effects may not require SSCS. If the FP calibration model is to be optimized or if empirical calibration is necessary, then SSCSs must be collected, prepared, and analyzed.

7.2.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of ten samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.2.2 Each sample should be oven-dried for 2 to 4 hours at a temperature of less than 150°C. If mercury is to be analyzed, a separate sample portion must remain undried, as heating may volatilize the mercury. When the sample is dry, all large, organic debris and

nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be ground with a mortar and pestle and passed through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.2.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 grams of the dried, sieved sample on a piece of kraft or butcher paper about 1.5 by 1.5 feet in size. Each corner of the paper should be lifted alternately, rolling the soil over on itself and toward the opposite corner. The soil should be rolled on itself 20 times. Approximately 5 grams of the sample should then be removed and placed in a sample cup for FPXRF analysis. The rest of the prepared sample should be sent off site for ICP or AA analysis. The method use for confirmatory analysis should meet the data quality objectives of the project.

7.3 Blank Samples: The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the method detection limits. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.4 Standard Reference Materials: Standard reference materials (SRM) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample handling and preservation procedures used in FPXRF analyses should follow the guidelines in Chapter Three, Inorganic Analytes.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance protocols. All field data sheets and quality control data should be maintained for reference or inspection.

9.2 Energy Calibration Check: To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting, which would indicate drift within the instrument. As discussed in Section 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (> 10 to 20°F).

The energy calibration check should be run at a frequency consistent with manufacturers recommendations. Generally, this would be at the beginning of each working day, after the batteries are changed or the instrument is shut off, at the end of each working day, and at any other time when the instrument operator believes that drift is occurring during analysis. A pure element such as iron, manganese, copper, or lead is often used for the energy calibration check. A manufacturer-recommended count time per source should be used for the check.

9.2.1 The instrument manufacturer's manual specifies the channel or kiloelectron volt level at which a pure element peak should appear and the expected intensity of the peak.

The intensity and channel number of the pure element as measured using the radioactive source should be checked and compared to the manufacturer's recommendation. If the energy calibration check does not meet the manufacturer's criteria, then the pure element sample should be repositioned and reanalyzed. If the criteria are still not met, then an energy calibration should be performed as described in the manufacturer's manual. With some FPXRF instruments, once a spectrum is acquired from the energy calibration check, the peak can be optimized and realigned to the manufacturer's specifications using their software.

9.3 Blank Samples: Two types of blank samples should be analyzed for FPXRF analysis: instrument blanks and method blanks. An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window.

9.3.1 The instrument blank can be silicon dioxide, a Teflon block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the method detection limits should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. To be acceptable, a method blank must not contain any analyte at a concentration above its method detection limit. If an analyte's concentration exceeds its method detection limit, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

9.4 Calibration Verification Checks: A calibration verification check sample is used to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. A check sample should be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. The frequency of calibration checks during active analysis will depend on the data quality objectives of the project. The check sample should be a well characterized soil sample from the site that is representative of site samples in terms of particle size and degree of homogeneity and that contains contaminants at concentrations near the action levels. If a site-specific sample is not available, then an NIST or other SRM that contains the analytes of interest can be used to verify the accuracy of the instrument. The measured value for each target analyte should be within ± 20 percent (%D) of the true value for the calibration verification check to be acceptable. If a measured value falls outside this range, then the check sample should be reanalyzed. If the value continues to fall outside the acceptance range, the instrument should be recalibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

9.5 Precision Measurements: The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It

is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent.

The equation for calculating RSD is as follows:

$$\text{RSD} = (\text{SD}/\text{Mean Concentration}) \times 100$$

where:

RSD	=	Relative standard deviation for the precision measurement for the analyte
SD	=	Standard deviation of the concentration for the analyte
Mean Concentration	=	Mean concentration for the analyte

The precision or reproducibility of a measurement will improve with increasing count time, however, increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing return. Increasing the count time also improves the detection limit, but decreases sample throughput.

9.6 Detection Limits: Results for replicate analyses of a low-concentration sample, SSCS, or SRM can be used to generate an average site-specific method detection and quantitation limits. In this case, the method detection limit is defined as 3 times the standard deviation of the results for the low-concentration samples and the method quantitation limit is defined as 10 times the standard deviation of the same results. Another means of determining method detection and quantitation limits involves use of counting statistics. In FPXRF analysis, the standard deviation from counting statistics is defined as $\text{SD} = (\text{N})^{1/2}$, where SD is the standard deviation for a target analyte peak and N is the net counts for the peak of the analyte of interest (i.e., gross counts minus background under the peak). Three times this standard deviation would be the method detection limit and 10 times this standard deviation would be the method quantitation limit. If both of the above mentioned approaches are used to calculate method detection limits, the larger of the standard deviations should be used to provide the more conservative detection limits.

