COVERSHEET
STANDARD OPERATING PROCEDURE

Operation Title: **PROTOCOL FOR COLLECTING DATA USING AN INNOV-X FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETER FOR CERTAIN METALS IN SOLID MEDIA**

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Standard Operating Procedure: **DRWM-DR-025**
Revision: **01**
Date: **February 20, 2009**
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Five Year Review No Changes Needed:

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1.0 PURPOSE

The purpose of this document is to describe the Maine Department of Environmental Protection, Bureau of Remediation and Waste Management, Division of Remediation's (MEDEP/DR) procedure for collecting data using a Innov-X portable x-ray fluorescence spectrometer (XRF) for certain metals in solid media, paint and dust wipe samples.

2.0 APPLICABILITY

MEDEP/DR is responsible for the investigation and subsequent remediation of hazardous substance, petroleum, and landfill Sites throughout Maine. Part of the investigation of these sites is analysis of samples for metals; the XRF is a useful tool in providing this analysis. This SOP applies to all staff that may use the XRF.

3.0 RESPONSIBILITIES

All MEDEP/DR Staff must follow this procedure when using the Innov-X XRF. All managers and supervisors within MEDEP/DR are responsible for ensuring that their staff are familiar with and adhere to this procedure. *Additionally, before any person is allowed to use the Innov-Xx XRF they* ***MUST:*** *have completed a radiation training course (proof of completion must be submitted to the DR Radiation Safety Officer (RSO)), wear a radiation dosimeter badge and have 8 hours of supervised field use with the instrument by approved Division of Remediation staff.* Safety procedures are described in detail in DR SOP #24 Safety Protocol for Use of the Innov-X X-Ray Fluorescence Metals Analyzer.

A current list of qualified supervisors and operators will be maintained by the DR RSO.

4.0 INTRODUCTION

This standard operating procedure (SOP) is designed to be a guideline for data collection with Innov-X XRF for solid media (e.g. soil, sediment and sludge), lead in painted surfaces and dust wipe samples. This is a field screening method used for: profiling an area, locating sources of contamination, determining the horizontal or vertical extent of contamination or collecting preliminary data that will be used to design a sampling plan. Samples can be analyzed either in-situ methods or by intrusive sample preparation methods. This SOP will outline collecting data using both methods.

5.0 PREPARATION AND GENERAL INFORMATION

5.1 PREPARATION

Prior to conducting any sampling event, a sampling plan should be developed (see SOP DR#014 - Development of a Sampling and Analysis Plan). Clean containers must be used for each sampling event unless in-situ sampling is to be performed.

An evaluation of the site and the elements of concern should be made prior to using the XRF on a site. Then determine if the XRF can analyze for the elements of concern and if the detection limits are acceptable to meet the Data Quality Objectives for the project.

Before sampling, a decision must be made whether to test the material:
- in-situ (in-place),
- as bagged samples (or for sludge, in cups) with a minimum of preparation, or
- in an XRF cup after preparation as described in Section 5.4.

If the primary objective of the sampling event is to determine whether an element is present (rather than accurately measuring how much is present), in-situ or bagged samples are the quickest, simplest way to proceed. (Note: Preparing a sample by drying, milling and sieving will yield greater accuracy.) Even if the objective is to collect samples and prepare them prior to analysis, preliminary direct measurements can help to survey the site.

5.2 EQUIPMENT

Equipment required for this SOP may include:

-- **XR**F – Innov-X X-Ray Fluorescence Spectrum Analyzer
  a) XRF
  b) Batteries and charger
  c) standardization clip
  d) Sample test stand
  e) in-situ sample test stand
  f) standards
  g) Grinder
  h) Mortar and pestle
  i) various size sieves

-- **Sampling implements** - This includes shovels, Geoprobe® soil boring system, dredges, etc, as outlined in the site specific sampling plan. Please refer to the following MEDEP/DR SOPs for using this equipment:
  -- DR#004 - Sampling Surface Water and Sediment
  -- DR#006 - Soil Sampling
  -- DR#007 - Soil Sampling with a Geoprobe Large Bore Sampler

-- **Sample containers** – Whirl pack bags, zipper locking bags or sample cups.
-- **Radiation dosimeter** – must be worn by any department staff using the XRF.

