QUALITY ASSURANCE PROJECT PLAN

GOLD KING MINE SPILL LONG-TERM MONITORING PLAN

NEW MEXICO ANIMAS AND SAN JUAN RIVER SEDIMENT ASSESSMENT SAMPLING AND ANALYSIS

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ACRONYMS AND ABBREVIATIONS

ARD	Acid Rock Drainage
°C	degrees Celsius
CO	Colorado
DQO	Data Quality Objective
DI	Dionized
EPA	U.S. Environmental Protection Agency
GIS	Geographic Information System
GKM	Gold King Mine
GPS	Global Positioning System
in	Inch(es)
LCS	Laboratory Control Samples
LTMP	Long-Term Monitoring Plan
MDL	Method Detection Limit
mg/kg	Milligrams per kilograms
NM	New Mexico
NMED	New Mexico Environment Department
oz	Ounce(s)
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RL	Reporting Limit
RPD	Relative Percent Difference
RSL	Regional Screening Level
SOP	Standard Operating Procedure
SLD	Scientific Laboratory Division
XRF	X-Ray Fluorescence

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1. INTRODUCTION

The purpose of the **New Mexico Animas and San Juan River Sediment Assessment Sampling and Analysis** is to collect a robust and defensible data set that delineates the nature and extent of contamination of sediment and soil released to the river basins during the August 5, 2015 Gold King Mine (GKM) spill along with impacts to sediment from over a century of mining in the Upper Animas River Basin. This project will collect data using the U.S. Environmental Protection Agency (EPA) Method 6200 for handheld X-Ray Fluorescence (XRF) device(s) and EPA Method 846 for analysis of sediment collected at sample locations in the Animas and San Juan Rivers, extending from Silverton, Colorado (CO) to Farmington, New Mexico (NM). These data will supplement and enhance the existing dataset from both the EPA and U.S. Geological Survey (USGS) collected within the watershed historically and as part of the GKM spill response.

This Quality Assurance Project Plan (QAPP) has been prepared for the sampling and analysis of soil and sediment within the Animas and San Juan River Watersheds as part of the New Mexico (NM) Long-Term Monitoring Plan (LTMP) Work Elements 3 and 4. As part of the LTMP, soil and sediment samples will be collected along the length of the Animas River, extending from the confluence of Cement Creek and the Animas River near Silverton, Colorado (CO) continuting downstream to the confluence of the Animas River and San Juan River near Farmington, NM. Samples will be collected for on-site and off-site analysis to define the nature and extent of contaminated soil and sediment resulting from the Gold King Mine (GKM) spill that occurred on August 5, 2015.

The principal elements of the proposed sampling and analysis associated with this work element in the NM LTMP are summarized in this QAPP which also describes the quality assurance, quality control, and other technical activities that will be implemented to ensure that the results of the sampling to be performed will meet project requirements. NMED is responsible for ensuring the QAPP is followed on-site.

The QAPP is organized into the following sections:

Section 2.0 Project/Task Organiziation

Section 3.0 Problem Definition/Background

Section 4.0 Data Generation and Acquisition

Section 5.0 Assessment and Oversight

Section 6.0 Data Validation and Reporting

2. PROJECT/TASK ORGANIZATION

This section lists the roles and responsibilities of persons that will collect and/or use the information gathered for the GKM spill sediment assessment sampling and analysis. A project organizational chart is included in this section, displaying the hierarchy of the project.

Name	Organization	Role	Responsibilities	Contact Information
Bruce Yurdin	NMED	GKM Program Manager	Reviewing and approving QAPP, project management oversight	bruce.yurdin@state.nm.us 505.827.1758
Dennis McQuillan	NMED	Chief Scientist	Reviewing and approving QAPP; technical project oversight and management.	dennis.mcquillan@state.nm.us 505.827.4120
Diane Agnew	NMED	GKM Project Manager	Producing and implementing QAPP, principal project management, maintaining project files and datasets, reporting.	diane.agnew@state.nm.us 505.222.9555
Kristine Pintado	NMED	GKM Field Sampling and Data Collection Team Lead	Set-up, principle data collection, performance of sampling plan	kristine.pintado@state.nm.us 505.827.2822

Operation of the handheld XRF analyzer will be conducted by NMED staff members with manufacturer training certification or 1-day of supervised operation of the instrument by a ceritified staff member. Sample team members will be provided with on-site training in the use of the Global Positioning System (GPS) equipment by an NMED staff member trained and competent in the use of the equipment.

3. PROBLEM DEFINTION/BACKGROUND

The central problem of this project is to quantitatively identify the nature and distribution of contaminated sediment resulting from the August 5, 2015 GKM spill event and historic mining activity in the Upper Animas River Basin. The EPA estimates that approximately 1.1 million pounds of sediment, primarily as suspended solids, were released during the spill (EPA, 2016). Modeling results presented by the EPA indicate that the majority of the impacted sediment was deposited between Baker's Bridget and Durango, CO, with smaller amounts traveling downstream into New Mexico. These solids have the potential to be transported further downstream and potentially pose a long-term concern to water users in New Mexico as these sediments are resuspeneded into the water column during storms and spring runoff.

The principal elements of the proposed sampling and analysis associated with this project include the following:

- Measurement of on-site soil and sediment samples for heavy metal concentrations using handheld XRF device(s) to identify "hot spots" of impacted soil and sediment within the Animas River and its floodplain;
- Correlated sampling of soil and sediment for off-site laboratory analysis of metals;
- Off-site laboratory analysis for hazardous characteristics; and
- Global Positioning System (GPS) and photographs at each sampling location.

The basic assumption underlying this assessment of contaminated sediment in the Animas and San Juan Rivers is that impacted sediment would be preferentially deposited in low-energy fluvial environments where the stream flow deposits sediment but is insufficient at low flows to maintain the sediment in water as suspended solids. Deposition of sediment can therefore be anticipated to vary along the distance of the two river systems. The resulting distribution of impacted sediment can also be assessed based on an evaluation of fluvial geomorphology in combination with visible field metrics.

3.1 Data Quality Objectives

The data quality objective (DQO) process is a planning approach that can be used to prepare for a data collection activity. The DQO process includes the seven steps presented in Table 3-1. The output from each step influences the choices that will be made later in the DQO process. Though the process is presented in a linear form, it is in practice an iterative approach as the outputs from one step may lead to reconsideration for prior steps.

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Table 3-1. Data Quality Objectives

Data Quality Objective Process Step	**GKM Question Description**
Step 1: State the Problem – Concisely describe the problem to be studied and existing information to gain a sufficient understanding to define the problem.	Since the 1860's mining activities have occurred in the Upper Animas River Basin, resulting in over a century of enhanced acid rock drainage (ARD) into the Animas River. Historic data collected by Church et al. (2007) and USGS have shown that ARD resulting from historic mining activities resulted in the transport of heavy-metal contaminated sediment downstream, into New Mexico eventually reaching the San Juan River. Additionally, on August 5, 2016 the GKM Spill resulted in an estimated 1.1 million kilograms of contaminated sediment being released into the Animas River. Sediment samples collected by the EPA during the immediate spill response and the 2016 Spring Runoff indicates the presence of sediment with elevated aluminum, arsenic, lead, and zinc concentrations resulting from the GKM Spill event in both rivers. ***Sediment associated with historic mine releases and the August 2015 GKM Spill contains concentrations of heavy metals that potentially pose a risk to human health and the environment in and adjacent to the Animas and San Juan Rivers.***
Step 2: Identify the Decision – Identify the questions the study will attempt to resolve and what actions may result.	1. What are the contaminants of concern exist in and along the Animas and San Juan Rivers? 2. What is the horizontal distribution of contaminated sediment in and along the Animas and San Juan Rivers, resulting from historic mining activities and the GKM Spill event? 3. What is the vertical distribution of contaminated sediment along the Animas and San Juan Rivers? 4. Is it possible to identify and map the estimated 1.1 million kg of sediment resulting from the GKM Spill event? 5. Can on-site handheld XRF analysis be used to quantitatively screen sediment concentrations? 6. Can the soil moisture interference on handheld XRF measurements be bounded?
Step 3: Identify the Inputs to the Decision – Identify the information that needs to be obtained and the measurements that need to be taken to resolve the decision statement.	1. Documentation of soil and sediment characteristics, including color; documentation of occurrence of discolored sediment and depositional environment (visual observation); and co-location of sample locations where Church, EPA, and other stakeholders have collected and analyzed samples for metals along the lengths of the Animas and San Juan Rivers during the GKM spill response and 2016 Spring Runoff. 2. On site, handheld XRF measurements; dried sample handheld XRF sample measurements and laboratory sample analysis for metals in soil and sediment samples collected along both the Animas and San Juan Rivers. 3. Wet and dry sample weights: on-site handheld XRF measurements of wet/moist samples; dry sample handheld XRF measurements; and off-site laboratory analysis. 4. Results of sample analysis for those collected both at the ground surface and at depth at