This SD based detection limit criteria must be used by the operator to evaluate each measurement for its useability. A measurement above the average calculated or manufacturer's detection limit, but smaller than three times its associated SD, should not be used as a quantitative measurement. Conversely, if the measurement is below the average calculated or manufacturer's detection limit, but greater than three times its associated SD. It should be coded as an estimated value.

9.7 Confirmatory Samples: The comparability of the FPXRF analysis is determined by submitting FPXRF-analyzed samples for analysis at a laboratory. The method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The confirmatory samples must be splits of the well homogenized sample material. In some cases the prepared

sample cups can be submitted. A minimum of 1 sample for each 20 FPXRF-analyzed samples should be submitted for confirmatory analysis. This frequency will depend on data quality objectives. The confirmatory analyses can also be used to verify the quality of the FPXRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the FPXRF. They should also include samples with analyte concentrations at or near the site action levels. The results of the confirmatory analysis and FPXRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r^2) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r^2 is 0.9 or greater and inferential statistics indicate the FPXRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Calibration: Instrument calibration procedures vary among FPXRF instruments. Users of this method should follow the calibration procedures outlined in the operator's manual for each specific FPXRF instrument. Generally, however, three types of calibration procedures exist for FPXRF instruments: FP calibration, empirical calibration, and the Compton peak ratio or normalization method. These three types of calibration are discussed below.

10.2 Fundamental Parameters Calibration: FP calibration procedures are extremely variable. An FP calibration provides the analyst with a "standardless" calibration. The advantages of FP calibrations over empirical calibrations include the following:

- No previously collected site-specific samples are required, although site-specific samples with confirmed and validated analytical results for all elements present could be used.
- Cost is reduced because fewer confirmatory laboratory results or calibration standards are required.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Section 7.2. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

10.2.1 Effective Energy FP Calibration: The effective energy FP calibration is performed by the manufacturer before an instrument is sent to the analyst. Although SSCS can be used, the calibration relies on pure element standards or SRMs such as those obtained from NIST for the FP calibration. The effective energy routine relies on the spectrometer response to pure elements and FP iterative algorithms to compensate for various matrix effects.

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured

x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

The working effective energy FP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of sampling. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. A manufacturer-recommended count time per source should be used for the calibration check. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A percent difference (%D) is then calculated for each target analyte. The %D should be within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

$$\%D = ((C_s - C_k) / C_k) \times 100$$

where:

%D = Percent difference

C_k = Certified concentration of standard sample

C_s = Measured concentration of standard sample

10.2.2 BFP Calibration: BFP calibration relies on the ability of the liquid nitrogen-cooled, Si(Li) solid-state detector to separate the coherent (Compton) and incoherent (Rayleigh) backscatter peaks of primary radiation. These peak intensities are known to be a function of sample composition, and the ratio of the Compton to Rayleigh peak is a function of the mass absorption of the sample. The calibration procedure is explained in detail in the instrument manufacturer's manual. Following is a general description of the BFP calibration procedure.

The concentrations of all detected and quantified elements are entered into the computer software system. Certified element results for an NIST SRM or confirmed and validated results for an SSCS can be used. In addition, the concentrations of oxygen and silicon must be entered; these two concentrations are not found in standard metals analyses. The manufacturer provides silicon and oxygen concentrations for typical soil types. Pure element standards are then analyzed using a manufacturer-recommended count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

The working BFP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of the analysis. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. The standard sample is analyzed using a manufacturer-recommended count time per source to check the

calibration curve. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A %D is then calculated for each target analyte. The %D should fall within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line the y-intercept value for the analyte. The standard sample is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

10.3 Empirical Calibration: An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Section 7.2; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is required. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

An empirical calibration using SSCS involves analysis of SSCS by the FPXRF instrument and by a conventional analytical method such as ICP or AA. A total acid digestion procedure should be used by the laboratory for sample preparation. Generally, a minimum of 10 and a maximum of 30 well characterized SSCS, site-typical standards, or prepared metal oxide standards are required to perform an adequate empirical calibration. The number of required standards depends on the number of analytes of interest and interfering elements. Theoretically, an empirical calibration with SSCS should provide the most accurate data for a site because the calibration compensates for site-specific matrix effects.

The first step in an empirical calibration is to analyze the pure element standards for the elements of interest. This enables the instrument to set channel limits for each element for spectral deconvolution. Next the SSCS, site-typical standards, or prepared metal oxide standards are analyzed using a count time of 200 seconds per source or a count time recommended by the manufacturer. This will produce a spectrum and net intensity of each analyte in each standard. The analyte concentrations for each standard are then entered into the instrument software; these concentrations are those obtained from the laboratory, the certified results, or the gravimetrically determined concentrations of the prepared standards. This gives the instrument analyte values to regress against corresponding intensities during the modeling stage. The regression equation correlates the concentrations of an analyte with its net intensity.

