

**Port Site Characterization
Sampling and Analysis Plan**

**DeLong Mountain Regional
Transportation System, Alaska**

Prepared for

Teck Cominco Alaska Inc.
Anchorage, Alaska

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Sampling and Analysis Plan**

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Transportation System, Alaska**

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July 2002

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Acronyms and Abbreviations

CSB	concentrate storage building
DMTS	DeLong Mountain Regional Transportation System
EPA	U.S. Environmental Protection Agency
GPS	global positioning system
IDW	investigation-derived waste
PAC	personnel accommodation complex
PSMP	port site monitoring program
QAPP	quality assurance project plan
SAP	sampling and analysis plan
SOP	standard operating procedure
Teck Cominco	Teck Cominco Alaska Inc.
TUB	truck unloading building
XRF	x-ray fluorescence

Port Site Characterization Sampling and Analysis Plan

Introduction

The Red Dog Mine is located approximately 50 miles east of the Chukchi Sea, in the western end of the Brooks Range of northern Alaska (Figure 1). Ore containing lead and zinc is milled at the Red Dog Mine to produce lead and zinc concentrates in a powder form. These concentrates are hauled year-round from Red Dog Mine via the DeLong Mountain Regional Transportation System (DMTS) road to concentrate storage buildings (CSBs) at the DMTS Port facility, where they are stored for later loading onto ships via a conveyor system during the summer months.

The port site is located 52 miles (by road) southwest of Red Dog Mine on the Chukchi Sea. Because the shipping season is confined to a few months when the waters are ice-free, the concentrates are stored at the port site for most of the year. Trucks haul the concentrates from the mine, along the DMTS road, and to the CSBs at the port. The CSBs are used to store the concentrates until shipping season begins. Enclosed conveyor belts transfer the concentrates from the CSBs to the barges, which are covered by fixed tarps. The barges carry the concentrates to deep-sea vessels 3 to 4 miles offshore, where they use a self-contained conveyor system to load the concentrates into the ships. Once the concentrates are loaded into the ships, they are delivered throughout North America, Europe, and Asia.

The DMTS Port facility includes the following features:

- Shallow-water dock
- Fueling/staging area
- Two CSBs and a truck unloading building (TUB)
- Road loop for trucks to enter and exit the CSBs
- Conveyors that transport ore concentrates from the TUB to the CSBs, and from the CSBs to the bargeloader conveyor at the dock
- Maintenance buildings
- Generator building
- Housing facilities for Teck Cominco Alaska Inc. (Teck Cominco) personnel at the personnel accommodation complex (PAC).

In the baseline port site monitoring program (PSMP) in June 1990, the port site was studied to determine “baseline” conditions prior to the shipping of concentrates. In 1991, the PSMP began to monitor lead, zinc, and diesel-range organic concentrations at the port site facilities. In 1992, Teck Cominco implemented mitigative measures to minimize fugitive lead and zinc. Onshore

and marine water and sediment sample analyses were also added to the program in 1992. The program was replaced by an air monitoring program in 1997.

Teck Cominco also commissioned a characterization of sediments in the port area in 1998 as part of the DeLong Mountain Terminal Project. The purpose of this project was to investigate the feasibility of extending the dock and dredging a ship channel, to allow for direct loading of the concentrates onto the barges. The characterization specifically targeted the areas proposed for the dredge material disposal and for the dredge channel. The U.S. Army Corps of Engineers performed an additional sediment study in 2000.

The purpose of this sampling and analysis plan (SAP) is to evaluate the current extent of lead, zinc, and cadmium concentrate deposition in the vicinity of the DMTS port site. The sampling will include areas where metal concentrations may be elevated, including historical source areas and areas where materials and/or structures were temporarily stored or relocated. This SAP provides a protocol for screening lead, zinc, and cadmium levels in soil at the dock, conveyor areas, road loop, and miscellaneous buildings at the port site, as well as in surrounding tundra areas. Surface soil metals concentrations near selected port site features will be measured in the field using a portable x-ray fluorescence (XRF) detector and confirmed through laboratory analysis of a subset of samples. Tundra soils in areas surrounding the port site features will be collected and submitted for laboratory analysis. Water samples and sediment samples will be collected from four lagoons and the nearshore marine stations that were previously sampled in the PSMP. All sampling activities and laboratory work will be conducted in general accordance with the U.S. Environmental Protection Agency's (EPA's) *Environmental Investigations, Standard Operating Procedure and Quality Assurance Manual* (U.S. EPA 1997). Specific methods for performing field tasks are described in subsequent sections.

This SAP is organized into the following sections:

- Introduction
- Summary of Existing Port Site Data
- Port Site Sampling Program
- Equipment Decontamination
- Sample Identification System
- Field Data Reporting
- Analytical Methods
- Disposal of Investigation-Derived Waste
- Field Sampling Schedule
- References.

Sample locations are shown in figures at the end of the main text. In addition, EPA Method 6200 for field portable XRF spectrometry is provided in Appendix A, portable XRF operator qualifications and training are provided in Appendix B, and a standard operating procedure (SOP) for sample packaging and shipping is provided in Appendix C. The quality assurance project plan (QAPP) is provided separately (Exponent 2001).

Summary of Existing Port Site Data

Soil Data

Data from the PSMP in 1996 are the most recent, and therefore the most representative of cumulative effects over the 1990–1996 period. In the 1996 program, 87 soil samples were taken near the CSB, 196 at the conveyor area, 40 at the dock area, 73 in the roadway area, 38 in the unloading area, and 39 in the fuel storage area. Table 1 shows the mean, median, and maximum concentrations of lead and zinc at each of the port facility areas.

The highest concentrations were observed in samples located close to operational features around the port site, and concentrations rapidly decline with distance. Figures 2 and 3 show the extent of lead and zinc concentration in the port facility area in 1996. Areas up to 500 ft from the conveyors, CSB, and roadway loop exceed the 1,000 ppm lead arctic zone soil cleanup level in Alaska Administrative Code, Section 18 AAC 75. Zinc concentrations exceeding the arctic zone soil cleanup level of 41,000 ppm were identified in three areas: two locations along the conveyor system and one location near the CSB and roadway loop.

Water Data

In the 1996 PSMP, five unfiltered water samples were collected from each of the four lagoons (seven samples were collected from Port Lagoon South). Twenty-six unfiltered water samples were collected from the marine sampling station and one unfiltered water sample was collected from the control marine sampling station (Figure 4). Table 2 shows the mean, median, and maximum concentrations of lead and zinc at each of the water sampling stations.