	sample locations.
Step 4: Define the Study Boundaries – Specify the time periods and spatial area to which decisions will apply. Determine when and where data should be collected.	A river has a finite capacity for sediment load and transport of sediment downstream that is a function of stream flow rate and fluvial geomorphology. In low energy environments along a river, it can be expected that sediment will be deposited as the river loses its ability to suspend and transport sediment. These low energy environments can be identified through an evaluation of topography, aerial photographs, and watershed studies. For this study, soil/sediment data should be collected from locations based on evaluation of the following criteria: • Fluvial geomorpohology using satellite imagery (dated October 2015) and aerial photography; • Sampling locations and data presented in the Church report (Church et al., 2007); • EPA fate and transport modeling presentation and data (EPA, 2016); and • Existing USGS and EPA data Low flow conditions will provide the highest rate of access to these low energy environments for sampling. A review of USGS stream gage data shows that flow conditions exist in the Animas and San Juan Rivers, particularly within New Mexico, during the summer growing season. There is measurable increase in flow in the Animas and San Juan rivers when irrigation ends and river water is no longer diverted for agricultural use; October is typically the final month of irrigation in New Mexico. Low flow in the Upper Animas River Basin extends through November/December when freezing of the river can occur. Due to the dynamic nature of rivers and their varying load capacity, sampling should occur in a single sampling event during low flow conditions so that a “snapshot” can be obtained of the sediment distribution. This will also minimize the impact of sediment being transported during high flow events associated with storms in the watersheds.
Step 5: Develop a Decision Rule – Define the statistical parameter of interest, specify the action level, and integrate the previous DQO outputs into a single statement that describes the logical basis for choosing among alternative actions.	The origin of the contaminated sediment is from mining activities in the Upper Animas River and therefore the contaminants of concern are limited to metals. The primary use of the Animas and San Juan Rivers vary across state lines. In the Upper Animas River, south of Silverton, CO and near Durango, CO, the primary use of the Animas River is recreational. As the river flows downstream into La Plata County and then into New Mexico, users of the river expand to include agricultural and residential users. In New Mexico, multiple private residences have property immediately adjacent to the Animas and San Juan Rivers and the most protective screening level applicable is a residential risk scenario. Additionally, sediment located

	along the reach of the Animas River has the potential to be mobilized into New Mexico where there is a residential exposure pathway. Therefore, all sediment sample results will be screened against the EPA residential regional screening level (RSL).
Step 6: Specify Tolerable Limits on Decision Errors – Define the decision maker's tolerable decision error rates based on a consideration of the consequences of making an incorrect decision.	The limits of detection of the handheld XRF analyzer for metals are sufficiently low to allow for the screening of results against the EPA residential RSLs. Based on a review of existing data, the following metals have been preliminarily identified as contaminants of concern: aluminum, arsenic, lead, and zinc. Sample locations have been selected to meet a range of criteria in order to identify sediment deposited within the rivers (Step 4). Access, weather, and depth of digging could result in a planned sample not being collected and a depositional area not being mapped. This limitation is being bounded through schedule (sampling will occur during low flow conditions) and pre-coordination of access with tribal governments and EPA. Chemical and moisture content can have an impact on measured metals concentrations. Chemical interferences can be result in both false positives and false negatives. When lead concentrations are ten times greater than the arsenic concentrations, it is possible to get a false negative for arsenic with the handheld XRF analyzer, outputting nondetect or zero read concentrations for arsenic. This type of error is considered low probability and will be further limited through the collection of off-site laboratory samples when on-site XRF analyzer measurements indicate lead concentrations ten times greater (or more) than arsenic. Moisture content can result in a biased low concentration for metals depending on the saturation of the sample. For metals with lower concentrations, increased moisture content could result in a low to nondetect concentration output.
Step 7: Optimize the Design – Evaluate information from the previous steps and generate alternative data collection designs. Choose the most resource-effective design that meets all DQOs.	Soil/sediment samples collected along the Animas and San Juan Rivers, along with upstream samples on tributaries and above confluences, will provide a robust dataset for understanding the nature and extent of contamination resulting from historic and GKM Spill sediment releases to the rivers. Sampling will be completed at locations based on a set list of criteria (Step 4) in order to provide the ability to obtain information on deposition and comparison with existing data. On-site and dry handheld XRF measurements will be collected, along with off-site laboratory analysis in order to determine correlation between the methods of measurement.

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The principle DQOs requiring quality assurance are to determine:

- Presence or absence of heavy metals at detection limits that are equal to or less than screening criteria for the residential risk scenario (EPA, 2016);
- Presence or absence of heavy metals that are equal to or less than the screening criteria for the residential risk scenario (EPA, 2016); and
- Potential hazardous characteristics of soil and sediment resulting from the GKM spill in and surrounding the Animas River.

Figures 1 through 8 illustrates the proposed sample location. Locations include tributary samples located upstream of where North Fork Cement Creek joins Cement Creek; upstream of Silverton, CO on the Animas River, upstream of the junction of Mineral Creek and the Animas River; and upstream of the confluence of the Animas and San Juan Rivers, on the San Juan River.

The handheld XRF has manufacturer defined detection limits (Table 3-2). These detection limits are below respective EPA residential RSLs with the exception of tungsten and zirconium; neither tungsten nor zirconium is considered a contaminant of concern in this assessment. The handheld XRF results can therefore be screened against the EPA residential RSLs in order to identify the distribution and character of sediment sampled along the Animas and San Juan Rivers.

Table 3-2. Limits of Detection for the DELTA Premium GeoChem Plus XRF Analyzer

Element	Symbol	Limit of Detection (mg/kg)	EPA Residential RSL (mg/kg)
Magnesium	Mg	3,000-10,000	N/A
Aluminum	Al	450-1,400	7,700
Silicon	Si	250-800	N/A
Phosphorus	P	10-120	N/A
Sulfur	S	50-150	N/A
Potassium	K	20-50	N/A
Calcium	Ca	10-35	N/A
Titanium	Ti	5-10	N/A
Vanadium	V	4-10	39
Chromium (total)	Cr	2-9	N/A
Manganese	Mn	3-7	180
Iron	Fe	5-20	5,500
Nickel	Ni	4-10	N/A
Copper	Cu	2-6	310
Zinc	Zn	1-3	2,300
Tungsten	W	4-10	6.3
Mercury	Hg	2-5	1.1
Gold	Au	2-4	N/A
Arsenic	As	1-3	3.5
Selenium	Se	1-2	39
Lead	Pb	1-4	400
Rubidium	Rb	1-2	N/A
Uranium	U	1-6	23
Strontium	Sr	1-2	4,700
Yttrium	Y	1-2	N/A
Zirconium	Zr	1-2	0.63
Niobium	Nb	1	N/A
Thorium	Th	2-6	N/A
Molybdenum	Mo	1-2	
Silver	Ag	5-12	39
Cadmium	Cd	5-9	7.1
Tin	Sn	9-14	4,700
Antimony	Sb	10-13	3.1

The quantitative DQOs will be determined by the method detection limits (MDLs) and reporting limits (RLs) to be specified by the analytical laboratory, the New Mexico Department of Health Scientific Laboratory Division (SLD). MDLs and RLs are highly dependent upon the sample matrix and concentrations of target constituents present. The MDL is a statistically derived value, representing the theoretical minimum level at which a particular analyte can be detected. The MDL studies are performed annually at SLD. The RL is a detection limit that the laboratory is confident can be accurately achieved consistent over time. Laboratory instruments are usually capable of detecting constituent concentrations less than the RL and therefore, laboratory convention is to report these concentrations with a flag. The RLs are values that the method may achieve under ideal conditions; actual limits may vary by sample due to matrix interference.

3.2 Use of Data

On-site XRF data will be used as a screening tool for the collection of samples for laboratory analysis, in addition to the samples collected at a rate of 1 for every 20 XRF samples for off-site analyses. Handheld XRF data and laboratory analytical data will be screened against the EPA residential regional screening level (RSL) for a given metal. Samples with concentrations greater than the EPA residential RSL will be denoted in bold, italic font in reporting tables.

A correlation analysis will be completed for metals that have handheld XRF and/or laboratory concentrations greater than their respective EPA residential RSL. At a minimum, the correlations will be completed for the primary contaminants of concern: aluminum (Al), arsenic (As), lead (Pb), and zinc (Zn).

GPS coordinate data collected at each sample location will be used to map soil/sediment concentration results using geographic information system (GIS). A separate map will be created for the surface samples and for the samples collected at depth. Photographs of samples and locations will be georeferenced in GIS for evaluating potential geomorphological affects on observed concentration trends.

4. DATA GENERATION AND ACQUISITION

The nature and extent of contaminated soil and sediment resulting from the GKM spill that occurred on August 5, 2015 will be defined by observation, portable XRF, and off-site laboratory analysis. Samples will be collected at the surface and at depth in order to define both the horizontal and vertical distribution of impacted soil/sediment. In addition, some analytical characterization of the soil and sediment may be performed to determine hazardous characteristics. The following subsections describe how these methods will be applied.