The calibration equation is developed using a least squares fit regression analysis. After the regression terms to be used in the equation are defined, a mathematical equation can be developed to calculate the analyte concentration in an unknown sample. In some FPXRF instruments, the software of the instrument calculates the regression equation. The software uses calculated intercept and slope values to form a multiterm equation. In conjunction with the software in the instrument, the operator can adjust the multiterm equation to minimize interelement interferences and optimize the intensity calibration curve.

It is possible to define up to six linear or nonlinear terms in the regression equation. Terms can be added and deleted to optimize the equation. The goal is to produce an equation with the smallest regression error and the highest correlation coefficient. These values are automatically computed by the software as the regression terms are added, deleted, or modified. It is also possible to delete data points from the regression line if these points are significant outliers or if they are heavily weighing the data. Once the regression equation has been selected for an analyte, the equation can be entered into the software for quantitation of analytes in subsequent samples. For an empirical calibration to be acceptable, the regression equation for a specific analyte should have a correlation coefficient of 0.98 or greater or meet the DQOs of the project.

In an empirical calibration, one must apply the DQOs of the project and ascertain critical or action levels for the analytes of interest. It is within these concentration ranges or around these action levels that the FPXRF instrument should be calibrated most accurately. It may not be possible to develop a good regression equation over several orders of analyte concentration.

10.4 Compton Normalization Method: The Compton normalization method is based on analysis of a single, certified standard and normalization for the Compton peak. The Compton peak is produced from incoherent backscattering of x-ray radiation from the excitation source and is present in the spectrum of every sample. The Compton peak intensity changes with differing matrices. Generally, matrices dominated by lighter elements produce a larger Compton peak, and those dominated by heavier elements produce a smaller Compton peak. Normalizing to the Compton peak can reduce problems with varying matrix effects among samples. Compton normalization is similar to the use of internal standards in organics analysis. The Compton normalization method may not be effective when analyte concentrations exceed a few percent.

The certified standard used for this type of calibration could be an NIST SRM such as 2710 or 2711. The SRM must be a matrix similar to the samples and must contain the analytes of interests at concentrations near those expected in the samples. First, a response factor has to be determined for each analyte. This factor is calculated by dividing the net peak intensity by the analyte concentration. The net peak intensity is gross intensity corrected for baseline interference. Concentrations of analytes in samples are then determined by multiplying the baseline corrected analyte signal intensity by the normalization factor and by the response factor. The normalization factor is the quotient of the baseline corrected Compton K_{α} peak intensity of the SRM divided by that of the samples. Depending on the FPXRF instrument used, these calculations may be done manually or by the instrument software.

11.0 PROCEDURE

11.1 Operation of the various FPXRF instruments will vary according to the manufacturers' protocols. Before operating any FPXRF instrument, one should consult the manufacturer's manual. Most manufacturers recommend that their instruments be allowed to warm up for 15 to 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems later on in analysis.

11.2 Each FPXRF instrument should be operated according to the manufacturer's recommendations. There are two modes in which FPXRF instruments can be operated: in situ and intrusive. The in situ mode involves analysis of an undisturbed soil sediment or sample. Intrusive analysis involves collection and preparation of a soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

11.3 For in situ analysis, one requirement is that any large or nonrepresentative debris be removed from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Another requirement is that the soil surface be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide data for this method, this modest amount of sample preparation was found to take less than 5 minutes per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for *in situ* analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on required detection limits.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 grams or 250 cm³, which is enough soil to fill an 8-ounce jar. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Section 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the homogenization procedure using the fluorescein dye required 3 to 5 minutes per sample. As demonstrated in Sections 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, it can be used without the more labor intensive steps of drying, grinding, and sieving given in Sections 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps must be followed.

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

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 minutes per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 µm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle,

and sieves must be thoroughly cleaned so that any cross-contamination is below the MDLs of the procedure or DQOs of the analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in parts per million and can be downloaded to a PC, which can provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation.

13.0 METHOD PERFORMANCE

13.1 This section discusses four performance factors, field-based method detection limits, precision, accuracy, and comparability to EPA-approved methods. The numbers presented in Tables 4 through 9 were generated from data obtained from six FPXRF instruments. The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from nondetect to tens of thousands of mg/kg.

13.2 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a HgI₂ detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.3 All data presented in Tables 4 through 9 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source. The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

13.4 Field-Based Method Detection Limits: The field-based method detection limits are presented in Table 4. The field-based method detection limits were determined by collecting ten replicate measurements on site-specific soil samples with metals concentrations 2 to 5 times the expected method detection limits. Based on these ten replicate measurements, a standard deviation on the replicate analysis was calculated. The method detection limits presented in Table 4 are defined as 3 times the standard deviation for each analyte.

The field-based method detection limits were generated by using the count times discussed earlier in this section. All the field-based method detection limits were calculated for soil samples that had been dried and ground and placed in a sample cup with the exception of the MAP Spectrum Analyzer. This instrument can only be operated in the in situ mode, meaning the samples were moist and not ground.