Although the lead concentrations did not exceed the EPA water quality criteria for acute freshwater and saltwater aquatic life, some lagoon and marine water samples exceeded the lead criteria for chronic freshwater and saltwater aquatic life of 0.003 and 0.0085 mg/L, respectively (64 Fed. Reg. 19,781). Zinc concentrations in the lagoon water samples did not exceed the freshwater acute and chronic criteria of 0.12 and 0.11 mg/L, respectively. However, the maximum zinc concentration in the marine stations exceeded the saltwater acute and chronic criteria of 0.095 and 0.086 mg/L, respectively.

Sediment Data

In the 1996 PSMP, sediment samples were collected in each of the four lagoons and in the nearshore marine zone. Five sediment samples were collected in each lagoon (with the

exception of seven samples from Port Lagoon South). Three sediment samples were obtained from the control marine station, and a total of 78 samples were taken from the nearshore marine zone stations (Figure 4). Table 3 shows the mean, median, and maximum concentrations of lead and zinc at each of the sediment sampling stations.

The maximum concentrations of lead in the lagoons and nearshore marine sediments did not exceed the Washington State Sediment Management Standard of 450 mg/kg (Ecology 2002). The maximum zinc concentration in the North Lagoon and both the maximum and mean concentrations in Port Lagoon North all exceeded the zinc standard of 410 mg/kg. The comparisons were made with Washington State standards because the State of Alaska has not established sediment criteria.

In 2000, Teck Cominco also characterized the marine sediment in the area of proposed dredging and dredged material disposal, as part of the Feasibility Stage of the DeLong Mountain Terminal Project. Sediments were collected at 23 stations: 9 in the proposed Channel and Turning Basin, 4 adjacent to the Loading Dock, and 10 in the proposed Marine Disposal area (locations nearest the shore are shown in Figure 4). The sediment samples were analyzed for metals, including lead, zinc, and cadmium.

The highest average lead concentration measured in sediment at the Loading Cell was 17.4 mg/kg, while the average in the proposed Channel was 8.9 mg/kg. Sediments collected from the proposed Marine Disposal area had average lead concentrations of 5.5 mg/kg. All sampled areas had similar zinc concentrations averaging 52.5 mg/kg. The maximum zinc concentration was 83 mg/kg in a Loading Cell sample. Cadmium concentrations among all the sampling locations averaged 2.0 mg/kg (Corps 2001). A comparison to the Washington State Sediment Management Standard of 450, 410, and 5.1 mg/kg for lead, zinc, and cadmium, respectively, indicates that the metals concentrations were below criteria. The lead and zinc concentrations in the nearshore marine sediments appeared to be lower in samples collected in 2000 than in samples collected during the 1996 PSMP.

Port Site Sampling Program

The sampling program planned for summer 2002 includes soil, water, and sediment sampling. The protocols for this work will be described in detail in the following sections. Figure 5 shows the proposed soil, sediment, and water sampling stations, with detailed views in Figures 6 and 7.

Soil Sampling

The soil sampling for this characterization study will include both soil samples analyzed by XRF, and soil samples collected for laboratory analysis. XRF measurements of lead, zinc, and cadmium concentrations at selected port facilities will be measured primarily *in situ* using a field portable XRF detector according to EPA Method 6200, *Field Portable XRF Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*, which is provided in Appendix A of this SAP. The locations planned for XRF sampling (Figures 6 and 7) include the two laydown areas that were historically used as temporary storage areas at the dock and racetrack roadway. XRF sampling will also be performed around the surge bin and in the

vicinity of the PAC building. *In situ* XRF analysis is a rapid testing method that can generate a large quantity of screening-level quality data over a short time period and allows field personnel to adapt the sampling strategy in reaction to XRF readings produced in real time. EPA Method 6200 recommends that at least 5 percent of XRF field measurements be confirmed through laboratory testing (see Appendix A). At 10 percent of the sampling stations, XRF measurements will be made *ex situ* on surface soil samples, which will then be submitted to the offsite laboratory for confirmatory analysis.

Sample soil cores will be sampled at the toe of the embankment at each of the road transects. Cores will be taken by hand with a hammer-driven split- spoon sampler. Each core will be at a depth of 1 ft below the surface. The core will be divided between a surface layer that consists of accumulated fines and fill material, and an organic matter layer that consists of peat and other naturally occurring soil material. Samples of the two layers of the soil core will be sent to an offsite laboratory for metals analyses.

Soil samples from the tundra, and from transects located along the racetrack, the road, the two CSBs, and the conveyor will be analyzed in an offsite laboratory. Lead, zinc, and cadmium will be analyzed by inductively coupled plasma analysis using EPA Method 6010B. Soil samples for XRF confirmation analysis and soil cores will also be analyzed by EPA Method 6010B. Blind field duplicate samples will be collected at 10 percent of the sampling locations. Additional discussion of analytical methods is provided in the *Analytical Methods* section below.

XRF Sampling Stations

- *In situ* XRF measurements will be recorded at approximately 125 stations at the port facility, as illustrated in Figures 6 and 7.
- Twelve stations will fall on a 200-ft spaced grid on the dock storage pad, which has historically been used as a temporary storage area (Figure 6).
- Forty-seven stations will fall on a 100-ft spaced grid oriented around the surge bin (which historically has been a source of fugitive dust), including the PAC area (Figure 6).
- Approximately 112 stations will fall on the CSB area grid. The area covered by this grid includes the laydown area east of CSB2 that has historically been used for temporary storage of equipment and material stockpiles, and it also includes the areas outside the doors of the CSBs (Figure 7).
- Five stations will be located next to the TUB (Figure 7), in the area planned for an additional structure.
- Soils will also be collected at a minimum of 5 percent of the XRF stations, and sent to an offsite laboratory for confirmatory analysis, to comply with EPA Method 6200. For these soil stations, metals concentrations in surface soil samples will be determined by both *in situ* and *ex situ* XRF analyses and confirmed by laboratory analysis.

- If samples are deemed too moist for XRF analysis (at the discretion of the sampler), a soil sample will be collected and submitted for laboratory analysis.
- For the convenience of the field crew, station IDs and their locations are provided in Table 4. However, exact station locations will be determined in the field. Station coordinates will be recorded using a handheld global positioning system (GPS) receiver.
- Stations will be identified with a letter and number designation, based on their position on the grid or transect, as illustrated in Figures 6 and 7 and as discussed in the *Sample Identification System* section of this report.