Figures 1 through 8 show planned sampling locations for this project; GPS coordinates for the sample locations are included in Appendix A. NMED will coordinate with and obtain prior approval from the Southern Ute Indian Tribe and the Navajo Nation for the sample locations proposed on those lands. The NMED will also coordinate access with EPA Region 8 for sample locations located near and upstream of the GKM adit and the Gladstone Water Treatment Facility. Actual sample locations may vary from those presented in this QAPP based on accessibility and field condition; for example sample locations located in sand bars and along the river banks could be inaccessible during higher flow conditions in the river(s).

4.1 Sampling Methods

The planned sampling location coordinates are in Appendix A. Sampling procedures and collection techniques follow the standard operating procedures presented in the the Standard Operating Procedures – Soil Sampling and Equipment Decontamination (SOP) in Appendix B to assure consistent collection and reliable data generation. Appendix C provides EPA Method 6200 for using a portable XRF for analysis and Appendix D includes the manufacturer standard operating procedure for the Olympus DELTA Premium GeoChem Plus Handheld XRF analyzer.

Samples will be collected during low flow conditions at locations along the Animas and San Juan Rivers. The field team will navigate to the sample location by pre-entering the location XY coordinates into the GPS unit. The sample team will utlilize the handheld XPRF to record surface sediment results as described in Appendices B and C. The sample team will also use a 2-ounce (oz) sterile disposable scoop to collect a sample for XRF analysis (Section 4.1.1) from the surface soil/sediment [(0-3-inches (in)]. If a laboratory sample is required, the same 2-oz scoop will be used to collect a sample for the laboratory (Section 4.1.2). Once the surface soil/sediment sample has been collected, the sample team will use a shovel and/or auger to collect a sample at depth. The depth of the second sample will be based on field conditions with the targeted sample interval to be just above when refusal ((e.g., cobblestone layer that cannot be penetrated with shovel or auger) is encountered or 18-in below surface, whichever is encountered first.

The GPS coordinates for the location of samples will be recorded (Trimble Geoexplorer II unit). Photographs will be taken at each sample location, at surface and at depth. Additional photographs will be taken to capture the sample and the sample location environment. Sample location environment photographs will be taken facing upstream. Photo number, location, day and time, direction facing, and any relevant notes will be documented in the photo tracking log.

This section describes the approaches necessary for collecting representative samples. Field sampling activities include soil and sediment sampling. Field staff will refer to this QAPP and standard operating procedures when conducting field sampling activities. Field logbooks will be maintained to document all activities performed in the field. General information to be recorded each day include time of each activity performed, weather conditions, and other pertinent observations (e.g., color of soil and sediment, etc.). The referenced procedures contained in this QAPP will be used to guide or direct field personnel in decision making and collecting practices. Actual procedures will be determined in the field and may follow one or more of the referenced procedures or be modified in response to field conditions. The type of and rationale for any modifications to procedures will be recorded in a field logbook.

4.1.1 XRF Screening Analytical Methodology

In-situ results from the application of the handheld XRF will be recorded on field sheets for primary contaminants of concern Al, As, Pb and Zn.Results for all analytes recorded on the XRF will be uploaded to a computer at the end of each day. Approximately 350-grams (or sufficient volume to fill an 8-oz jar) will be scooped into a quart-sized ziplock bag. The ziplock bag will be handled following the procedures outlined in Section 4.2 of this QAPP. Any large, nonrepresentative debris will be removed from the sample; debris includes leaves, vegetation, and roots. A visual inspection of the sample will be logged in the field note book, recording (at a minimum) the following features:

- Moisture content using the Unified Soil Classification System field classification (Dry – No sign of water and soil dry to touch; Moist – Signs of water and soil is relatively dry to touch; and Wet – Signs of water and soil is definitely wet to touch; granular soil exhibits some free water when touched);
- Color; and
- Consistency.

The sample will then be spread evenly, within the ziplock bag, and analyzed using the handheld XRF analyzer. Analysis will be completed with all 3-beams activated with 30-seconds per beam and concentrations will be recorded for the full range of elements measured by handheld XRF analyzer. The procedures used to prepare samples and conduct the XRF analyses are in Appendix C.

For on-site handheld XRF measurements indicating a lead concentration ten times greater than the arsenic concentration, as read directly from the instrument at the time of measurement, a laboratory sample will be collected for off-site laboratory analysis. The field measurement will be flagged in the logbook for potential chemical matrix interferences (Appendix B).

Samples will be stored and transported to an on-site NMED laboratory where the samples will be dried, homogenized, and measured following the procedures in the SOP (Appendix B) and EPA Method 6200 (Appendix C).

Appendix C provides the details of EPA Method 6200 (EPA, 2007) for the application of a handheld XRF analyzer. Handheld XRF analyzer(s) will be utilized to screen soil and sediment for metals, specifically lead the primary constituent of concern. Correlation between XRF and analytical results will be established. Calibration of the XRF equipment will be documented in a field calibration tracking sheet.

4.1.2 Soil and Sediment Sampling Methodology for Laboratory Analysis

Off-site laboratory confirmation analysis for metals (EPA Method 846 200.7 and 200.8) will be conducted at a frequency of one laboratory analysis for every 20 XRF samples (5%) and for on-site XRF measurements indicating lead concentrations ten time or more greater than the arsenic concentration. This frequency is based on the specifications in EPA Method 6200 (EPA, 2007). A disposable 2-oz disposable, plastic scoop will be used to collected approximately 350-grams (or sufficient volume to fill an 8-oz jar) in a quart-sized ziplock bag. The sample will be packaged and handled according to the procedures outlined in Section 4.2 of this QAPP.

4.1.3 Decontamination of Sampling Equipment

The following decontamination procedure is applicable for any non-disposable sampling equipment used for the collection of field and laboratory soil/sediment samples.

1. Wash and scrub samples with brush and detergent (Alconox Liquinox® and water).
2. Rinse with deionized (DI) water.
3. Air-dry.

4.2 Sampling Handling and Custody

Samples will be handled in a manner that maintains the original chemical composition. Table 4-1 outlines the sample preservation requirements for the various sample matrices and analytical methods (40 CRF 136, Table II).

Table 4-1. Sample Requirements for Analytical Testing

Matrix	Parameter	Container	Preservation	Maximum Holding Times
Soils/Sediments	Metals	1 x 5.6-oz ziplock	Ice to 4°C	6 months
Soils/Sediments	Handheld XRF	1 x 5.6-oz ziplock	None	6 months

Samples in the field will have the necessary sample labeling, chain-of-custody forms, and packaging to maintain the proper integrity and custody of samples collected in the field. Samples delivered for laboratory analysis shall follow the laboratory custody requirements that starts with the receipt of samples and continues through sample storage, analysis, data reporting, and data archiving.

4.2.1 Field Custody Procedures

The following elements will be tracked for the field custody of samples:

Sample Identification

Sample Labels

Custody Records

Packaging Procedures

Samples will be identified using a unique alphanumeric identifier. Samples will be labeled by sample type, location, and date of collection. An example of a field sample number is as follows:

20160805-AR1

The following bullet items present information to be used in assigning sample identifications:

Digits 1-8	Date written in terms of Year/Month/Date (201XYYZZ)
Digit 9	Hyphen
Digits 11, 12	River identifier for Animas River (AR) and San Juan River (SJ)
Digits 12, 13	Numeric designation that increases sequentially

Sample labels will be written on the sample zip lock bags with indelible ink. An entry will be made for each sample on the custody record. The custody record will include sampler names and signatures, sample location, date, time, type of sample, and analysis. After samples are carefully collected, sample containers will be tightly sealed and the outside wiped clean to maintain sample integrity during transport. The chain-of-custody will be placed in a separate plastic bag and included in the container used for sample transportation. For samples delivered to SLD for analysis, one copy of the custody record will stay with the field team while the remaining copies will accompany the samples.

4.2.2 Laboratory Custody Procedures

Unless otherwise specified by the field team, SLD will employ EPA custody protocols to track the samples through their facility. Sample custody is maintained from sample receipt to delivery of the data to archiving of sample data.

4.3 Quality Control

Data quality will be maintained through compliance with the analytical, field, and project management procedures set forth in this QAPP. The purpose of this section is to detail the analytical quality assurance program for this project. All data generate by the analytical laboratory will be required to meet the quality standards for the methods used. Sample holding times are provided in Table 4-1. Analytical methods, detection limits, and analytical quality control procedures are outlined in this section.

4.3.1 Analytical Methods

Soil/sediment samples will be analyzed on-site for heavy metals by EPA Method 6200 using the Delta Premium Handheld XRF instrument. The procedures to conduct the XRF analyses are described in the SOP (Appendix B).

Samples for off-site laboratory confirmation will be analyzed by the SLD for total metals following EPA Method 846 200.7 and 200.8.

4.3.2 XRF Analysis and Quality Control

Daily operation of the XRF instrument will include the following quality control (QC) measures: instrument standardization resolution check standard, initial and continuing calibration check standards, and field duplicate samples.

Standardization Resolution Check Standard: The XRF instrument operating condition will be checked during the instrument startup procedure, with a manufacturer provided standardization resolution check standard. This standard will be analyzed each time the instrument is powered up from the off-mode. The standard will check x-ray tube and detector performance.