Some of the analytes such as cadmium, mercury, silver, selenium, and thorium were not detected or only detected at very low concentrations such that a field-based method detection limit could not be determined. These analytes are not presented in Table 4. Other analytes such as calcium, iron, potassium, and titanium were only found at high concentrations (thousands of mg/kg) so that reasonable method detection limits could not be calculated. These analytes also are not presented in Table 4.

13.5 Precision Measurements: The precision data is presented in Table 5. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from nondetects to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from in situ (no preparation) to dried and ground in a sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 5 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the MDL for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 5. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the MDLs so that an RSD value calculated at 5 to 10 times the MDL was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 6 shows these results. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the detection limit of the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the *in situ* homogenized samples. The FPXRF analyzer conducted five replicate measurements of the in situ field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 6 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square, measurements of different soil samples were actually taking place within the square. Table 6 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five versus ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy Measurements: Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 7 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 7 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 7. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 7.

Table 8 provides a more detailed summary of accuracy data for one FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. Table 8 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

13.7 Comparability: Comparability refers to the confidence with which one data set can be compared to another. In this case, FPXRF data generated from a large study of six FPXRF instruments was compared to SW-846 Methods 3050 and 6010 which are the standard soil extraction for metals and analysis by inductively coupled plasma. An evaluation of comparability was conducted by using linear regression analysis. Three factors were determined using the linear regression. These factors were the y-intercept, the slope of the line, and the coefficient of determination (r^2).

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 9. Similar trends in the data were seen for all instruments.

Table 9 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. The soil types are as follows: soil 1--sand; soil 2--loam; and soil 3--silty clay. The preparation methods are as follows: preparation 1--in situ in the field; preparation 2--in situ, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not ground; and preparation 4--sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

For arsenic, copper, lead, and zinc, the comparability to the confirmatory laboratory was excellent with r^2 values ranging from 0.80 to 0.99 for all six FPXRF instruments. The slopes of the regression lines for arsenic, copper, lead, and zinc, were generally between 0.90 and 1.00 indicating the data would need to be corrected very little or not at all to match the confirmatory laboratory data. The r^2 values and slopes of the regression lines for barium and chromium were

not as good as for the other for analytes, indicating the data would have to be corrected to match the confirmatory laboratory.

Table 9 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 9 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

Section 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time required to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 minutes. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 minutes per sample. Lastly, when grinding and sieving is conducted, time must be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

13.8 The following documents may provide additional guidance and insight on this method and technique:

13.8.1 Hewitt, A.D. 1994. "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_{α} Peak Normalization Analysis." *American Environmental Laboratory*. Pages 24-32.

13.8.2 Piorek, S., and J.R. Pasmore. 1993. "Standardless, In Situ Analysis of Metallic Contaminants in the Natural Environment With a PC-Based, High Resolution Portable X-Ray Analyzer." *Third International Symposium on Field Screening Methods for Hazardous Waste and Toxic Chemicals*. Las Vegas, Nevada. February 24-26, 1993. Volume 2, Pages 1135-1151.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Metorex. X-MET 920 User's Manual.
2. Spectrace Instruments. 1994. Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction.
3. TN Spectrace. Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.
4. Unpublished SITE data, recieved from PRC Environment Management, Inc.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 9 and a method procedure flow diagram.

**TABLE 1
INTERFERENCE FREE DETECTION LIMITS**

Analyte	Chemical Abstract Series Number	Detection Limit in Quartz Sand (milligrams per kilogram)
Antimony (Sb)	7440-36-0	40
Arsenic (As)	7440-38-0	40
Barium (Ba)	7440-39-3	20
Cadmium (Cd)	7440-43-9	100
Calcium (Ca)	7440-70-2	70
Chromium (Cr)	7440-47-3	150
Cobalt (Co)	7440-48-4	60
Copper (Cu)	7440-50-8	50
Iron (Fe)	7439-89-6	60
Lead (Pb)	7439-92-1	20
Manganese (Mn)	7439-96-5	70
Mercury (Hg)	7439-97-6	30
Molybdenum (Mo)	7439-93-7	10
Nickel (Ni)	7440-02-0	50
Potassium (K)	7440-09-7	200
Rubidium (Rb)	7440-17-7	10
Selenium (Se)	7782-49-2	40
Silver (Ag)	7440-22-4	70
Strontium (Sr)	7440-24-6	10
Thallium (Tl)	7440-28-0	20
Thorium (Th)	7440-29-1	10
Tin (Sn)	7440-31-5	60
Titanium (Ti)	7440-32-6	50
Vanadium (V)	7440-62-2	50
Zinc (Zn)	7440-66-6	50
Zirconium (Zr)	7440-67-7	10

Source: References 1, 2, and 3

**TABLE 2
SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS**

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
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