General Procedures for XRF Analysis

- The field portable XRF detector will be operated and maintained in accordance with procedures outlined in the operator's manual accompanying the instrument.
- A 15-minute warm-up period will precede any calibration, standardization, or operation of the XRF detector. The warm-up, calibration, standardization, and operation of the XRF detector will be performed in outside ambient air temperatures to avoid effects of temperature fluctuation.
- Calibration and standardization of the XRF detector will be performed according to the instrument manufacturer's instructions and at a frequency consistent with the manufacturer's recommendations.
- Field personnel will follow all quality assurance and quality control protocols defined in EPA Method 6200 (Appendix A), including energy calibration checks, blank samples analysis, calibration verification checks, precision sample analysis, calculation of site-specific method detection and quantitation limits, and collection of confirmatory samples.
- Field personnel will avoid calibrating, standardizing, or operating the XRF detector in the vicinity of an active computer monitor.

Procedures for *In Situ* XRF Analysis

- At each station, a location will be selected that is relatively flat and dry. Ideally, soil moisture content should be between 5 and 20 percent (see Appendix A).
- XRF sampling stations may be leveled with a clean stainless-steel spoon as necessary to accommodate the placement of the XRF detector and to remove unrepresentative debris.

- Three 60-second readings of lead, zinc, and cadmium concentrations will be collected at each sampling station. At 60 seconds, concentration and standard deviation measurements will be recorded in the field logbook, and in instrument memory for later downloading.
- Mean lead, zinc, and cadmium concentrations for each station will be calculated and recorded in the field logbook. The mean concentration will be the average of the XRF results obtained from three measurements per station.
- Information on the condition of the port site feature or facility, how recently it has been changed, and the moisture content (dry, moist, or wet) will be recorded in the field logbook for each sampling point.

Surface and Tundra Soil Sampling Stations

Soil samples will be collected from both surface soils near port site facilities and from tundra soils. Surface soil consists of fill material near the port facilities. Two types of tundra soil samples will be collected. Shallow tundra soil samples will consist of peat or decaying organic matter beneath the vegetative cover, at the root zone. Deeper tundra soil samples will be collected at the top of the inorganic layer, if present, beneath the organic layer. Transects that extend from the port site facilities out toward the tundra may have both surface soil and tundra soil samples (Figure 8). Transects extending into the tundra will have additional stations at 250 and 500 ft.

- Approximately 144 shallow tundra soil sampling stations will be spaced 1,000 ft apart on a grid, beginning 100 ft away from port site features. This will provide greater coverage than the historical dustfall grid locations. At the sampler's discretion, if the soil at stations near the lagoons is dry enough to be deemed a soil sample, a sample will be collected (Figure 5). Deep tundra samples will be collected at approximately 10 of these stations (5 near port site facilities, and 5 in outlying areas). The deep samples will be co-located with shallow samples to evaluate the occurrence of fugitive metals with depth.
- Sixty-four stations within 100 ft of the racetrack loop will be along bi-directional transects and spaced at 0, 10, and 50 ft from the feature in one direction, and 0, 10, 50, 250, and 500 ft in the direction toward the tundra (Figure 7). The two 0-ft stations will be at the toe of the embankment and will be core samples. Transects will be perpendicular to the orientation of the racetrack road and will be spaced approximately 500 ft from each other.
- Nine transects will be placed along the edges of the two CSBs. The 0-ft station will be located outside of the drainage ditches that surround the CSBs, as shown in Figure 8. Transects located on CSB1 extend into the tundra and will have stations at 250 and 500 ft added on (for a total of 35 stations). All transects will be spaced approximately 500 ft from each other, with one

transect extending out from the two northwest corners of each CSB (Figure 8).

- One hundred and forty-four stations within 100 ft of the conveyor system and road will be along bi-directional transects and spaced at 0, 10, 50, 250, and 500 ft from the conveyor or road, out towards the tundra, and spaced at 0, 10, and 50 ft in the opposite direction (Figure 8). The 0-ft stations on conveyor transects will be located directly below the outer edge of the conveyor on the surface of the foundation pad. The 0-ft station on road transects will be at the toe of embankment and will be soil core samples. Transects will be placed perpendicular to the orientation of the conveyor and road, and will be spaced approximately 500 ft from each other.
- For the convenience of the field crew, station IDs and their locations on the 1,000-ft grid are provided in Table 4. However, exact station locations will be determined in the field, as they are expected to vary based on field conditions. Station coordinates will be recorded using a handheld GPS receiver.
- Stations will be identified with a letter and number designation, based on their position on the grid or transect, as illustrated in Figures 5, 7, and 8, and as discussed in the *Sample Identification System* section of this report.

Procedures for Surface and Tundra Soil Sampling

Soil samples collected for laboratory analyses will include surface soil samples and tundra soil samples. Surface soils (i.e., fill material) are found near port site facilities. Shallow tundra soils usually have a vegetation cover of mosses, lichens, or grasses. The tundra soil under the vegetation is peat or coarse, decaying organic material. Deep tundra soils are an inorganic layer of parent geologic material, where present.

- Surface soil samples will be taken at a depth of 0–1 in. from the surface.
- Shallow tundra soil samples will be taken at a depth 2–6 in. below the surface, depending on where the peat/organic material is present below the vegetation.
- If surface vegetation is present, it will be removed. The layer of peat or decaying organic matter beneath the vegetation will be collected as the shallow tundra soil sample.
- With a fresh set of gloves for each sample, the sampler will collect a handful of material and place it in a precleaned 8-oz sample container. As material is added to the jar, it will be compressed to squeeze out excess water. If a field duplicate is required at the station, soil will be split between two sample jars.
- Deep tundra soil samples will be collected by exposing the top of the inorganic soil layer, using a precleaned stainless steel spoon to sample the top

1–2 in. of the layer, and placing the sample into a precleaned 8-oz sample container. Where an inorganic layer is not found, a sample of organic tundra soil will be collected at a depth of approximately 1 ft below the shallow sample (above the permafrost).