Initial and Continuing Calibration Checks: Calibration check standards will be analyzed at the beginning and middle of each day to verify instrument sensitivity and factory calibration. If the unit is powered down during the course of the day, calibration check standards will be run with operation of the unit is resumed.

The QC acceptance criteria (percent difference from the known concentration) for the initial and continuing calibration checks is 20%. The National Institute of Standards and Technology (NIST) Standard will be used to perform the initial and continuing calibration checks. The NIST standards were provided by the manufacturer and are comprised of multiple target elements.

Field Duplicates: Field duplicates for XRF analysis is 5% for the confirmatory samples. A relative percent difference goal of less than 50% for soil analysis by XRF has been established for the project. The relative percent difference (RPD) between the field sample result and field duplicate result will be calculated for both the XRF and EPA 846 methods.

4.3.3 XRF and Off-Site Laboratory Correlation Analysis

This section presents the statistical analysis that will be performed to verify correlation of field XRF data with laboratory analysis data, using EPA Method 846 200.7 and 200.8.

Statistical Analysis: The onsite XRF and off-site data results will be compared and analyzed for correlation and accuracy.

Correlation: Correlation indicates strength and direction of a linear relationship between two variables. A linear correlation plot of XRF results versus off-site laboratory results will be constructed for aluminum, arsenic, lead, and zinc; these heavy metals have been identified as the primary constituents of concern for human health and the environment based on spill response and spring runoff data. A plot of the data will include points for XRF, a best-fit linear regression equation, and the correlation coefficient (r^2) to illustrate the relationship between the XRF and laboratory results. A good correlation will be represented by an r^2 value greater than 0.9.

Accuracy: The RPD between the off-site laboratory and the XRF result will be calculated as a measure of accuracy. An RPD of 50% will be considered as acceptable.

4.3.4 Off-Site Sample Quality Control Procedures

4.3.4.1 Laboratory Quality Control Samples

Method Blanks: Laboratory method blanks will be run at a rate of one per every 12 hours of equipment run time; one at the start of the day and one at the midway point of the analytical sequence. Inorganic blanks will contain less than one-tenth the concentration of a compound detected in a corresponding environmental sample.

Laboratory Control Samples: Laboratory control samples (LCS) will be run for each method used per batch of samples. An LCS is blank laboratory DI water spiked with compounds being analyzed by a particular method. Percent recoveries of each compound are used as quality control measure of method and instrument performance.

4.4 Instrument/Equipment Testing, Inspection, and Maintenance

4.4.1 Field Equipment

Preventative maintenance of field equipment is performed routinely before each sampling event; more extensive maintenance is performed based on hours of use. The Project Manager and project task leads will oversee and implement maintenance programs as applicable.

4.4.2 Laboratory Equipment

The SLD Standard operating procedures (SOPs) for preventative maintenance include details on equipment log records, routine maintenance, and troubleshooting. Equipment maintenance schedules, problem identification procedures, and failure analysis protocols are provided with the preventative maintenance protocols in the laboratory's SOP manual.

4.5 Instrument/Equipment Calibration and Frequency

4.5.1 Field Equipment Calibration Check Procedures

Each field instrument will be initially calibrated prior to the start of field work and thereafter at a frequency specified by the manufacturer. Dates and times of calibration, serial numbers, and calibration techniques as well as the signature of the person conducting the calibration will be entered into the instrument's log book and field log book. The XRF instrument will be calibrated as specified in Section 2.3.2.

4.5.2 Laboratory Calibration Procedures

The laboratory, SLD, will employ appropriate methods for calibration of all instruments used for sample analysis. The frequency and procedures will be derived from the analytical methods being requested.

4.6 Documentation

Field teams will use a permanently bound field notebook indicating the time, date, and location of sample collection (including a written description and location references), description of the sample preservation, sample identification number, analyses requested, and the name of the laboratory where off-site samples are sent. The notebook, associated maps, laboratory analytical reports, and copies of chain-of-custody and analysis request forms will be maintained as part of the project records.

The field logbook will record pertinent information and observations. The sampling team will record physical measurements, field analyses, and any observations made on field sheets in the log book. Since auxiliary data often proves useful in interpretation of results, the observation of color, odor, changes in the sample, equipment problems, weather conditions, and relative moisture (e.g., saturated, moist, etc.) or any other observations could prove helpful.

5. ASSESSMENT AND OVERSIGHT

5.1 Assessments and Response Actions

Field and laboratory performance and laboratory system assessments will be used to monitor project activities to ensure compliance with quality assurance (QA) objectives and procedures.

5.1.1 Field Assessments and Response Actions

At the discretion of the Project Manager, internal assessments of field observations may be performed during the project. Field assessments will monitor field quality control, equipment calibration, and sampling. If the field assessments yield results that do not satisfy the QA objectives of this project, the Project Manager will initiate corrective actions.

5.2 Reports

The analytical laboratory will validate data prior to submitting the final data report. Outlying data will be flagged in accordance with the laboratory SOPs and corrective action will be taken to rectify any problems.

Corrective actions, data assessment results, and validation results will be documented in a manner consistent with EPA protocols.

6. DATA VALIDATION AND REPORTING

6.1 Analytical Data Review, Verification, and Validation

The NMED staff will perform verification and validation of data. The field team leader will perform a QC of field documentation at the completion of each day to ensure completeness of documentation. An NMED technical staff person will match XRF data to the laboratory results to identify outliers and potential data concerns.

The laboratory analyst who generates the analytical data will have the primary responsibility for the correctness and completeness of data. Each step of this verification and review process will involve the evaluation of data quality based on both the results of the QC data and the professional judgment of those conducting the review. This application of technical knowledge and experience to the evaluation of data is essential in ensuring that data of known quality are generated consistently. All data generated and produced will follow well-documented in-house protocols.