Source: Reference 1, 2, and 3

**TABLE 3
SUMMARY OF X-RAY TUBE SOURCE CHARACTERISTICS**

Anode Material	Recommended Voltage Range (kV)	K-alpha Emission (keV)	Elemental Analysis Range	
Cu	18-22	8.04	Potassium to Cobalt Silver to Gadolinium	K Lines L Lines
Mo	40-50	17.4	Cobalt to Yttrium Europium to Radon	K Lines L Lines
Ag	50-65	22.1	Zinc to Technicium Ytterbium to Neptunium	K Lines L Lines

Source: Reference 4

Notes: The sample elements excited are chosen by taking as the lower limit the same ratio of excitation line energy to element absorption edge as in Table 2 (approximately 0.45) and the requirement that the excitation line energy be above the element absorption edge as the upper limit (L2 edges used for L lines). K-beta excitation lines were ignored.

TABLE 4
FIELD-BASED METHOD DETECTION LIMITS (mg/kg)^a

Analyte	Instrument					
	TN 9000	TN Lead Analyzer	X-MET 920 (SiLi Detector)	X-MET 920 (Gas-Filled Detector)	XL Spectrum Analyzer	MAP Spectrum Analyzer
Antimony	55	NR	NR	NR	NR	NR
Arsenic	60	50	55	50	110	225
Barium	60	NR	30	400	NR	NR
Chromium	200	460	210	110	900	NR
Cobalt	330	NR	NR	NR	NR	NR
Copper	85	115	75	100	125	525
Lead	45	40	45	100	75	165
Manganese	240	340	NR	NR	NR	NR
Molybdenum	25	NR	NR	NR	30	NR
Nickel	100	NR	NA	NA	NA	NR
Rubidium	30	NR	NR	NR	45	NR
Strontium	35	NR	NR	NR	40	NR
Tin	85	NR	NR	NR	NR	NR
Zinc	80	95	70	NA	110	NA
Zirconium	40	NR	NR	NR	25	NR

Source: Reference 4

^a MDLs are related to the total number of counts taken. See Section 13.3 for count times used to generate this table.

NR Not reported.

NA Not applicable; analyte was reported but was not at high enough concentrations for method detection limit to be determined.

**TABLE 5
PRECISION**

Analyte	Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the MDL					
	TN 9000	TN Lead Analyzer	X-MET 920 (SiLi Detector)	X-MET 920 (Gas-Filled Detector)	XL Spectrum Analyzer	MAP Spectrum Analyzer
Antimony	6.54	NR	NR	NR	NR	NR
Arsenic	5.33	4.11	3.23	1.91	12.47	6.68
Barium	4.02	NR	3.31	5.91	NR	NR
Cadmium	29.84 ^a	NR	24.80 ^a	NR	NR	NR
Calcium	2.16	NR	NR	NR	NR	NR
Chromium	22.25	25.78	22.72	3.91	30.25	NR
Cobalt	33.90	NR	NR	NR	NR	NR
Copper	7.03	9.11	8.49	9.12	12.77	14.86
Iron	1.78	1.67	1.55	NR	2.30	NR
Lead	6.45	5.93	5.05	7.56	6.97	12.16
Manganese	27.04	24.75	NR	NR	NR	NR
Molybdenum	6.95	NR	NR	NR	12.60	NR
Nickel	30.85 ^a	NR	24.92 ^a	20.92 ^a	NA	NR
Potassium	3.90	NR	NR	NR	NR	NR
Rubidium	13.06	NR	NR	NR	32.69 ^a	NR
Strontium	4.28	NR	NR	NR	8.86	NR
Tin	24.32 ^a	NR	NR	NR	NR	NR
Titanium	4.87	NR	NR	NR	NR	NR
Zinc	7.27	7.48	4.26	2.28	10.95	0.83
Zirconium	3.58	NR	NR	NR	6.49	NR

Source: Reference 4

^a These values are biased high because the concentration of these analytes in the soil samples was near the detection limit for that particular FPXRF instrument.

NR Not reported.

NA Not applicable; analyte was reported but was below the method detection limit.

**TABLE 6
PRECISION AS AFFECTED BY SAMPLE PREPARATION**

Analyte	Average Relative Standard Deviation for Each Preparation Method		
	In Situ-Field	Intrusive- Undried and Unground	Intrusive- Dried and Ground
Antimony	30.1	15.0	14.4
Arsenic	22.5	5.36	3.76
Barium	17.3	3.38	2.90
Cadmium ^a	41.2	30.8	28.3
Calcium	17.5	1.68	1.24
Chromium	17.6	28.5	21.9
Cobalt	28.4	31.1	28.4
Copper	26.4	10.2	7.90
Iron	10.3	1.67	1.57
Lead	25.1	8.55	6.03
Manganese	40.5	12.3	13.0
Mercury	ND	ND	ND
Molybdenum	21.6	20.1	19.2
Nickel ^a	29.8	20.4	18.2
Potassium	18.6	3.04	2.57
Rubidium	29.8	16.2	18.9
Selenium	ND	20.2	19.5
Silver ^a	31.9	31.0	29.2
Strontium	15.2	3.38	3.98
Thallium	39.0	16.0	19.5
Thorium	NR	NR	NR
Tin	ND	14.1	15.3
Titanium	13.3	4.15	3.74
Vanadium	NR	NR	NR
Zinc	26.6	13.3	11.1
Zirconium	20.2	5.63	5.18

Source: Reference 4

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

ND Not detected.