- Each sample and field duplicate will be properly labeled with a unique sample identification number (see *Sample Identification System* section of this report) and submitted to the offsite analytical laboratory for analysis. Chain-of-custody forms will be completed and signed by the field representative and submitted with the samples to the analytical laboratory. Sample packaging and chain-of-custody procedures are provided in SOP 2 (Appendix C). Field documentation is discussed in the *Field Data Reporting* section of this report.
- Soil samples will be analyzed for lead, zinc, cadmium, and moisture content at an offsite laboratory.
- Information on the condition of the soil in the port area, and moisture content (dry, moist, or wet), will be recorded in the field logbook for each station.

Procedures for *Ex Situ* XRF Analysis

- XRF samples will be hand-collected with the same method used for surface soil samples. At each station, a sample will be collected and homogenized using a precleaned stainless-steel spoon and bowl.
- Approximately 5 g of homogenized soil will be placed in a clean 31.0-mm polyethylene sample cup (or equivalent) for XRF analysis. The sample cup will be filled at least one-half to three-quarters full and covered with 2.5 μm Mylar (or equivalent) film.
- Lead, zinc, and cadmium concentration data will be collected for 60 seconds by the XRF operator. At 60 seconds, concentration and standard deviation measurements will be recorded in the field logbook, and in instrument memory for later downloading.
- After XRF analysis, soil in the sample cup will be returned to the bowl and re-homogenized with the rest of the sample. The sample will then be transferred to a precleaned 8-oz jar. If a field duplicate is planned at the station, the re-homogenized soil will be split between two sample jars.
- Each sample and field duplicate will be properly labeled with a unique sample identification number and submitted to the offsite analytical laboratory for analysis. Chain-of-custody forms will be completed and signed by the field representative and submitted with the samples to the analytical laboratory. Sample packaging and chain-of-custody procedures are provided in SOP 2 (Appendix C). Field documentation is discussed in the *Field Data Reporting* section of this report.

- Soil samples will be analyzed for lead, zinc, cadmium, and moisture content at an offsite laboratory.
- Information on the condition of the soil in the port area and moisture content (dry, moist, or wet) will be recorded in the field logbook for each station.

Procedures for Soil Core Samples

Soil cores will be collected from the toe of the embankment at each of 0-ft stations on road transects.

- The cores will be collected with a split-spoon sampler driven by a hand-operated power hammer. The split-spoon will be driven to a depth of 1 ft. Samples will be collected from two depth intervals: a surface sample, and an organic matter sample beneath the surface sample. The segregation of the two samples from the core will be at the discretion of the sampler.
- The surface sample will consist of accumulated fine-grained materials and fill materials. The organic matter sample will consist of peat or naturally occurring soil material.
- Each interval sample will be homogenized using a precleaned stainless-steel spoon and bowl, and a representative portion of the sample transferred to a precleaned 8-oz sample jar. If a field duplicate is required at the station, a representative portion of each homogenized sample will be placed into a second set of sample jars.
- Each sample and field duplicate will be properly labeled with a unique sample identification number (see *Sample Identification System* section of this report) and submitted to the offsite analytical laboratory for analysis. Chain-of-custody forms will be completed and signed by the field representative and submitted with the samples to the analytical laboratory. Sample packaging and chain-of-custody procedures are provided in SOP 2 (Appendix C). Field documentation is discussed in the *Field Data Reporting* section of this report.
- Core samples will be submitted for laboratory analysis for lead, zinc, and cadmium.

Water Sampling

Water samples will be collected from the lagoons and submitted to an offsite laboratory for lead, zinc, and cadmium analysis. Stations will be identical to historical PSMP water sampling stations, however, marine water samples will not be collected. The water samples will be co-located with lagoon sediment samples (see *Sediment Sampling* section of this report). Water samples will be sent to an offsite laboratory for metals analyses. Lead will be analyzed by

graphite furnace atomic absorption spectrometry using EPA Method 7421, and zinc and cadmium will be analyzed by inductively coupled plasma analysis using EPA Method 6010B.

Description of Water Sampling Stations

- Two water samples will be taken in each of the four lagoons, which have been previously identified (from north to south) in the PSMP as North Lagoon, Port Lagoon North, Port Lagoon South, and Control Lagoon (Figure 5)
- In each lagoon, one water sample will be taken in a location closer to and one farther away from the port facility.

Procedures for Surface Water Sampling

- Field personnel in diving dry suits will wade out into the lagoon to the station location. Water samples will be collected before sediment samples are collected.
- Surface water sampling in the lagoons will be collected by vertically submersing a precleaned 1-L polyethylene sample bottle below the water surface and allowing only the upper portion of the water to enter.
- Water samples for dissolved metal analysis will be collected in a separate bottle, filtered through a 0.45 μm filter into a precleaned disposable flask, and transferred to another sample bottle.
- Both filtered and unfiltered water samples will be preserved with 2 mL of HNO_3 after collection.
- Each sample and field duplicate will be properly labeled with a unique sample identification number (identical to PSMP identification numbers) and submitted to the offsite analytical laboratory for analysis. Chain-of-custody forms will be completed and signed by the field representative and submitted with the samples to the analytical laboratory. Sample packaging and chain-of-custody procedures are provided in SOP 2 (Appendix C). Field documentation is discussed in the *Field Data Reporting* section of this report.
- At each water sample station, conductivity, pH, and temperature readings will be collected with a field meter to describe the basic properties of the waters sampled.
- Station IDs and locations from the PSMP can be found in Table 5. This table is provided for the convenience of the field crew, but it is expected that exact locations will vary, depending on the field conditions. Station coordinates will be recorded using a handheld GPS receiver.

Sediment Sampling

Sediment samples will be collected and sent to an offsite laboratory for lead, zinc, and cadmium analysis. Sediment samples will be obtained by a team member or a diver (at stations with large depths) using a hand-held sample container. Some of the sediment samples to be collected in the lagoons will have co-located water samples (see Figure 5 and the *Water Sampling* section of this report). The samples will be sent to an offsite laboratory for metals analyses. Lead, zinc, and cadmium will be analyzed by inductively coupled plasma analysis using EPA Method 6010B.

Description of Sediment Sampling Stations

- Twenty-six sediment samples will be taken in the nearshore marine waters at the port site. Locations of these sediment samples will be identical to sediment samples taken in the PSMP (Figure 5).
- Twenty-two sediment samples will be taken in the four onshore lagoons. Locations of these sediment samples will be identical to sediment samples taken in the PSMP (Figure 5).
- Three sediment samples will be taken from the drainage ditch surrounding CSB1. Ditch sample locations shown in Figure 7 are approximate and may be adjusted based on field conditions.