5.3 GENERAL INFORMATION

5.3.1 Radiation Sources

The Innov-X XRF does not contain a radioactive source, which would constantly emit ionizing radiation. The Innov-X has an x-ray tube which can only emit ionizing radiation when the instrument is powered. The instrument will not power the x-ray tube without the battery or handheld computer installed.

5.3.2 Radiation License and Training Requirements

The Innov-X XRF is registered with the Department of Human Services. Only staff who have completed radiation training and are issued a radiation dosimeter badge may use the XRF. Additionally, staff using the XRF must have 8 hours of supervised field use by approved DR Oil and Hazardous Materials Specialists (OHMS).

5.3.3 Detection Limits

An element will only be shown as detected by the XRF if the measured concentration of the sample is at least three times the standard deviation of the measurement. This detection limit will depend on the composition of the sample.

Detection limits depend on several factors: the analyte of interest, times the sample is irradiated, physical matrix effects, chemical matrix effects, and interelement spectral interferences. For more of an explanation of detection limits see Attachment A "EPA Method 6200". Detected elements are displayed as in the Measurement screen. Non-detected elements are shown as **< xx**, where **xx** is the detection limit for that sample. The detection limit for each element is calculated from each sample.

5.3.4 Interferences

Physical matrix interferences result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition.

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.

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.

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.

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.

5.3.5 Precision

The measurement precision for each element displayed appears to the right of the measured concentration, under the heading "**+-**". The **precision** of each measurement is three times the standard deviation.

5.3.6 Maintenance

If there are any problems with how the XRF is working, stop using the instrument and report the problem to the DR's SASS. **Do not attempt to fix the XRF yourself.** Opening the instrument may expose the user to the radiation and will void the warrantee.

5.4 GENERAL PROCEDURE FOR OPERATING THE INNOV-X XRF

Refer to the attached Innov-X User Manual for additional information and figures showing the features of the instrument (Attachment B).

5.4.1 Place a battery in the unit and install the iPAQ. Turn on both the iPAQ (top left hand side) and the XRF (back of the unit).

5.4.2 Make sure the date and time are set correctly on the iPAQ. Data is stored on the instrument by date.

5.4.3 On the iPAQ drop down menu, located at the top left hand side of the screen, choose Innov-X. Note the red light on the end of the instrument will be on when the instrument is on and ready for use. It will flash once the trigger is pulled which indicates the instrument is emitting radiation.

5.4.4 Choose the test mode (soil, paint or dust wipe) from the menu.

5.4.5 The instrument will require you to perform the standardization test at this point. The instrument will not operate without passing this test. Place the standardization clip securely over the sample window, and tap the instruction box on the screen. A small red light on the end of the XRF will begin to flash. This indicates the instrument is operating and emitting radiation. This test will take approximately 1 minute. ***KEEP ALL YOUR BODY PARTS AWAY FROM THE END OF THE INSTRUMENT. MAKE SURE THE INSTRUMENT IS NOT POINTED AT ANYONE AT ANYTIME.*** **All reasonable measures, including labeling, and the concepts of time, distance and shielding should be implemented to limit radiation exposure to as low as reasonably achievable (ALARA).**

Once the standardization is complete, the results will be shown on the screen. If the resolution result is within tolerance limits proceed to the next step. Otherwise run the standardization test again. If the test fails again, turn off the instrument and try again. If the instrument fails a third time you will be prompted to perform a soft restart on the iPAQ. If this fails replace the battery and try again. If you still do not pass call Innov-X customer support (781-938-5005).

5.4.6 Once the instrument has passed the standardization you are ready to begin testing samples.

5.4.7 A padlock icon is also shown on the bottom of the screen. This indicates if the software has been locked or is ready to test. The software will automatically lock when the

instrument has not been used for several minutes. This will prevent anyone from inadvertently activating the instrument. To unlock the software, tap on the icon.