NR Not reported.

**TABLE 7
ACCURACY**

Analyte	Instrument															
	TN 9000				TN Lead Analyzer				X-MET 920 (SiLi Detector)				XL Spectrum Analyzer			
	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD
Sb	2	100-149	124.3	NA	--	--	--	--	--	--	--	--	--	--	--	--
As	5	68-115	92.8	17.3	5	44-105	83.4	23.2	4	9.7-91	47.7	39.7	5	38-535	189.8	206
Ba	9	98-198	135.3	36.9	--	--	--	--	9	18-848	168.2	262	--	--	--	--
Cd	2	99-129	114.3	NA	--	--	--	--	6	81-202	110.5	45.7	--	--	--	--
Cr	2	99-178	138.4	NA	--	--	--	--	7	22-273	143.1	93.8	3	98-625	279.2	300
Cu	8	61-140	95.0	28.8	6	38-107	79.1	27.0	11	10-210	111.8	72.1	8	95-480	203.0	147
Fe	6	78-155	103.7	26.1	6	89-159	102.3	28.6	6	48-94	80.4	16.2	6	26-187	108.6	52.9
Pb	11	66-138	98.9	19.2	11	68-131	97.4	18.4	12	23-94	72.7	20.9	13	80-234	107.3	39.9
Mn	4	81-104	93.1	9.70	3	92-152	113.1	33.8	--	--	--	--	--	--	--	--
Ni	3	99-122	109.8	12.0	--	--	--	--	--	--	--	--	3	57-123	87.5	33.5
Sr	8	110-178	132.6	23.8	--	--	--	--	--	--	--	--	7	86-209	125.1	39.5
Zn	11	41-130	94.3	24.0	10	81-133	100.0	19.7	12	46-181	106.6	34.7	11	31-199	94.6	42.5

Source: Reference 4

- n Number of samples that contained a certified value for the analyte and produced a detectable concentration from the FPXRF instrument.
- SD Standard deviation.
- NA Not applicable; only two data points, therefore, a SD was not calculated.
- %Rec. Percent recovery.
- No data.

**TABLE 8
ACCURACY FOR TN 9000^a**

Standard Reference Material	Arsenic			Barium			Copper			Lead			Zinc		
	Cert. Conc.	Meas. Conc.	%Rec.												
RTC CRM-021	24.8	ND	NA	586	1135	193.5	4792	2908	60.7	144742	149947	103.6	546	224	40.9
RTC CRM-020	397	429	92.5	22.3	ND	NA	753	583	77.4	5195	3444	66.3	3022	3916	129.6
BCR CRM 143R	--	--	--	--	--	--	131	105	80.5	180	206	114.8	1055	1043	99.0
BCR CRM 141	--	--	--	--	--	--	32.6	ND	NA	29.4	ND	NA	81.3	ND	NA
USGS GXR-2	25.0	ND	NA	2240	2946	131.5	76.0	106	140.2	690	742	107.6	530	596	112.4
USGS GXR-6	330	294	88.9	1300	2581	198.5	66.0	ND	NA	101	80.9	80.1	118	ND	NA
NIST 2711	105	104	99.3	726	801	110.3	114	ND	NA	1162	1172	100.9	350	333	94.9
NIST 2710	626	722	115.4	707	782	110.6	2950	2834	96.1	5532	5420	98.0	6952	6476	93.2
NIST 2709	17.7	ND	NA	968	950	98.1	34.6	ND	NA	18.9	ND	NA	106	98.5	93.0
NIST 2704	23.4	ND	NA	414	443	107.0	98.6	105	106.2	161	167	103.5	438	427	97.4
CNRC PACS-1	211	143	67.7	--	772	NA	452	302	66.9	404	332	82.3	824	611	74.2
SARM-51	--	--	--	335	466	139.1	268	373	139.2	5200	7199	138.4	2200	2676	121.6
SARM-52	--	--	--	410	527	128.5	219	193	88.1	1200	1107	92.2	264	215	81.4

Source: Reference 4

^a All concentrations in milligrams per kilogram.

%Rec. Percent recovery.

ND Not detected.

NA Not applicable.

-- No data.