Procedures for Sediment Sampling

- Field personnel will don a diving dry suit and a breathing apparatus (when necessary in deep waters) to collect the sediment samples. Personnel should ensure that the fine sediments on the surface are not stirred up or disturbed.
- Personnel will uncap the sampling jar and use it to skim along the sediment surface (until the jar is full) to obtain the top 2 cm of sediment. The lid will be immediately replaced, being careful not to lose any fine sediment.
- The collection jar will be a precleaned 4-oz glass jar with Teflon[®] lid. The collection jar will also become the sample container.
- Alternatively, sediment samples may be collected in the winter by coring through the ice and using a Shelby tube to collect the sediment sample. If this approach is taken, a separate sampling procedure will be provided in a document to follow.
- The sample container will be properly labeled with a unique sample identification number (identical to the PSMP identification number) and submitted to the offsite analytical laboratory for analysis.
- Station IDs and locations from the PSMP can be found in Table 5. This table is provided for the convenience of the field crew but it is expected that exact

locations will vary, depending on the field conditions. Station coordinates will be recorded using a handheld GPS receiver.

- Chain-of-custody forms will be completed and signed by the field representative and submitted with the samples to the analytical laboratory. Sample packaging and chain-of-custody procedures are provided in SOP 2 (Appendix C). Field documentation is discussed in the *Field Data Reporting* section of this report.
- Sediment pH levels will be taken for each sediment sample and recorded.

Equipment Decontamination

All reusable sampling equipment will be decontaminated prior to collection of each sample. Procedures for management and disposal of waste generated during equipment decontamination are described in the *Disposal of Investigation-Derived Waste* section of this report.

Sampling equipment (such as stainless-steel spoons, bowls, and split-spoon samplers) will be washed using a scrub brush in a solution of Alconox[®] and water. Following the wash, equipment will be rinsed in tap water and then rinsed with deionized or distilled water.

Equipment rinsate blanks will be used to help identify possible contamination from the sampling environment and/or from decontaminated sampling equipment. Equipment rinsate blanks will be prepared at least once per sampling event per the type of sampling equipment used. Equipment rinsate blanks will be prepared by pouring laboratory distilled/deionized water through, over, and into the decontaminated sample collection equipment, then transferring the water to the laboratory-prepared sample containers. Each blank will be assigned a unique sample number and submitted to the offsite laboratory for analysis. Equipment rinsate blanks will be analyzed for lead, zinc, and cadmium.

Field blanks will be collected at a minimum frequency of once per day in order to evaluate potential background concentrations present in the air and in the distilled/deionized water used for the final decontamination rinse. Field blanks will be prepared at the sample collection site by filling the laboratory-prepared sample bottle with distilled/deionized water, sealing the bottle, assigning a unique sample number to the field blank, and submitting the bottle to the offsite laboratory for analysis. Field blanks will be analyzed for lead, zinc, and cadmium.

Sample Identification System

Each sample and field duplicate will be assigned a unique sample number. Soil samples will be named based on their grid location, as illustrated in Figures 5, 6, and 7. Water and sediment samples will have the same sample identities as the PSMP (see Table 5). Transects will be numbered in sequential order in the field. Bi-directional transects will be numbered individually. Field duplicates (to be collected at 10 percent of the sample stations) will be

identified in the same way, except that the station number will be a number beyond the expected range of actual station numbering. Samples will be identified using the following nomenclature:

- PG-A1, PG-A2, PG-A3, ... = Tundra soil on the 1,000-ft port grid, collected for laboratory analysis recorded for a station based on its location on the grid (Table 4).
- RAT1-0, RAT1-10, RAT1-50, ... = Soil sample collected from racetrack transect, numbered sequentially in the field. A suffix of 0, 10, or 50 will be added to identify individual stations at 0, 10, and 50 ft.
- ROT1-0, ROT1-10, ROT1-50, ... = Soil samples collected from road transects, numbered sequentially in the field. A suffix of 0, 10, 50, 250, or 500 will be added to identify individual stations at 0, 10, 50, 250, and 500 ft.
- CVT1-0, CVT1-10, CVT1-50, ... = Soil samples collected from conveyor transects, numbered sequentially in the field. A suffix of 0, 10, 50, 250, or 500 will be added to identify individual stations at 0, 10, 50, 250, and 500 ft.
- C1T1-0, C1T1-10, C1T1-50, ... = Soil samples collected from CSB1 transects, numbered sequentially in the field. A suffix of 0, 10, 50, 250, or 500 will be added to identify individual stations at 0, 10, 50, 250, and 500 ft.
- DD1, DD2, DD3, ... = Sediment samples collected from the drainage ditch around CSB1, numbered sequentially in the field.
- DSP-A1-A, DSP-A1-B, ... = *In situ* XRF analysis recorded for dock storage pad stations, including areas around the surge bin and PAC stations, based on its location on the grid (a suffix of A, B, or C will be added to identify the three individual measurements recorded at that station) (Table 4).
- CAG-A1-A, CAG-A1-B, ... = *In situ* XRF analysis recorded for CSB area grid stations, based on their location on the grid (a suffix of A, B, or C will be added to identify the three individual measurements recorded at that station) (Table 4).
- TU-1, TU-2, TU-3, ... = *In situ* XRF analysis recorded for TUB stations; stations will be numbered sequentially in the field.
- RB-1, RB-2, ... = Rinsate blank sample.
- FB-1, FB-2, ... = Field blank sample.

Water and sediment samples will be identified like the original nomenclature in the PSMP (RWJ 1997). Station IDs and locations are provided in Table 5.

Field Data Reporting

Sampling activities will be documented in a bound, waterproof field logbook, or on field forms. All daily field activities will be documented in indelible ink in the logbook or on the forms, and no erasures will be made. All corrections will consist of a single line-out deletion, followed by the sampler's initials and the date. Detailed information to be recorded in the logbook or on the forms will include:

- XRF measurements for lead, zinc, and cadmium taken at individual sampling points, as well as mean XRF measurements calculated for stations
- Date and time of sample collection or XRF measurement
- Sample number (as described in previous section)
- Cross-references of numbers for duplicate samples
- Location of sample, including station name, distance from the associated port facility, GPS coordinates, and a sketch of the transect in relation to the associated port feature
- Sample type (i.e., surface soil, tundra soil, XRF)
- Sample material description
- Unique sample tag number
- Date and time of equipment calibration
- Description of the sample, moisture content of soil (dry, moist, or wet)
- Weather conditions
- Description of any deviation from the SAP (as applicable)
- Personnel conducting the activity.