5.4.8 If you will be sampling in the soil mode see section 5.0 Soil Sampling and Analysis Procedure below.

6.0 SOIL SAMPLING AND ANALYSIS PROCEDURE

6.1 SOIL ANALYSIS MODEL

6.1.1 After completing the procedure described in section 5.4 there are two buttons shown on the bottom of the touch screen "Start" and "Info". Tap on the Info button to enter information specific to the samples you are analyzing. In soil mode there are preset options such as Operator, Sample method, Sample Number, Sample Depth and Comment. These can be customized to projects when necessary. Fill in the information for the sample before analysis. The analysis will be stored with this information. You need to change the information prior to each sample that is run.

6.1.2 The bottom menu on the screen shows 4 options: File, Edit, View, Options and Help. From these menus the operator can change the settings for the method of analysis (Standard or LEAP) and the time interval for testing. For a complete description of these menus and how to change the settings, see Attachment B.

6.1.3 To begin testing a sample the operator either taps the start button at the bottom of the screen or pulls the trigger. *Note: the software lock may have to be disabled if the instrument has not be used for more than 5 minutes.*

6.1.4 Check the XRF's calibration with testing standards before using the XRF to analyze samples, use standards that are closest to the levels of elements that are expected onsite. Recheck the standards at least once per hour during testing and after analysis has been completed for the day.

EPA Method 6200 Field Portable X-Ray Fluorescence spectrometry for the determination of elemental concentrations in soil and sediment (Attachment C) provides additional information regarding acceptable testing procedures and may be used in place of the procedure described below.

6.2 IN-SITU ANALYSIS

6.2.1 Clear the area selected for analysis of any surface debris or vegetation. Level the area so the XRF sample window will contact the area evenly. Keep in mind that a finer and more homogeneous material will yield more accurate the results. Increased accuracy can be obtained by loosening the soil and letting it dry in the sun before testing.

6.2.2 Hold the XRF on the ground and pull the trigger or place the XRF in the in-situ test stand and pull the trigger. The stand will allow the instrument to stand on its own. If the deadman trigger lock is engaged the trigger must be held for the duration of the analysis.

If the deadman trigger has been disengaged then the analysis will run for the preset time period. The test can be stopped by pulling the trigger again.

Warning: Always treat radiation with respect. Do not put your hand or any other body part on or near the sample window of the XRF while samples are being analyzed. Never point the XRF at yourself or anyone else. ALARA objectives must be considered whenever staff are using an XRF.

The operator is responsible for controlling access in the area in which the XRF is being used. When possible use signs, barricades or caution tape to restrict access. Never allow anyone to enter within 5 feet of the x-ray path.

6.2.3 Watch the results on the display screen to decide when the test has reached the desired level of accuracy or let the analysis run for the allotted time. NOTE: if the instrument is set to run both standard and LEAP analysis consecutively and the test is ended during the standard analysis mode and before the LEAP analysis has begun your data will not be stored.

6.3 IN-SITU DEPTH PROFILING

An in-situ XRF soil test examines only the top few millimeters of soil. To profile the depth of contamination, remove a vertical slice of soil and test several samples from different depths.

6.4 ANALYSIS OF BAGGED SOLID SAMPLES

Depending on the data quality objectives for your site it may be convenient to screen samples collected in plastic bags and analyze them without preparation. Because samples are tested through a bag, test results will tend to be 5-10% lower than test results obtained from direct analysis.

6.4.1 Place 50-100 grams of sample in a clean whirl pack or zipper locking bag. Remove any large stones or debris. Keep in mind that finer and more homogeneous material will yield more accurate results. Increased accuracy can be obtained by letting the sample dry in the sun before testing. Mix the sample thoroughly by kneading the bag.

6.4.2 The accuracy of measurements will be limited by the thickness of the plastic in the bag used. 1 mil-thick polyethylene bags offer a reasonable compromise between accurate readings and bag durability.

6.4.3 Flatten the bag of soil to form a continuous uniform layer of at least 1 cm. (0.4 inch) thickness. Place the sample window flat against the bag and pull the trigger. **Do not hold bagged samples in your hand during testing.**

Warning: Always treat radiation with respect. Do not put your hand or any other body part on or near the sample window of the XRF while samples are being analyzed. Never point the XRF at yourself or anyone else. ALARA objectives must be considered whenever staff is using an XRF.