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FIGURES


Figure 1: GKM and Gladstone Sample Locations

Figure 2: Cement Creek Sample Locations

Figure 3: Silverton, CO Animas River Sample Locations

Figure 4: Animas River Sample Locations

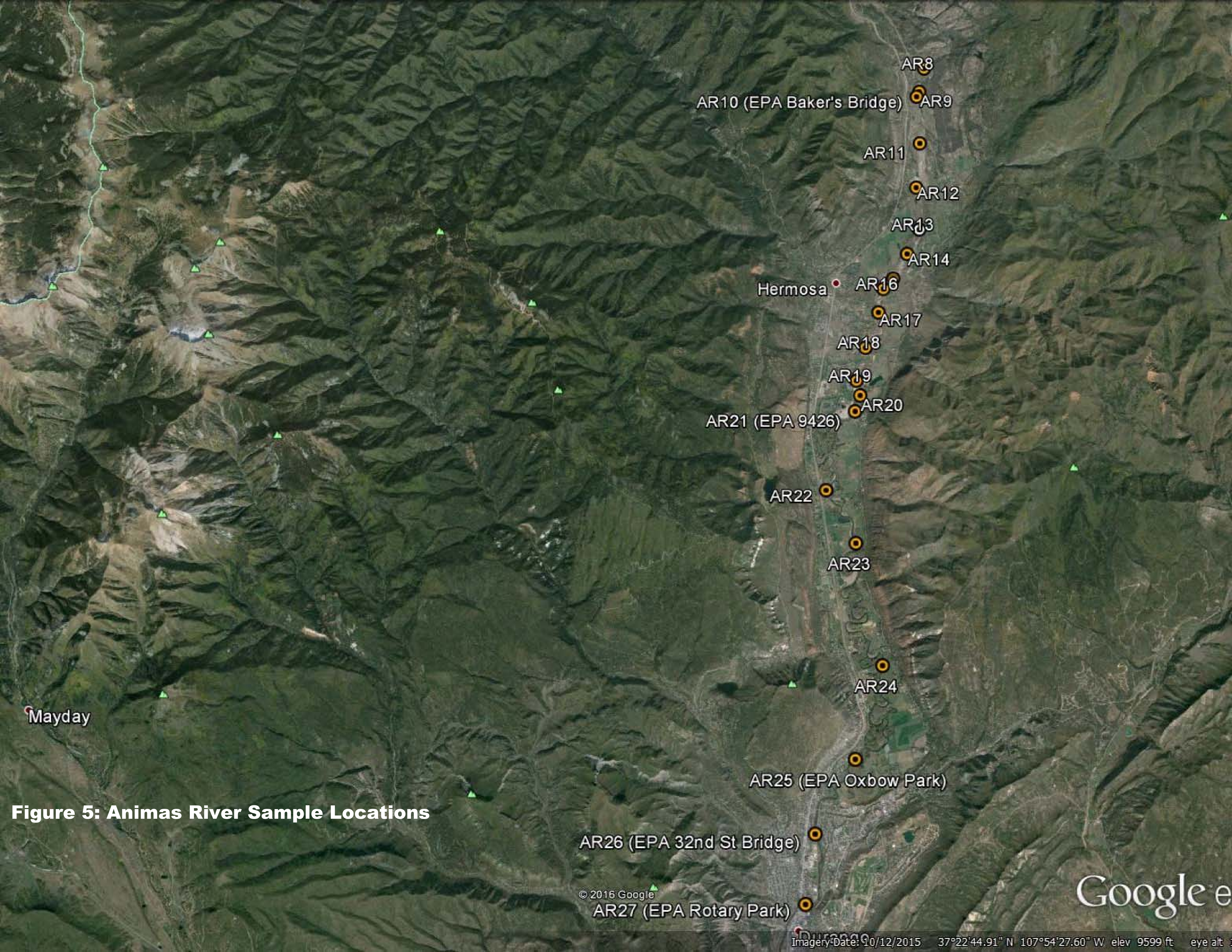

Figure 5: Animas River Sample Locations

Figure 6: Animas River Sample Locations

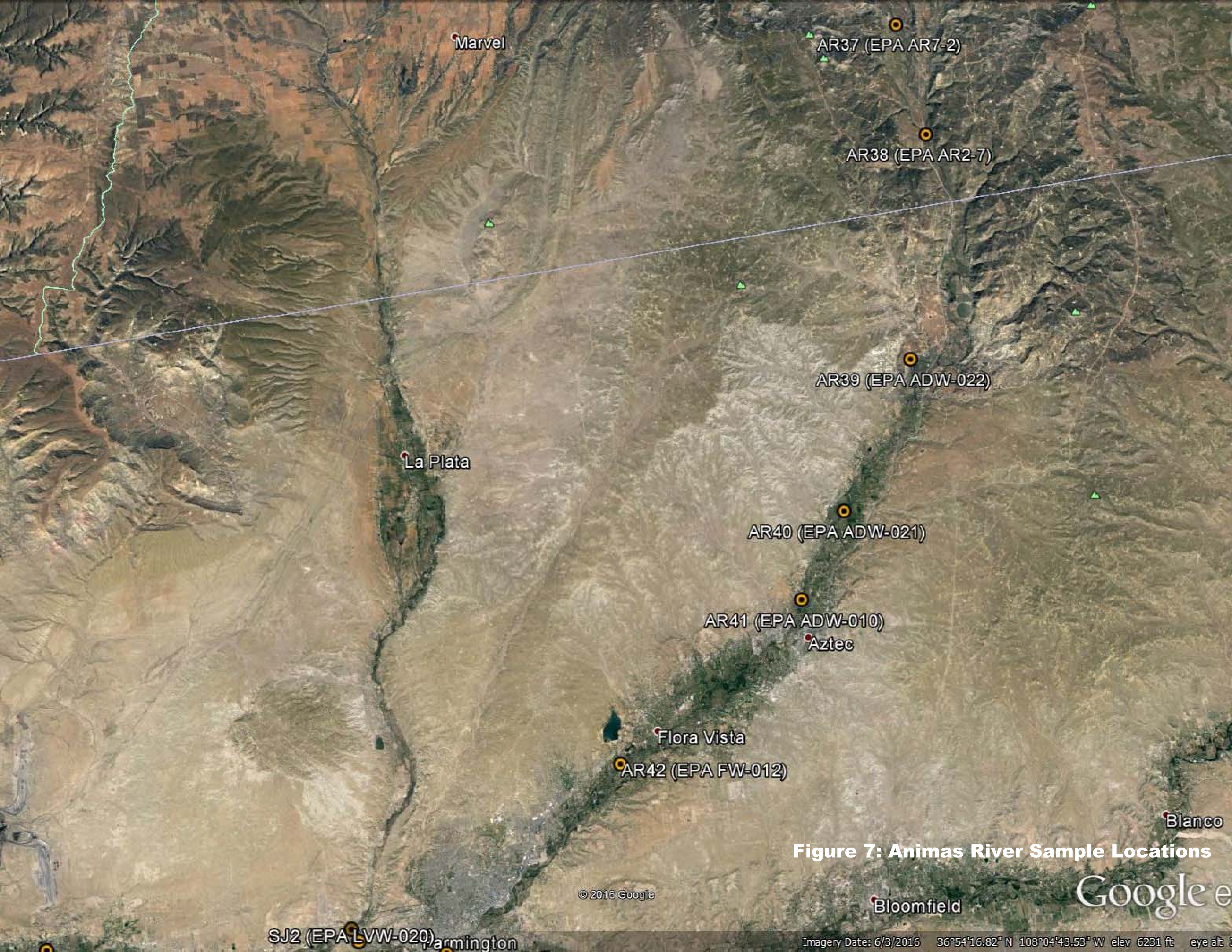

Figure 7: Animas River Sample Locations

Figure 8: Animas and San Juan River Sample Locations near Farmington, NM

APPENDICES

APPENDIX A

Proposed Sampling Location Coordinates

NAME	LATITUDE	LONGITUDE
USAR1	37.82593043	-107.6297391
USAR2	37.8188771	-107.644453
USAR3	37.81534747	-107.6521941
NFCC1	37.89420528	-107.6372947
NFCC2	37.89397466	-107.638611
NFCC3	37.89549617	-107.64484
NFCC4	37.8951311	-107.6467249
CC1	37.89610475	-107.6467932
CC2	37.89552564	-107.6470322
CC3	37.89470176	-107.6473928
CC4	37.8935323	-107.64792
CC5	37.89204206	-107.6487545
CC6	37.88989906	-107.6530163
CC7 (Church S20)	37.88766715	-107.6615894
CC8 (Church S21)	37.88585129	-107.6643869
CC9 (Church S22)	37.87569248	-107.6717714
CC11 (EPA CC48)	37.81811471	-107.6616781
CC10 (Church S23)	37.84576953	-107.6782203
AR1 (EPA A68)	37.81095838	-107.6593701
MC1 (EPA M34)	37.80286802	-107.6727475
AR2 (EPA A72)	37.790017	-107.667536
AR3 (Church S46)	37.72416803	-107.6541078
AR4 (EPA A75D)	37.59777839	-107.7756211
AR5	37.59689921	-107.7772089
AR6	37.59194053	-107.7794121
AR7	37.52868663	-107.7802352
AR8	37.46225451	-107.7971213
AR9	37.45681419	-107.8000008
AR10 (EPA Baker's Bridge)	37.45573037	-107.8010951
AR11	37.44465098	-107.802849
AR12	37.43431195	-107.8065756
AR13	37.4244047	-107.8081564
AR14	37.41921846	-107.8131018
AR15	37.41400909	-107.8185185
AR16	37.41200985	-107.821937
AR17	37.40680826	-107.8246842
AR18	37.39925148	-107.8303799
AR19	37.39205346	-107.8348417
AR20	37.38853625	-107.8346403

NAME	LATITUDE	LONGITUDE
AR21 (EPA 9426)	37.385148	-107.836946
AR22	37.3686039	-107.849401
AR23	37.35570867	-107.8440114
AR24	37.32803816	-107.843255
AR25 (EPA Oxbow Park)	37.30903703	-107.855714
AR26 (EPA 32nd St Bridge)	37.29480855	-107.8704678
AR27 (EPA Rotary Park)	37.280534	-107.876622
AR28 (EPA GKM05)	37.268704	-107.885857
AR29	37.23773416	-107.8675443
AR30 (EPA AR19-3)	37.22129385	-107.8596002
AR31	37.20378717	-107.8468358
AR32	37.19997953	-107.8507125
AR33	37.19467464	-107.8626906
AR34	37.18504759	-107.8791086
AR35	37.16866227	-107.874119
AR36	37.11288366	-107.8926277
AR37 (EPA AR7-2)	37.08514326	-107.8792317
AR38 (EPA AR2-7)	37.032292	-107.875455
AR39 (EPA ADW-022)	36.933295	-107.909073
AR40 (EPA ADW-021)	36.872838	-107.960741
AR41 (EPA ADW-010)	36.838545	-107.992183
AR42 (EPA FW-012)	36.78363539	-108.1021108
AR43 (EPA FW-040)	36.71967218	-108.2071116
SJ1 (EPA SJAR)	36.70747012	-108.1508222
SJ2 (EPA LVW-020)	36.730556	-108.251046
SJ4 (EPA SJFP)	36.74815615	-108.4120162
SJ3 (EPA SJLP)	36.73588713	-108.2539884
SJBB	37.25737015	-109.6185856
SJCH	37.29333599	-110.3992927
SJMC	37.25814839	-109.3104452
AR2-7a	37.14999308	-109.8662834
AR (optional)	37.56497286	-107.7820058
Gladstone EPA WTF	37.89018712	-107.6506578
Gold King Mine	37.89456696	-107.6383403

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APPENDIX B

Standard Operating Procedures – Soil Sampling and Equipment Decontamination

Revision Date: 9 September 2016

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Section **Page**

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures to be used at the Gold King Mine (GKM) Spill Site to analyze soil and sediment samples for metals using the DELTA Premium Handheld X-ray Fluorescence (XRF) analyzer. This SOP will be used in conjunction with the DELTA Family Handheld XRF Analyzer Manual.