Any other pertinent data or observations identified during sampling will also be recorded. Quality assurance and quality control documentation, including sample labels and chain-of-custody forms, will be completed. Samples will be delivered to the offsite analytical laboratory using standard chain-of-custody procedures.

Analytical Methods

Surface soil metals concentrations will be measured in the field by XRF analysis following EPA Method 6200. Surface soil, tundra soil, and core samples that are submitted to the offsite laboratory will be tested for total lead, zinc, and cadmium. Lead, zinc, and cadmium in soil will be measured by inductively coupled plasma analysis using EPA Method 6010B. Zinc and cadmium in water will also be analyzed with Method 6010B. Lead in water will be quantified by graphite furnace atomic absorption spectrometry using EPA Method 7421. Analytical methods, detection limits, and sample volume requirements are summarized in the QAPP (Exponent 2001).

Disposal of Investigation-Derived Waste

Wastes generated during the sampling program are expected to be non-hazardous. Investigation-derived waste (IDW) generated during sampling is expected to include disposable XRF sample cups and Mylar film, decontamination water containing residual solid materials, and used personal protective equipment (e.g., gloves, paper towels). Liquid IDW generated from decontamination will be disposed of on the road surface or in the mine or port site wastewater treatment systems. Solid IDW (e.g., used personal protective equipment) will be placed in plastic garbage bags and disposed of at the Red Dog Mine or at the port solid waste collection facilities.

Field Sampling Schedule

The field effort is expected to begin in late June 2002 and should be completed within 2 to 3 weeks.

References

Corps. 2001. Pre-dredge sediment characterization DeLong Mountain Terminal Project, Red Dog, Alaska, August 2000. Draft. U.S. Army Corps of Engineers, Alaska District, Engineering Services Branch, Materials Section.

Ecology. 2002. http://www.ecy.wa.gov/programs/tcp/smu/sed_chem.htm.

Exponent. 2001. Quality assurance project plan, haul road fugitive dust study, Red Dog Mine, Alaska. Prepared for Teck Cominco Alaska Inc., Anchorage, AK. Exponent, Bellevue, WA.

RWJ. 1997. Red Dog port site monitoring program. August 1996 Final Report. Prepared for Cominco Alaska, Inc., Kotzebue, AK. RWJ Consulting.

U.S. EPA. 1997. Environmental investigations, standard operating procedure and quality assurance manual. U.S. Environmental Protection Agency, Washington, DC.

Appendix A

EPA Method 6200

METHOD 6200

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

1.0 SCOPE AND APPLICATION

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

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

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

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use sealed radioisotope sources to irradiate samples with x-rays. X-ray tubes are used to irradiate samples in the laboratory and are beginning to be incorporated into field portable instruments. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This 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 K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

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

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

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

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

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

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly

proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

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

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

3.0 DEFINITIONS

3.1 FPXRF: Field portable x-ray fluorescence.

3.2 MCA: Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS: Site specific calibration standard.

3.4 FP: Fundamental parameter.

3.5 ROI: Region of interest.

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

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

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

4.0 INTERFERENCES

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

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup, the analyte concentration measurement will be higher than if the fine particles are not

mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

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

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

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

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

The most common spectrum overlaps involve the K_{β} line of element Z-1 with the K_{α} line of element Z. This is called the K_{α}/K_{β} interference. Because the $K_{\alpha}:K_{\beta}$ intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V K_{α} and K_{β} energies are 4.95 and 5.43 keV, respectively, and the Cr K_{α} energy is 5.41 keV. The Fe K_{α} and K_{β} energies are 6.40 and 7.06 keV, respectively, and the Co K_{α} energy is 6.92 keV. The difference between the V K_{β} and Cr K_{α} energies is 20 eV, and the difference between the Fe K_{β} and the Co K_{α} energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively. The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

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

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

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

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

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method, the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r^2 often exceeding 0.95, except for barium and chromium. See Table 9 in Section 17.0). The critical factor is that the digestion procedure and analytical reference method used should meet the data quality objectives (DQOs) of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make

periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Section 9.2.

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

5.0 SAFETY

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

5.2 Radiation monitoring equipment should be used with the handling of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs should be worn in the area of most frequent exposure. The maximum permissible whole-body dose from occupational exposure is 5 Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

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

6.0 EQUIPMENT AND SUPPLIES

6.1 FPXRF Spectrometer: An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-

ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

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

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

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum required for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of accelerating voltage is governed by the anode material, since the electrons must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

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

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

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

6.1.4 Data Processing Units: The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in parts per million on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 100 to 500 sets of numerical analytical results. Most FPXRF instruments are menu-driven from software built into the units or from PCs. Once the data-storage memory of an FPXRF unit is full, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery chargers.

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

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

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

6.6 Containers: glass or plastic to store samples.

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

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

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

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

7.0 REAGENTS AND STANDARDS

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

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

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

7.2.2 Each sample should be oven-dried for 2 to 4 hours at a temperature of less than 150°C. If mercury is to be analyzed, a separate sample portion must remain undried, as heating may volatilize the mercury. When the sample is dry, all large, organic debris and nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be ground with a mortar and pestle and passed through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

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

7.3 Blank Samples: The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the method detection limits. These

samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

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

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

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

9.0 QUALITY CONTROL

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

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

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

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

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

9.3.1 The instrument blank can be silicon dioxide, a Teflon block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An

instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the method detection limits should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

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

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

9.5 Precision Measurements: The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent.

The equation for calculating RSD is as follows:

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

where:

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

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

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

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

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

10.0 CALIBRATION AND STANDARDIZATION

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

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

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

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

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

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

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

A percent difference (%D) is then calculated for each target analyte. The %D should be within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the

line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

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

where:

%D = Percent difference

C_k = Certified concentration of standard sample

C_s = Measured concentration of standard sample

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

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

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

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

10.3 Empirical Calibration: An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Section 7.2; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards

by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is required. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

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

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

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

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

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

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

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

11.0 PROCEDURE

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

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

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

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

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

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

12.0 DATA ANALYSIS AND CALCULATIONS

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

13.0 METHOD PERFORMANCE

13.1 This section discusses four performance factors, field-based method detection limits, precision, accuracy, and comparability to EPA-approved methods. The numbers presented in Tables 4 through 9 were generated from data obtained from six FPXRF instruments. The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States.