The operator is responsible for controlling access in the area in which the XRF is being used. When possible use signs, barricades or caution tape to restrict access. Never allow anyone to enter within 5 feet of the x-ray path.

6.4.3 If you are analyzing many samples at one time the easiest way to analyze samples to set up the test stand. See Attachment B for directions to set up the test stand.

6.4.4 When the XRF is in the test stand all operations are conducted from the iPAQ. The red light on top of the test stand will operate in the same way as the red light on top of the XRF. When the instrument is on and capable of emitting radiation the red light will be on constantly. When the light is flashing the instrument is emitting radiation. The instrument cannot emit radiation while the cover is open. The stand is constructed so that all radiation is absorbed by the stand, however, no one should stand behind the test stand while the XRF is being used. The deadman trigger lock cannot be used while the instrument is in the test stand.

6.4.5 Place the sample over the XRF sample window so that the sample is indirect contact with the window. Start the test from the iPAQ.

Signs must be posted restricting access to the area where the XRF is being used while in the test stand. The operator is responsible for restricting access near the XRF while it is being used. No one should be allowed within 5 feet of the x-ray path.

6.4.6 Watch the display screen results to decide when the test has reached the desired level of accuracy and stop the test through the iPAQ or the test will automatically stop when the preset time has expired. NOTE: if the instrument is set to run both standard and LEAP analysis consecutively and the test is ended during the standard analysis mode and before the LEAP analysis has begun your data will not be stored.

6.5 ANALYSIS OF PREPARED SAMPLES

Prepared sample analysis is the most accurate method for determining the concentration of elements in a solid media. Sample preparation minimizes the effects of moisture, large particle size and variations in particle size.

Following this protocol for preparing and testing samples is vital for achieving a level of accuracy comparable with laboratory results. See Attachment B for EPA's approved method for analyzing samples using and XRF (EPA 6200). MEDEP has developed the following preparation method for samples to be analyzed by an XRF.

6.5.1 Collect 50-100 grams of sample to insure that there is enough sample to be representative and unbiased after mixing, grinding, and sieving it. You must have enough sample to half fill the XRF sample cup.

6.5.2 Place the sample in a clean bowl and mix the sample thoroughly by stirring and by rotating the bowl. Gently break up any dirt clods. Don't shake the sample because the sample may become stratified by weight.

6.5.3 If the sample is moist it should be dried. To best prepare a sample for analysis the material should be dry and well homogenized. Ideally, the entire sample should be dried to constant weight, sieved to remove gravel and debris, and ground or milled to a fine powder.

The sample can be dried in several ways:

- Oven dry the sample for approximately 2 hours at 150° C., until the sample reaches a constant weight;
- air dry the sample overnight at room temperature in a shallow pan;
- gently stir and warm the sample in a pan over a hot plate or burner.

Oven, hot plate or burner drying is inappropriate when volatile compounds may be present in the sample. For example, lead present as tetraethyl lead would be driven off by the heat of drying. Some forms of mercury and arsenic are volatile. If mercury is to be analyzed the sample must be air dried.

6.5.4 Sieve the dried sample with the #10 (2mm) mesh and separate out the larger pieces (stones, organic matter, metallic objects).

6.5.5 Grind the sample with a mortar and pestle or electric grinder until the soil particles are fine and homogenous.

6.5.6 Sieve at least 10 grams of the sample through #60 (250 um) and #120 (125 um) mesh. Re-grind the unpassed material until the required fraction is able to pass. Mix the resulting sample.

6.5.7 Place the sample in a sample cup. To assemble a sample cup: *1)* place a circle of mylar film on top of an XRF sample cup. The window goes on the end of the cup with the indented ring. *2)* Secure the film with the collar. The flange inside the collar faces down and snaps into the indented ring of the cup. Inspect the installed film window for continuity and smooth, taut appearance. *3)* Set the cup, window-side down, on a flat surface. Fill it with at least three grams of the prepared sample (no more than half-full). Take care that there are no voids or layering. *4)* Placing the cup film-side down on a flat surface, tamp the sample into the cup. *5)* Fill the cup with polyester fiber stuffing to prevent sample movement. Use aquarium filter or pillow filling as stuffing. A small supply of stuffing comes with the bulk sample kit. *6)* Fasten the cap on the cup.