EPA Method 6200 will be used to analyze soil and sediment samples using the XRF. A listing of elements and reporting limits of metals analyzed by the XRF is presented in Table 1 of this SOP.

Table 1. Limits of Detection for the DELTA Premium GeoChem Plus XRF Analyzer

Element	Symbol	Limit of Detection (mg/kg)
Magnesium	Mg	3,000-10,000
Aluminum	Al	450-1,400
Silicon	Si	250-800
Phosphorus	P	10-120
Sulfur	S	50-150
Potassium	K	20-50
Calcium	Ca	10-35
Titanium	Ti	5-10
Vamadium	V	4-10
Chromium (total)	Cr	2-9
Manganese	Mn	3-7
Iron	Fe	5-20
Nickel	Ni	4-10
Cooper	Cu	2-6
Zinc	Zn	1-3
Tungsten	W	4-10
Mercury	Hg	2-5
Gold	Au	2-4
Arsenic	As	1-3
Selenium	Se	1-2
Lead	Pb	1-4
Rubidium	Rb	1-2
Uranium	U	1-6
Strontium	Sr	1-2
Yttrium	Y	1-2
Zirconium	Zr	1-2
Niobium	Nb	1
Thorium	Th	2-6
Molybdenum	Mo	1-2
Silver	Ag	5-12
Cadmium	Cd	5-9
Tin	Sn	9-14
Antimony	Sb	10-13

2. METHOD SUMMARY

2.1 Principles of Operation

XRF is a nondestructive qualitative and quantitative analytical technique used to determine the chemical composition of metals in a sample. In an XRF analysis, primary X-rays emitted from an X-ray tube are utilized to irradiate a sample. The primary X-rays incident on the sample cause the elements present in the sample to emit their characteristic X-ray line spectra. The elements may be identified by the energies of the wavelengths of their spectral lines. The X-ray energy is proportional to the wavelength. There will also be backscattering of the primary X-rays. Energies of the fluorescent and primary X-rays are converted within the detector. An electronic multi-channel analyzer measures the 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 concentrations in a sample and is the basis for quantitative analysis.

2.2 Sample Preparation and Analysis Summary

Soil samples will be collected in plastic bags in the field, and screened with the XRF initially as wet weight samples. The soil samples will be homogenized as thoroughly as possible inside the plastic bag, and a minimum of three readings will be taken. Results for lead, arsenic, and aluminum will be recorded in the field logbook; sample data is stored locally to the handheld XRF analyzer and will be transferred to the project computer at the end of each day.

Sticks, stones, and other matter that is non-representative of the sample will be removed. Once placed in the plastic bag, the sample will be homogenized and a wet reading will be taken. Sample bags will be labeled with Sample ID, Date, and Location and placed in a cooler on ice.

A dry measurement will also be taken for samples collected in the field. Upon arrival in the laboratory, samples will be weighed, in the plastic bag, and then transferred to an oven-safe pan. The sample will be dried in an oven at 150^{o}C for up to 4 hours, weighed, and then sieved through a No. 60 mesh sieve. The fraction that passes the No. 60 sieve is then re-homogenized and transferred to the XRF sample cup.

3. HEALTH AND SAFETY

The DELTA Premium Handheld XRF analyzer uses an X-ray tube to generate ionizing radiation for sample analysis. During all measurements, the sample must be positioned under the analyzer and hands must be on the analyzer handle for safe operation. Whenever possible, the docking station will be used for sample analysis as it is the most protective with shielding. The probe must not be opened except by authorized personnel. Proper training for the safe operation of the instrument and radiation training will be completed prior to field operations. Radiation safety information on the DELTA Premium Handheld XRF analyzer can be found in the operator’s manual and startup guide. The analyst should be aware of the local, state, and federal regulations that pertain to the use of radiation-producing equipment. The radiation registration certificate should be kept with the instrument at all times. All reasonable measures, including labeling, operator training, and the concepts of time, distance, and shielding will be implemented to limit radiation exposure to *as low as reasonable achievable* (ALARA).

4. INTERFERENCES AND POTENTIAL PROBLEMS

4.1 Chemical Matrix Interferences

An interference occurs when the spectral speak from one element overlaps either partially or complete with the spectral speak of another. If the XRF is calibrated for both elements, it is generally capable of correcting handling the interference. In this case, the element being interfered with may be measured with a poorer detection limit or poorer precision, but the analytical results should still be acceptable for field-portable XRF. IF the XRF is not calibrated for the element causing the interference, then the XRF may report the presence of elements not in the sample, or greatly elevated concentrations of elements in or not in the sample.

Interferences between elements can be broadly categorized into: A) Z, Z-1, Z+1 interferences; and B) K/L interferences. Interference type "A" occurs when high levels of an element of atomic number Z are present. This can cause elevated levels of elements with atomic number Z-1 or Z+1. Generally, portable XRF analyzers have good correction methods, so this interference only causes problems with very high levels of the element in question .The type "B" interference occurs when the L-shell line of one element overlaps with the K-shell spectral line of another element. The most common example is the lead/arsenic interference where the L-alpha line of lead is in nearly the exact same location as the K-alpha line of arsenic.

Interferences can also happen, though less commonly, from K/L, K/M, and L/M overlaps. The primary example of this type of overlap involve arsenic and lead as well as sulfur and lead. Due to the mathematical corrections in the instrument software, concentrations of arsenic cannot be efficiently calculated for samples with lead:arsenic rations of 10:1 or more. When lead concentrations are ten times or more greater than the arsenic concentration the instrument may result in a false negative (read a "nondetect" concentration) for arsenic regardless of the actual concentration present.

4.2 Moisture Content

Sample moisture content will affect the accuracy of the sample results. The measurement error may be minor when the moisture content is small or it may be significant when measuring surface soils that are saturated with water. For this reason, wet and dry measurements will be taken on each sample and the moisture content will be estimated.

5. PERSONNEL QUALITIFCATIONS

Sample analysis will be performed by qualified personnel with training and/or experience in the operation of the XRF analyzer and knowledgeable in X-ray fluorescence. The analyst must be familiar with this SOP and the DELTA Family Handheld XRF Operations Manual supplied by the instrument manufacturer.

6. EQUIPMENT AND SUPPLIES

6.1 DELTA Premium Handheld Instrument and accessories

- DELTA Premium GeoChem (Plus) Handheld XRF Analyzer with Soil Plus package
- (2) Lithium ion batteries

- Docking station
- Battery charger and AC adaptor
- Standardization cap

6.2 Computer

- Olympus software for remote operating of instrument

6.3 Supplies

- Ziploc, quart-sized bags for sample collection
- 8 ounce glass jars for off-site split samples (QC clean quality)
- Oven – drying of soil and sediment samples
- Sieve – No. 60 (250 µm) stainless steel
- Sample cups
- Disposable scoops
- Polystyrene drying pans
- Nitrile gloves
- Safety glasses
- Logbook
- NIST standards for instrument calibration checks
- Instrument blank standard provided by Olympus

7. CALIBRATION

Procedures for calibration and operation of the DELTA Premium Handheld XRF analyzer are taken from EPA Method 6200 and updated to be specific to the DELTA Premium Handheld XRF analyzer.

8. QUALITY ASSURANCE AND QUALITY CONTROL

The following section details the quality assurance for sediment and soil samples using the XRF analyzer. All operators will perform QA/QC procedures as described in this SOP.

8.1 Verification of Instrument Operation

The following procedure s were taken from the EPA Method 6200 and updated to be specific to the DELTA Premium Handheld XRF analyzer. Quality assurance here consists of testing known standards to verify calibration.

1. ENERGY CALIBRATION: An energy calibration check sample will be analyzed at the beginning of each day. The DELTA Premium XRF analyzer performs this automatically; this is the purpose of the standardization check when the analyzer is started. The software does not allow the analyzer to be used if the standardization is not completed. The energy calibration check is performed by placing the check standard under the analyzer or by docking the instrument and turning the unit on. If the energy calibration fails, the analyst will shut down the instrument, replace the battery with a full charged backup, and restart the instrument. An energy calibration will be performed after restarting the XRF.

2. INSTRUMENT BLANK: An instrument blank will be analyzed at the beginning of each day, and for every 20 environment samples. The operator should use the silicon dioxide blank provided with the analyzer. The purpose of this test is to verify there is no contamination on the window of the analyzer or any other component that is “seen” by the X-rays. EPA Method 6200 recommends an instrument blank at least once per day, preferably every 20 samples. If target analytes are reported in the instrument blank, all contact surfaces of the instrument will be wiped down with a soft cloth to remove any contamination on the detector window. If the instrument continues to detect target analytes with the instrument blank, the window covering the detector should be replaced.

3. CALIBRATION VERIFICATION: A calibration check, using an NIST check standard, will be analyzed at the beginning of each day or every 4 hours. The operator will perform a 2-minute test on a NIST standard. The percent difference between the handheld XRF result for an element and the value of the standard should be 20% or less. If the calibration check is greater than 20% of the standard value, the operator will adjust the calibration factor of the instrument and re-analyze the standard.

9. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Soil and sediment samples will be collected in press-seal plastic bags (Ziploc® or equivalent). Initial homogenization of the sample and removal of non-representative material should take place at the time of sampling. To maintain sample integrity, documentation of sample locations, dates, times, depths, and associated field sample identification numbers will be recorded in field logbooks at the time of sample collection. If a sample is collected for off-site laboratory analysis, the corresponding sample ID will also be noted.

10. SAMPLE PRESERVATION AND ANALYSIS

10.1 Sample preservation

Soil and sediment samples will be collected in plastic bags in the field and screened with the XRF initially as wet weight samples. The soil samples will be homogenized as thoroughly as possible inside the plastic bag, and a minimum of three readings will be taken. Results will be stored locally on the instrument and downloaded to the project laptop at the end of each day. Readings for lead, arsenic, and aluminum will be recorded in the field logbook.

Field samples will be transported back to the NMED on-site laboratory for dry weight analysis. Samples will weighed in the plastic bag and then spread out in polystyrene drying pan. The sample will be allowed to air-dry and sample weight will be measured daily. A sample will be considerd dry when there is no measured difference between the daily sample weights. The dried sample will be sieved through a No. 60 (250 µm) mesh stainless steel sieve. At no time should material be forced through the sieve. The sieved fraction will be collected in sample cup and the cup will be labeled appropriately. The stainless steel sieve must be wiped clean with a paper town between sample preparations. A disposable plastic scoop will be used for each sample.

10.2 Sample Analysis

Analysis of sample, blanks, and check standards will be performed using the DELTA Premium Handheld XRF analyzer and the associated GeoChem (Plus) and Soils (Plus) software. Refer to the DELTA Family Handheld XRF Operator Manual for sample analysis using the analyzer software.

10.3 Analysis Sequence

- Install battery in the XRF unit. Battery should remain charging overnight when the instrument is not in use.

- Turn on instrument and allow to warm-up.

- Perform the standardization procedure with the standardization clip, using either the coin provided by the manufacturer or the chip mounted in the unit docking station.

- Analyze the initial calibration check using the NIST standards provided with the instrument. The percent difference of the calibration of the check standard must be ≤20 to continue with analysis. If the percent difference is greater than 20, the instrument will need to be recalibrated, per manufacturer’s specifications.

- Analyze the instrument blank (provided with the instrument). There should be no detections greater than reporting limits.

- Analyze field samples.

- Analyze a calibration sample standard after every 20 samples and a method blank with every batch of 20 samples.

11. DOCUMENTATION AND REPORTING RESULTS

Sample raw results will be recorded in the field logbook for lead, arsenic, aluminum. Results for each sample will be recorded locally on the instrument and downloaded to the project laptop at the end of each day. The data will be exported and analyzed by analyst for detections above the reporting limit established for the project. Values less than the reporting limit will be reported with a “U” qualifier flag in an Excel spreadsheet.

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APPENDIX C

EPA Method 6200

METHOD 6200

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

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed below for soil and sediment samples. Some common elements are not listed in this method because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). These light elements are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed below 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. The following RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-0
Barium (Ba)	7440-39-3
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Thallium (Tl)	7440-28-0
Tin (Sn)	7440-31-5

Analytes	CAS Registry No.
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

In addition, the following non-RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Calcium (Ca)	7440-70-2
Iron (Fe)	7439-89-6
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-93-7
Potassium (K)	7440-09-7
Rubidium (Rb)	7440-17-7
Strontium (Sr)	7440-24-6
Thorium (Th)	7440-29-1
Titanium (Ti)	7440-32-6
Zirconium (Zr)	7440-67-7

1.2 This method is a screening method to be used with confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)). This method’s main strength is that it is a rapid field screening procedure. The method's lower limits of detection are typically above the toxicity characteristic regulatory level for most RCRA analytes. However, when the obtainable values for precision, accuracy, and laboratory-established sensitivity of this method meet project-specific data quality objectives (DQOs), FPXRF is a fast, powerful, cost effective technology for site characterization.

1.3 The method sensitivity or lower limit of detection depends on several factors, including 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. Example lower limits of detection for analytes of interest in environmental applications are shown in Table 1. These limits apply to a clean spiked matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (100 -600 second) count times. These sensitivity values are given for guidance only and may not always be achievable, since they will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of performance-based sensitivity is presented in Sec. 9.6.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use either sealed radioisotope sources or x-ray tubes to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This latter 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 three electron shells include 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), beta (β), or gamma (γ) etc., 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 15.77 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, specifically, 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 standards.

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, Chapter Three, and the manufacturer's instructions for other definitions that may be relevant to this procedure.

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 (i.e., against the cup window), 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 reporting of a "nondetect" or a "less than" value (e.g., <300 ppm) for As, 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 using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)).

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 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-specific data quality objectives (DQOs).

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 (see Table 8), the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r often exceeding 0.95, except for barium and chromium). The critical factor is that the digestion procedure and analytical reference method used should meet the 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 Sec. 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° F. The operator should follow the manufacturer's recommendations for gain check frequency.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The user is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

NOTE: No MSDS applies directly to the radiation-producing instrument because that is covered under the Nuclear Regulatory Commission (NRC) or applicable state regulations.

5.2 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 operator's 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. 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.

Licenses for radioactive materials are of two types, specifically: (1) a general license which is usually initiated by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) a specific license which is issued to named persons for the operation of radioactive instruments as required by local, state, or federal agencies. A copy of the radioactive material license (for specific licenses only) 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. An additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply, however, if the tube is properly positioned within the instrument, this is only a negligible risk. Any instrument (x-ray tube or radioisotope based) is capable of delivering an electric shock from the basic circuitry when the system is inappropriately opened.

5.3 Radiation monitoring equipment should be used with the handling and operation 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 or badges should be worn in the area of maximum 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.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

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 -- FPXRF instruments use either a sealed radioisotope source or an x-ray tube to provide the excitation source. Many 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 (^{55}Fe), cadmium Cd-109 (^{109}Cd), americium Am-241 (^{241}Am), and curium Cm-244 (^{244}Cm). These sources may be contained in a probe along with a window and the detector; the probe may be 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. This is due to the ever increasing time required for the analysis rather than a decrease in instrument performance. 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 necessary 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 both 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 and by the instrument's ability to cool the x-ray tube. 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 FPXRF instruments operated in the intrusive mode, the probe may be rotated so that the window faces either upward or downward. 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 Si(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 Si(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 Si(Li) detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 L. 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; Si(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 ppm on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 3,000 to 5,000 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 or at any other time, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery and battery charger.

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

6.4 X-ray window film -- Mylar^{TM}, Kapton^{TM}, Spectrolene^{TM}, polypropylene, or equivalent; 2.5 to 6.0 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 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 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 designated 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.

7.3 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.

7.3.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of 10 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.

7.3.2 Each sample should be oven-dried for 2 to 4 hr at a temperature of less than 150 °C. If mercury is to be analyzed, a separate sample portion should be dried at ambient temperature 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 homogenized (see Sec. 7.3.3) and then a representative portion ground with a mortar and pestle or other mechanical means, prior to passing through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.3.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 g 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 g 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.

7.4 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 established lower limit of detection. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.5 Standard reference materials -- Standard reference materials (SRMs) 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. When these SRMs are unavailable, alternate standards may be used (e.g., NIST 2702).

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 Follow the manufacturer’s instructions for the quality control procedures specific to use of the testing product. Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

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 Sec. 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (more than 10 °F).

9.2.1 The energy calibration check should be run at a frequency consistent with manufacturer's 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.

9.2.2 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 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, specifically, instrument blanks and method blanks.

9.3.1 An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window. The instrument blank can be silicon dioxide, a polytetraflurorethylene (PTFE) 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 established lower limit of detection 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. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lowest level of detection or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, 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. If both in situ and intrusive analytical techniques are used during the course of one day, it is recommended that separate precision calculations be performed for each analysis type.

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 sensitivity, but decreases sample throughput.

9.6 The lower limits of detection should be established from actual measured performance based on spike recoveries in the matrix of concern or from acceptable method performance on a certified reference material of the appropriate matrix and within the appropriate calibration range for the application. This is considered the best estimate of the true method sensitivity as opposed to a statistical determination based on the standard deviation of replicate analyses of a low-concentration sample. While the statistical approach demonstrates the potential data variability for a given sample matrix at one point in time, it does not represent what can be detected or most importantly the lowest concentration that can be calibrated. For this reason the sensitivity should be established as the lowest point of detection based on acceptable target analyte recovery in the desired sample matrix.

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 project-specific 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) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r 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, namely: 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 necessary, 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 necessary.

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 Sec. 7.3. 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 Sec. 7.3; 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 necessary. 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 necessary to perform an adequate empirical calibration. The exact number of 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 reading. 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 during 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, remove any large or nonrepresentative debris from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Also, the soil surface must 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 example performance data for this method, this modest amount of sample preparation was found to take less than 5 min 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 the desired method sensitivity. Due to the heterogeneous nature of the soil sample, in situ analysis can provide only “screening” type data.