The soil samples contained several of the target analytes at concentrations ranging from nondetect to tens of thousands of mg/kg.

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

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

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

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

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

13.5 Precision Measurements: The precision data is presented in Table 5. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from nondetects to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from in situ (no preparation) to dried and ground in a

sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

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

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

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

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

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

Table 8 provides a more detailed summary of accuracy data for one FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. Table 8 shows the certified value, measured

value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

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

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

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

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

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

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

Section 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time required to dry and grind the sample for small improvements in comparability.

Homogenization requires 3 to 5 minutes. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 minutes per sample. Lastly, when grinding and sieving is conducted, time must be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

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

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

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

14.0 POLLUTION PREVENTION

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

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

1. Metorex. X-MET 920 User's Manual.

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

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

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

**TABLE 1
INTERFERENCE FREE DETECTION LIMITS**

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

Source: References 1, 2, and 3

**TABLE 2
SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS**

Source	Activity (mCi)	Half-Life (Years)	Excitation Energy (keV)	Elemental Analysis Range	
Fe-55	20-50	2.7	5.9	Sulfur to Chromium Molybdenum to Barium	K Lines L Lines
Cd-109	5-30	1.3	22.1 and 87.9	Calcium to Rhodium Tantalum to Lead Barium to Uranium	K Lines K Lines L Lines
Am-241	5-30	458	26.4 and 59.6	Copper to Thulium Tungsten to Uranium	K Lines L Lines
Cm-244	60-100	17.8	14.2	Titanium to Selenium Lanthanum to Lead	K Lines L Lines

Source: Reference 1, 2, and 3

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

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

Source: Reference 4

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

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

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

Source: Reference 4

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

NR Not reported.

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

**TABLE 5
PRECISION**

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

Source: Reference 4

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

NR Not reported.

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

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

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

Source: Reference 4

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

ND Not detected.

NR Not reported.

**TABLE 7
ACCURACY**

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

Source: Reference 4

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

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

Standard Reference Material	Arsenic			Barium			Copper			Lead			Zinc		
	Cert. Conc.	Meas. Conc.	%Rec.	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: Reference 4

- ^a All concentrations in milligrams per kilogram.
- %Rec. Percent recovery.
- ND Not detected.
- NA Not applicable.
- No data.

**TABLE 9
REGRESSION PARAMETERS FOR COMPARABILITY¹**

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

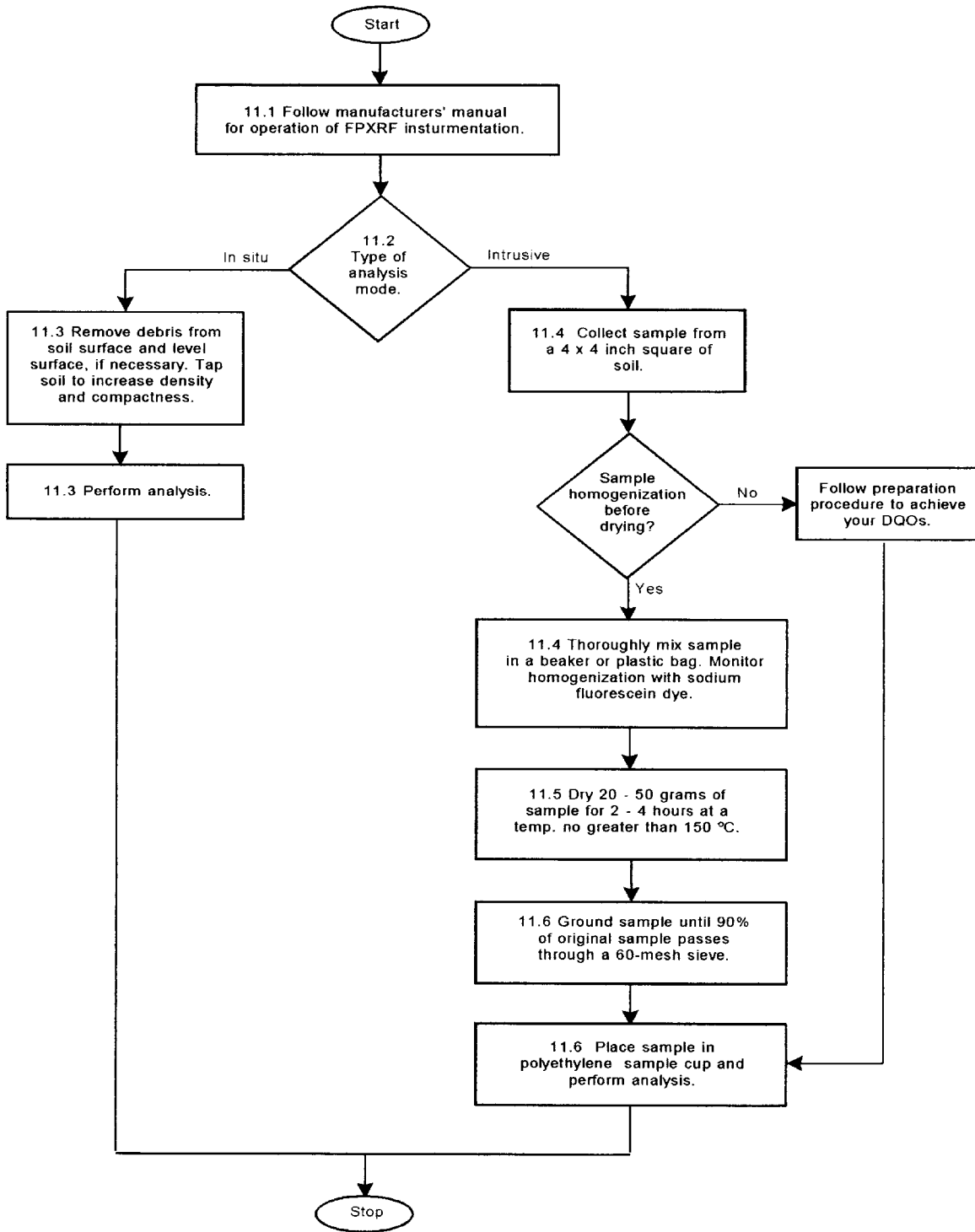
	Lead				Zinc				Chromium			
	n	r ²	Int.	Slope	n	r ²	Int.	Slope	n	r ²	Int.	Slope
All Data	1205	0.92	1.66	0.95	1103	0.89	1.86	0.95	280	0.70	64.6	0.42
Soil 1	357	0.94	1.41	0.96	329	0.93	1.78	0.93	—	—	—	—
Soil 2	451	0.93	1.62	0.97	423	0.85	2.57	0.90	—	—	—	—
Soil 3	397	0.90	2.40	0.90	351	0.90	1.70	0.98	186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