6.5.8 Analyze the sample with the XRF. The easiest way to analyze samples in cups is to set up the test stand. See Attachment B for directions to set up the test stand.

6.5.9 When the XRF is in the test stand all operations are conducted from the iPAQ. The red light on top of the test stand will operate in the same way as the red light on top of the XRF. When the instrument is on and capable of emitting radiation the red light will be on constantly. When the light is flashing the instrument is emitting radiation. The instrument cannot emit radiation while the cover is open. The stand is constructed so

that all radiation is absorbed by the stand, however, no one should stand behind the test stand while the XRF is being used.

6.5.10 Place the sample cup over the XRF sample window so that the cup is indirect contact with the window. Start the test from the iPAQ.

Warning: Always treat radiation with respect. Do not put your hand or any other body part on or near the sample window of the XRF while samples are being analyzed. Never point the XRF at yourself or anyone else. ALARA objectives must be considered whenever staff is using an XRF.

Signs must be posted restricting access to the area where the XRF is being used. The operator is responsible for restricting access near the XRF while it is being used. No one should be allowed within 5 feet of the x-ray path.

6.5.11 Watch the display screen results to decide when the test has reached the desired level of accuracy and stop the test through the iPAQ or the test will automatically stop when the preset time has expired. NOTE: if the instrument is set to run both standard and LEAP analysis consecutively and the test is ended during the standard analysis mode and before the LEAP analysis has begun your data will not be stored.

7.0 LEAD PAINT ANALYSIS AND PROCEDURE

7.1 LEAD PAINT ANALYSIS MODE

7.1.1 After completing the procedure described in section 4.4 there are two buttons shown on the bottom of the touch screen "Start" and "Info". Tap on the Info button to enter information specific to the samples you are analyzing. In there are preset options such as Operator, Location and Comment. These can be customized to projects when necessary. Fill in the information for the sample before analysis. The analysis will be stored with this information. You need to change the information prior to each sample that is run.

7.1.2 The bottom menu on the screen shows 4 options: File, Edit, View, Options and Help. From these menus the operator can change the settings for the method of analysis (Inspection or Fixed time). For a complete description of these menus and how to change the settings, see Attachment B.

7.1.3 Inspection mode automatically ends the test when the analyzer reaches a "Positive" or "Negative" determination with 95% confidence. This is based on a preset action level (the default is 1.0 mg/cm^2).

7.1.4 Fixed time mode always test up to the preset time (default 15 seconds). This returns actual results as opposed to the positive or negative results in the inspection mode.

7.1.5 To begin testing a sample the operator either taps the start button at the bottom of the screen or pulls the trigger. Note the software lock may have to be disabled if the instrument has not been used for more than 5 minutes.

7.1.6 Check the XRF's calibration with testing standard before using the XRF to analyze samples. Recheck the standards at least once every 4 hours during testing and after analysis has been completed for the day.

7.1.7 Hold the analyzer up to the sample to be analyzed. Make sure the sample window is as flat as possible against the sample. Start the analysis either from the iPAQ window or with the trigger. The red light on top of the instrument will flash while the analysis is performed and the instrument is emitting radiation. When at all possible use the instrument with the deadman trigger engaged. This means the operator must hold the trigger during the entire analysis. If the deadman trigger is not engaged the test can be stopped by pulling the trigger again or depending on the test mode the instrument will end the test when a positive or negative result is reached or the preset time period has elapsed.

Warning: Always treat radiation with respect. Do not put your hand or any other body part on or near the sample window of the XRF while samples are being analyzed. Never point the XRF at yourself or anyone else. ALARA objectives must be considered whenever staff are using an XRF.

The operator is responsible for controlling access in the area in which the XRF is being used. When possible use signs, barricades or caution tape to restrict access. Never allow anyone to enter within 5 feet of the x-ray path.

8.0 DUST WIPE ANALYSIS AND PROCEDURE

8.1 DUST WIPE TEST MODE

8.1.1 After completing the procedure described in section 4.4 there are two buttons shown on the bottom of the touch screen "Start" and "Info". Tap on the Info button to enter information specific to the samples you are analyzing. There are preset options such as Operator, Location and Comment to choose from. These can be customized to projects when necessary. Fill in the information for the sample before analysis. The analysis will be stored with this information. You need to change the information prior to each sample that is run.