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 g or 250 cm^3, which is enough soil to fill an 8-ounce jar. However, the exact dimensions and sample depth should take into consideration the heterogeneous deposition of contaminants and will ultimately depend on the desired project-specific data quality objectives. 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 Sec. 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 time necessary for homogenization procedure using the fluorescein dye ranged from 3 to 5 min per sample. As demonstrated in Secs. 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, the direct analysis through the plastic bag is possible without the more labor intensive steps of drying, grinding, and sieving given in Secs. 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps should 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 g) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hr in the convection or toaster oven at a temperature not greater than 150 °C. Samples may also be air dried under ambient temperature conditions using a 10- to 20-g portion. Regardless of what drying mechanism is used, the drying process is considered complete when a constant sample weight can be obtained. Care should be taken to avoid sample cross-contamination and these measures can be evaluated by including an appropriate method blank sample along with any sample preparation process.

CAUTION: 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 min 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 established lower limit of detection of the procedure or DQOs of the analysis. If all recommended sample preparation steps are followed, there is a high probability the desired laboratory data quality may be obtained.

12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in ppm and can be downloaded to a personal computer, which can be used to provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation. See the manufacturer's instructions regarding data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.</u>

13.2 The sections to follow discuss three performance evaluation factors; namely, precision, accuracy, and comparability. The example data presented in Tables 4 through 8 were generated from results obtained from six FPXRF instruments (see Sec. 13.3). 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. These data are provided for guidance purposes only.

13.3 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 HgI_2 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.

13.4 All example data presented in Tables 4 through 8 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.

13.5 Precision measurements -- The example precision data are presented in Table 4. These data are provided for guidance purposes only. 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 4 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the lower limit of detection 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 4. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the lower limit of detection so that an RSD value calculated at 5 to 10 times this limit 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 5 shows these results. These data are provided for guidance purposes only. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the lower limit of detection for 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 5 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 5 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 instead of 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 6 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 6 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 6. 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 6.

Table 7 provides a more detailed summary of accuracy data for one particular FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. These data are provided for guidance purposes only. Table 7 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 8. Similar trends in the data were seen for all instruments. These data are provided for guidance purposes only.

Table 8 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. These data are provided for guidance purposes only. 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--intrusive, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not ground; and preparation 4–intrusive, with 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 8 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 8 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.

Sec. 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 necessary to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 min. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 min per sample. Lastly, when grinding and sieving is conducted, time has to 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 A. D. Hewitt, "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_α Peak Normalization Analysis," American Environmental Laboratory, pp 24-32, 1994.

13.8.2 S. Piorek and J. R. Pasmore, "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, Vol 2, pp 1135-1151, 1993.

13.8.3 S. Shefsky, "Sample Handling Strategies for Accurate Lead-in-soil Measurements in the Field and Laboratory," *International Symposium of Field Screening Methods for Hazardous Waste and Toxic Chemicals*, Las Vegas, NV, January 29-31, 1997.

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 St., N.W. Washington, D.C. 20036, http://www.acs.org.

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, "Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction," 1994.

3. TN Spectrace, Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.

4. Unpublished SITE data, received from PRC Environment Management, Inc.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

EXAMPLE INTERFERENCE FREE LOWER LIMITS OF DETECTION

Analyte	Chemical Abstract Series Number	Lower Limit of Detection 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: Refs. 1, 2, and 3
These data are provided for guidance purposes only.

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	K Lines
				Molybdenum to Barium	L Lines
Cd-109	5-30	1.3	22.1 and 87.9	Calcium to Rhodium	K Lines
				Tantalum to Lead	K Lines
				Barium to Uranium	L Lines
Am-241	5-30	432	26.4 and 59.6	Copper to Thulium	K Lines
				Tungsten to Uranium	L Lines
Cm-244	60-100	17.8	14.2	Titanium to Selenium	K Lines
				Lanthanum to Lead	L Lines

Source: Refs. 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	K Lines
			Silver to Gadolinium	L Lines
Mo	40-50	17.4	Cobalt to Yttrium	K Lines
			Europium to Radon	L Lines
Ag	50-65	22.1	Zinc to Technicium	K Lines
			Ytterbium to Neptunium	L Lines

Source: Ref. 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

EXAMPLE PRECISION VALUES

Analyte	Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the Lower Limit of Detection					
	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

These data are provided for guidance purposes only.
Source: Ref. 4

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

NR Not reported.

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

TABLE 5

EXAMPLES OF 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

These data are provided for guidance purposes only.
Source: Ref. 4

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

ND Not detected.
NR Not reported.

TABLE 6

EXAMPLE ACCURACY VALUES

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: Ref. 4. These data are provided for guidance purposes only.
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 7

EXAMPLE ACCURACY FOR TN 9000[a]

Standard Reference Material	Arsenic			Barium			Copper			Lead			Zinc		
	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	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: Ref. 4. These data are provided for guidance purposes only.

[a] All concentrations in milligrams per kilogram.

%Rec.: Percent recovery; ND: Not detected; NA: Not applicable.

-- No data.

TABLE 8

EXAMPLE REGRESSION PARAMETERS FOR COMPARABILITY[1]

	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

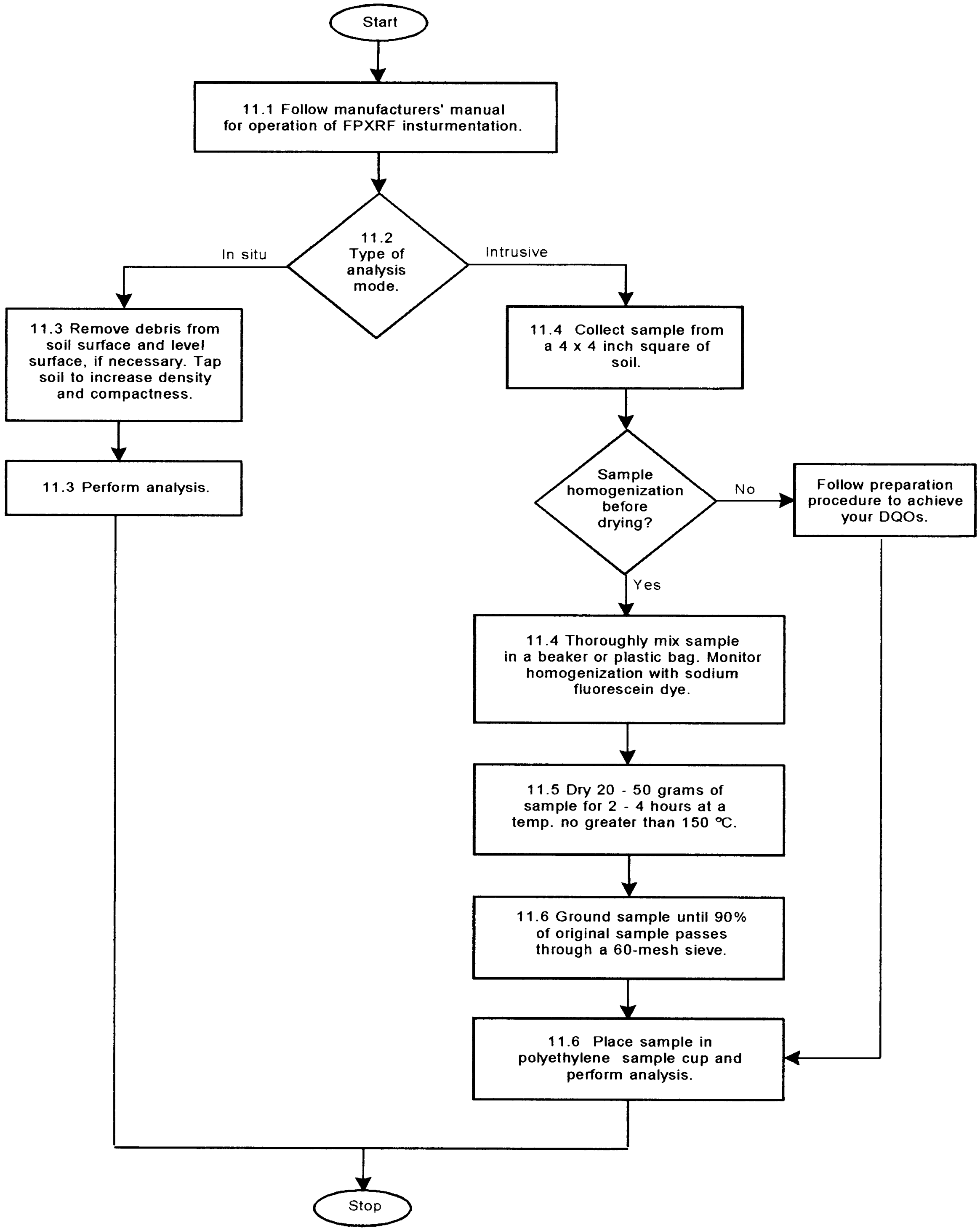
Source: Ref. 4. These data are provided for guidance purposes only.

[1] Log-transformed data

n: Number of data points; r^2: 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



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APPENDIX D

Olympus DELTA Family XRF Analyzer Guide
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