**TABLE 9
REGRESSION PARAMETERS FOR COMPARABILITY¹**

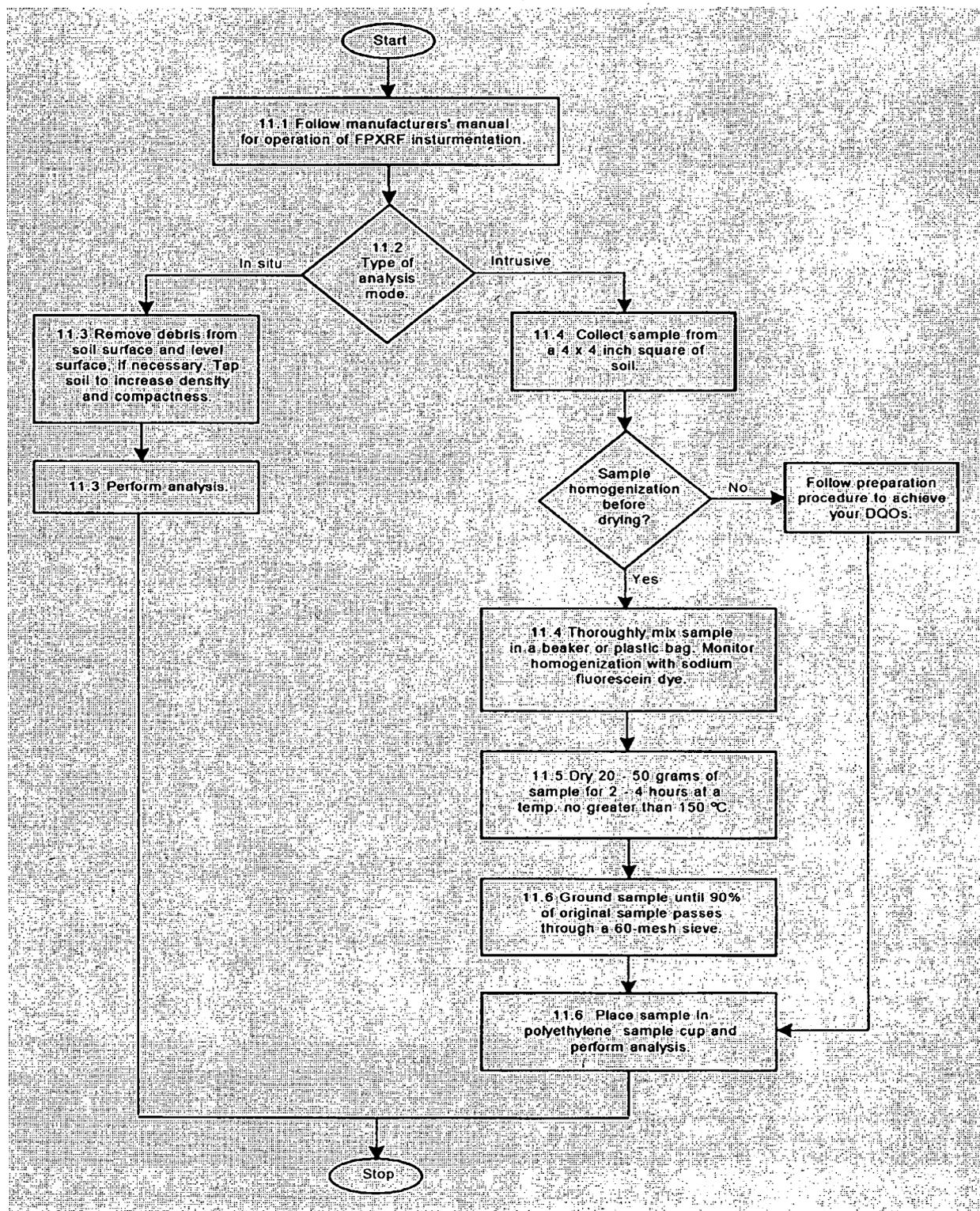
	Arsenic				Barium				Copper			
	n	r ²	Int.	Slope	n	r ²	Int.	Slope	n	r ²	Int.	Slope
All Data	824	0.94	1.62	0.94	1255	0.71	60.3	0.54	984	0.93	2.19	0.93
Soil 1	368	0.96	1.41	0.95	393	0.05	42.6	0.11	385	0.94	1.26	0.99
Soil 2	453	0.94	1.51	0.96	462	0.56	30.2	0.66	463	0.92	2.09	0.95
Soil 3	—	—	—	—	400	0.85	44.7	0.59	136	0.46	16.60	0.57
Prep 1	207	0.87	2.69	0.85	312	0.64	53.7	0.55	256	0.87	3.89	0.87
Prep 2	208	0.97	1.38	0.95	315	0.67	64.6	0.52	246	0.96	2.04	0.93
Prep 3	204	0.96	1.20	0.99	315	0.78	64.6	0.53	236	0.97	1.45	0.99
Prep 4	205	0.96	1.45	0.98	313	0.81	58.9	0.55	246	0.96	1.99	0.96