8.1.2 The bottom menu on the screen shows 4 options: File, Edit, View, Options and Help. From these menus the operator can change the settings for the analysis (e.g. 4 or 8 tests per wipe, area of wipe (default 1ft^2.)) For a complete description of these menus and how to change the settings, see Attachment B.

8.2 SAMPLE PREPARATION

8.2.1 Conduct wipe sample according to Attachment C "Settled Dust Sampling for Lead". However, instead of packaging the wipe for analysis at a laboratory continue as follows.

8.2.2 For best results dry the wipe before analysis.

8.2.3 Fold the wipe so that it will fit into the dust wipe holder as shown in Attachment B. Center the filter in the holder and secure the holder with tape.

8.3 ANALYZING THE DUST WIPE

8.3.1 The XRF can be set to analyze the dust wipe in either 4 or 8 positions on the wipe. If 4 positions are set then they are analyzed in four quadrants of the wipe on the same side. For 8 positions, four quadrants on each side are analyzed.

8.3.2 Place the dust wipe on a flat surface and position the sample window in 1 quadrant of the filter. Pull the trigger. The red light on top of the instrument will flash during analysis indicating the instrument is emitting radiation. When the first position is complete the iPAQ will prompt for the additional readings. Reposition the XRF and tap ok on the screen. Note: If you cancel instead of saying ok the wipe measurement will be aborted and no results will be saved. If you stop the test before any position reading has been completed, no results will be saved.

Warning: <u>Always</u> treat radiation with respect. Do not put your hand or any other body part on or near the sample window of the XRF while samples are being analyzed. Never point the XRF at yourself or anyone else. ALARA objectives must be considered whenever staff are using an XRF.

The operator is responsible for controlling access in the area in which the XRF is being used. When possible use signs, barricades or caution tape to restrict access. Never allow anyone to enter within 5 feet of the x-ray path.

8.3.3 After the last reading has been completed the analyzer will open the results screen and display an average of the readings taken on the dust wipe.

<u>9.0 DOWNLOADING DATA FROM THE XRF</u>

9.1 DOWNLOADING DATA

The Innov-X XRF stores thousands of measurements plus their spectra. This can be downloaded to a computer for reporting in a spreadsheet format. From the Innov-X menu screen choose view on the bottom and then choose results. This will open the last result entered into the iPAQ. Choose "File" on the bottom of the screen them choose "export results". From this screen you can choose the date and analysis mode for the results (analytical results are saved on the iPAQ by date). After these options have been chosen, click "OK" at the bottom of the screen. The next screen allows you to enter a file name and location to save the file to. The file can then be downloaded to your desk top computer by synchronizing the iPAQ with your computer and saving the data file in an excel format. You must have the iPAQ software installed on your computer. See Attachment B for complete directions on downloading data.

Note: Downloading data does not erase readings. To make room for the next set of data, erase readings after verifying that the data was downloaded successfully.

9.2 ERASING READINGS

Once your data has been downloaded from the i-PAQ the file should be erased. From the Innov-X menu screen choose "view" then "results". This will open the last analysis saved to the iPAQ. Choose "file" at the bottom of the screen then "erase readings". You must enter the administrator password (lower case z). Choose which readings you would like to delete then click "OK". Make sure your data has successfully transferred to your desk top prior to deleting data. See Attachment B for complete directions on erasing data.

10.0 DECONTAMINATION

Decontamination of equipment will follow the MEDEP DR SOP DR#017 - "Decontamination Procedures Protocol". Additionally the following methods may be used in the field:

The mortar, pestle, and grinding mill may be cleaned with dry paper towels. Water will also clean the mortar, pestle, and the mill's container, but be sure each is absolutely dry before they are used for another sample. The mortar and pestle may be cleansed by grinding clean dry sand in the mortar. Use the short bristle brushes (included in the Bulk Testing Kit) to clean the sieves.

11.0 CHAIN OF CUSTODY

For confirmatory samples that are submitted to a fixed laboratory, procedures for chain of custody outlined in MEDEP/DR SOP DR#012 - "Chain of Custody" must be followed.