Source: Reference 4

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

METHOD 6200

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



Appendix B

Portable XRF Operator Qualifications and Training

Portable XRF Operator Qualifications and Training

Kerry Adler	AAPG Certified Professional Geologist (10364) Wyoming Professional Geologist (PG-3293)
Education:	B.S., University of Alaska—Fairbanks, 1986
Experience:	Professional geologist working in mineral exploration for more than 20 years. Operated XRF survey at Red Dog Mine, September 2001. Operated XRF survey on North Slope (SAG 1, SAG 2, Kuparuk River surveys) for CH2MHill.
XRF Training:	Niton Certified Operator, September 2001 (#A1110150427). To be re-trained at Red Dog Mine site by Niton representative May 22–23, 2002.
James Devin Harbke	Geologist
Education:	B.S., University of Alaska—Anchorage, 2002
Experience:	Field geologist working in minerals exploration for two summers on geochemical sampling, geophysical, and GIS projects. Operated XRF survey at Red Dog Mine, September 2001.
XRF Training:	Niton Certified Operator, September 2001 (#A1110150688).
John Robinson	Washington State license pending
Education:	B.S., Western Illinois University, 1975 M.S., Eastern Washington University, 1991
Experience:	Professional geologist working in mineral exploration for more than 25 years, mainly in Alaska and western United States.
XRF Training:	To be trained at Niton (short course), Eagle River, June 7, 2002.
Kent Turner	Washington State Licensed Geologist (License #473)
Education:	B.S., Yale University, 1977 M.S., University of Arizona, 1983
Experience:	Professional geologist working in mineral exploration for more than 25 years. Responsibilities include design, implementation, and interpretation of geochemical surveys throughout the United States, including Alaska.
XRF Training:	To be trained at the Red Dog Mine site by Niton representative May 22–23, 2002.

Appendix C

Standard Operating Procedure

SOP 2 SAMPLE PACKAGING AND SHIPPING

Specific requirements for sample packaging and shipping must be followed to ensure the proper transfer and documentation of environmental samples collected during field operations. Procedures for the careful and consistent transfer of samples from the field to the laboratory are outlined herein.

EQUIPMENT REQUIRED

Specific equipment or supplies necessary to properly pack and ship environmental samples include the following:

- Sealable airtight bags
- Plastic garbage bags
- Coolers
- Ice packs in doubled, sealable bags
- Bubble wrap
- Fiber reinforced packing tape
- Scissors
- Chain-of-custody seals
- Airbills for overnight shipment
- Chain-of-custody record/sample analysis request forms.

PROCEDURE

The following steps should be followed to ensure the proper transfer of samples from the field to the laboratories:

1. Appropriately document all samples using proper logbooks and chain-of-custody record/sample analysis request forms (example provided in Attachment 2-1).

2. Make sure all applicable laboratory quality control sample designations have been made on the chain-of-custody record/sample analysis request forms. Samples that will be archived for future possible analysis should be clearly identified on the chain-of-custody record/sample analysis request form. Such samples should also be labeled on the chain-of-custody record/sample analysis request form as “Do Not Analyze: Hold and archive for possible future analysis” as some laboratories interpret “archive” to mean continue holding the residual sample after analysis.
3. Notify the laboratory contact and the project QA/QC coordinator that samples will be shipped and the estimated arrival time. Send copies of all chain-of-custody record/sample analysis request forms to the QA/QC coordinator.
4. Samples will be placed in secure onsite storage or remain in the possession of the sampling personnel before shipment. Any temporary sample storage areas will be locked and secured to maintain sample integrity and chain-of-custody requirements.
5. Clean the outside of all dirty sample containers to remove any residual material that may lead to cross-contamination.
6. Check sample containers against the chain-of-custody record/sample analysis request form to ensure all samples intended for shipment are accounted for.
7. Choose the appropriate size cooler (or coolers) and line with bubble wrap.
8. Fill the cooler with the samples, separating glass containers with bubble wrap. If the samples have a required storage temperature, add enough ice or Blue Ice[®] to keep the samples refrigerated during overnight shipping (i.e., 4°C). Always over-estimate the amount of ice that you think will be required. Ice should be enclosed in a sealable plastic bag and then placed in a second sealable plastic bag to prevent leakage. Avoid separating the samples from the ice with excess bubble wrap because it will insulate the containers from the ice. After all samples and ice have been added to the cooler, use bubble wrap to fill any empty space to keep the samples from shifting during transport.
9. If temperature blanks have been provided by the testing laboratory, include one temperature blank in each sample cooler.
10. After the cooler is sufficiently packed to prevent shifting of the containers, close the lid and seal it shut with fiber-reinforced packing tape. If the cooler has a drain at the bottom, it should be taped shut in the same manner.
11. Fill out the chain-of-custody/sample analysis request form and retain the back copy of the form for the project records before sealing the cooler. Store the signed chain-of-custody record/sample analysis request forms in a sealable

bag and tape them to the inside of the cooler lid. For a shipment containing multiple coolers, indicate on the outside of this cooler “Chain-of-Custody Inside.”

12. As security against unauthorized handling of the samples, apply one or two chain-of-custody seals across the opening of the cooler lid (example provided in Attachment 2-1). Be sure the seals are properly affixed to the cooler so they are not removed during shipment.
13. Label the cooler with destination and return addresses, and add other appropriate stickers, such as “This End Up,” “Fragile,” and “Handle With Care.”
14. If an overnight courier is used, fill out the airbill as required and fasten it to the top of the cooler. The identification number sticker should be taped to the lid, because tracking problems can occur if a sticker is removed during shipment.

ATTACHMENT 2-1

**Example Chain-of-Custody
Record/Sample Analysis
Request Form, and Label and
Custody Seal**

Exponent®
OFFICIAL SAMPLE SEAL

SAMPLE NO.

DATE

SIGNATURE

PRINT NAME AND TITLE

Exponent®

SAMPLE NO.

SITE NAME

DATE

TIME

SAMPLER

PRESERVATIVE

TAG NO. **25101**