	Lead				Zinc				Chromium			
	n	r ²	Int.	Slope	n	r ²	Int.	Slope	n	r ²	Int.	Slope
All Data	1205	0.92	1.66	0.95	1103	0.89	1.86	0.95	280	0.70	64.6	0.42
Soil 1	357	0.94	1.41	0.96	329	0.93	1.78	0.93	—	—	—	—
Soil 2	451	0.93	1.62	0.97	423	0.85	2.57	0.90	—	—	—	—
Soil 3	397	0.90	2.40	0.90	351	0.90	1.70	0.98	186	0.66	38.9	0.50
Prep 1	305	0.80	2.88	0.86	286	0.79	3.16	0.87	105	0.80	66.1	0.43
Prep 2	298	0.97	1.41	0.96	272	0.95	1.86	0.93	77	0.51	81.3	0.36
Prep 3	302	0.98	1.26	0.99	274	0.93	1.32	1.00	49	0.73	53.7	0.45
Prep 4	300	0.96	1.38	1.00	271	0.94	1.41	1.01	49	0.75	31.6	0.56

Source: Reference 4

- ¹ Log-transformed data
- n Number of data points
- r² Coefficient of determination
- Int. Y-intercept
- No applicable data

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT



APPENDIX B

**USEPA REGION 5'S QUALITY ASSURANCE GUIDANCE DOCUMENT
(APPENDIX Q)
SAMPLE PREPARATION OF SOILS/SOLIDS FOR METALS ANALYSIS**

matrix spike concentration from the matrix spiked value. An undesirable 2 to 3-fold variation in sample results is observed.

For the high concentration level lead measurements (ICP emission spectroscopy), precision of measurement was undesirable for 12 of 15 soil QC audits. Any analysis of variance would show that sample aliquot selection had a larger effect on data quality than analytical measurement. If sample homogenization, with particle size reduction had been practiced, desirable data quality would probably have been obtained. The cost/time of sample homogenization would have been small compared to the cost of sample collection, and any resampling. Desirable data quality can be defined as the difference in replicate sample aliquots being less than the 20% relative percent deviation.

The Environmental Protection Agency (EPA) does recognize, recommend, and specify homogenization of soils prior to sample aliquot selection. Please see the documents listed below for EPA's lead program:

3. "Residential Sampling for Lead: Protocols for Dust and Soil Sampling, Final Report", EPA 747-R-95-001, March 1995.
4. "Pb-Based Paint Laboratory Operations Guidelines: Analysis of Pb in Paint, Dust, and Soil Revision 1.0", EPA 747-R-92-006, May 1993.

Procedures for drying and homogenization of soils are described in these guidance documents.

Other references are available for soil preparation techniques. I have included a copy of Chapter 21 from:

Methods of Soil Analysis, Part II,
Second Edition,
American Society of Agronomy,
Soil Science Society of America,
Madison, Wisconsin,
1982

Section 21-3 of this reference discusses sample preparation techniques for lead in soil.

Attachments

cc: A. Debus, RCRA
J. Morris, CRL

MEMORANDUM

SUBJECT: Sample Preparation of Soils/Solids for Metals
Analysis

FROM: David A. Payne, Chemist
Toxics Program Section
Waste, Pesticides and Toxics Division

TO: Oliver Fordham, Chemist
SW-846 Methods Team
Office of Solid Waste (5307W)
U.S. EPA Headquarters

DATE: July 16, 1996

This memo is written to request SW-846 methodologies, (Method 3050 series) for sample preparation of soils/solids for metals analysis, be changed to recognize the utility of dried, homogenized soils/solids prior to acid digestion. Method 3050, and other succeeding methods in this series, specifies a 1 g. representative, "wet" aliquot be selected, but does not specify how this is to be done. Even smaller aliquots (0.2g.) are used for mercury analyses. One (1) gram of a "wet" soil is often not representative of the entire soil/solid sample.

I provide QA support to our Division's RCRA Facility Investigations for enforcement and permitting programs. The usability of metals data for soils/solids can not be assured unless representative portions are first dried at 60°C, or less (to prevent mercury loss), then homogenized with particle size reduction. Data usability is monitored through QC audits of matrix spikes and sample replicates. Present day analytical instruments (ICP emission spectrometers) are controlled with calibration errors and measurement repeatability of less than 10%. Data quality is more a function of sample aliquot selection, than analytical measurement, when soil/solid aliquots are not homogenized.

I have attached an example data set to illustrate the undesirable use of "wet" sample aliquots. Attachments 1 and 2 to this memo provide ICP and graphite furnace results, respectively, for lead in soil using triplicate, one (1) gram "wet" aliquots. The soil were from a Superfund lead site and were 10-15% moisture. The third soil replicate value is estimated by subtracting the lead