12.0 DOCUMENTATION

All sampling activities must be documented as outlined in MEDEP/DR SOP DR#013 – "Documentation of Field Activities and Development of a Trip Report". Each sample location will be given a unique sample number. This number will be entered into the XRF with the optical pen and or recorded in the field notes. If no number is entered into the XRF, the default number shown on the XRF screen for that sample will be recorded in the field notes.

13.0 QUALITY ASSURANCE/QUALITY CONTROL

13.1 QUALITY ASSURANCE SAMPLES

Depending on the DQO's for a project the following QA samples may be collected. Any QA sample analyzed will be documented in field notes or in a written report. Calculations for QA samples will also be documented and if QA samples are re analyzed the results of will be documented.

13.1.1 Energy Calibration Check

To determine whether the XRF is operating within resolution and stability tolerances, an energy calibration check should be run. Generally, this is run 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.

13.1.2 Blank Samples

Two types of blank samples should be analyzed for XRF 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.

13.1.2.1 Instrument Blank

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.

13.1.2.2 Method Blank

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.

13.1.3 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 samples used by the DR will be NIST or other SRM that contains the analytes of interest. These will 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 re-calibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

13.1.4 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. 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: RSD = (SD/Mean Concentration) x 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.

14.1.5 Confirmatory Samples

The comparability of the XRF analysis is determined by submitting XRF-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 XRF-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 XRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the XRF. They should also include samples with analyte concentrations at or near the site action levels. Acceptance criteria for comparison of field and lab samples will be 20% difference of sample results or stated in the site specific QAPP or sampling plan. If the acceptance criteria is exceeded the project manager will evaluate the results to determine if they meet the data quality objectives for the project. If the data quality objectives are not met samples will be re-run or collected again for analysis.

14.2 DEVIATIONS FROM SOPS

All deviations from the procedures outlined in this or in any other SOPs followed for XRF sampling must be documented in field notes.

15.0 REFERENCES

- Innov-X User Manual for Alpha Series XRF.
- EPA Method 6200 Field Portable X-Ray Fluorescence Spectrometry For the Determination of Elemental Concentrations in Soil and Sediment.

ATTACHMENT A

EPA Method 6200 Field Portable X-Ray Fluorescence Spectrometry For the Determination of Elemental Concentrations in Soil and Sediment.

METHOD 6200

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

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

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

1.0 SCOPE AND APPLICATION

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

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

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

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

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

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

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

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

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

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

2.0 SUMMARY OF METHOD

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

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

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

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

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than

the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.77 keV than to chromium, which has a K line energy of 5.41 keV.

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

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

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

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

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

3.0 DEFINITIONS

3.1 FPXRF -- Field portable x-ray fluorescence.

3.2 MCA -- Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS -- Site-specific calibration standards.

3.4 FP -- Fundamental parameter.

3.5 ROI -- Region of interest.

3.6 SRM -- Standard reference material; a standard containing certified amounts of metals in soil or sediment.

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

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

4.0 INTERFERENCES

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

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

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

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

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

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

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

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) K_α/lead (Pb) L_α and sulfur (S) K_α/Pb M_α. In the As/Pb case, Pb can be measured from the Pb L_β line, and As can be measured from either the As K_α or the As K_β line; in this way the interference can be corrected. If the As K_β line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As K_α line. If the As K_α line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in reporting of a "nondetect" or a "less than" value (e.g., <300 ppm) for As, regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-

atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)).

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

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

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method (see Table 8), the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r often exceeding 0.95, except for barium and chromium). The critical factor is that the digestion procedure and analytical reference method used should meet the DQOs of the project and match the method used for confirmation analysis.

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

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

5.0 SAFETY

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

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

5.2 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operator's manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals.

Licenses for radioactive materials are of two types, specifically: (1) a general license which is usually initiated by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) a specific license which is issued to named persons for the operation of radioactive instruments as required by local, state, or federal agencies. A copy of the radioactive material license (for specific licenses only) and leak tests should be present with the instrument at all times and available to local and national authorities upon request.

X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. An additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply, however, if the tube is properly positioned within the instrument, this is only a negligible risk. Any instrument (x-ray tube or radioisotope based) is capable of delivering an electric shock from the basic circuitry when the system is inappropriately opened.

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

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for

use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

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

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

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

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

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

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

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

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

6.1.4 Data processing units -- The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in ppm on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 3,000 to 5,000 sets of numerical analytical results. Most FPXRF instruments are menu-driven from software built into the

units or from PCs. Once the data–storage memory of an FPXRF unit is full or at any other time, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery and battery charger.

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

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

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

6.6 Containers -- Glass or plastic to store samples.

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

6.8 Trowels -- For smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags -- Used for collection and homogenization of soil samples.

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

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

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

7.3.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of 10 samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.3.2 Each sample should be oven-dried for 2 to 4 hr at a temperature of less than 150 °C. If mercury is to be analyzed, a separate sample portion should be dried at ambient temperature as heating may volatilize the mercury. When the sample is dry, all large, organic debris and nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be homogenized (see Sec. 7.3.3) and then a representative portion ground with a mortar and pestle or other mechanical means, prior to passing through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

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

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

7.5 Standard reference materials -- Standard reference materials (SRMs) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories. When these SRMs are unavailable, alternate standards may be used (e.g., NIST 2702).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

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

9.0 QUALITY CONTROL

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

9.2 Energy calibration check -- To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting,

which would indicate drift within the instrument. As discussed in Sec. 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (more than 10 °F).

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

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

9.3 Blank samples -- Two types of blank samples should be analyzed for FPXRF analysis, specifically, instrument blanks and method blanks.

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

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lowest level of detection or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

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

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

The equation for calculating RSD is as follows:

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

where:

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

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

9.6 The lower limits of detection should be established from actual measured performance based on spike recoveries in the matrix of concern or from acceptable method performance on a certified reference material of the appropriate matrix and within the appropriate calibration range for the application. This is considered the best estimate of the true method sensitivity as opposed to a statistical determination based on the standard deviation of

replicate analyses of a low-concentration sample. While the statistical approach demonstrates the potential data variability for a given sample matrix at one point in time, it does not represent what can be detected or most importantly the lowest concentration that can be calibrated. For this reason the sensitivity should be established as the lowest point of detection based on acceptable target analyte recovery in the desired sample matrix.

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

10.0 CALIBRATION AND STANDARDIZATION

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

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

- No previously collected site-specific samples are necessary, although site-specific samples with confirmed and validated analytical results for all elements present could be used.

- Cost is reduced because fewer confirmatory laboratory results or calibration standards are necessary.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Sec. 7.3. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

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

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

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

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

The equation to calibrate %D is as follows:

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

where:

%D = Percent difference
C_k = Certified concentration of standard sample
C_s = Measured concentration of standard sample

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

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

count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

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

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

10.3 Empirical calibration -- An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Sec. 7.3; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is necessary. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

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

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

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

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

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

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

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

11.0 PROCEDURE

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

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

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

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

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 g) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hr in the convection or toaster oven at a temperature not greater than 150 °C. Samples may also be air dried under ambient temperature conditions using a 10- to 20-g portion. Regardless of what drying mechanism is used, the drying process is considered complete when a constant sample weight can be obtained. Care should be taken to avoid sample cross-contamination and these measures can be evaluated by including an appropriate method blank sample along with any sample preparation process.

CAUTION: Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

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

12.0 DATA ANALYSIS AND CALCULATIONS

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

13.0 METHOD PERFORMANCE

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

13.2 The sections to follow discuss three performance evaluation factors; namely, precision, accuracy, and comparability. The example data presented in Tables 4 through 8 were generated from results obtained from six FPXRF instruments (see Sec. 13.3). The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from "nondetect" to tens of thousands of mg/kg. These data are provided for guidance purposes only.

13.3 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a HgI_2 detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode

detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.4 All example data presented in Tables 4 through 8 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source. The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

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

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 4 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the lower limit of detection for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 4. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the lower limit of detection so that an RSD value calculated at 5 to 10 times this limit was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 5 shows these results. These data are provided for guidance purposes only. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the lower limit of detection for the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the in situ homogenized samples. The FPXRF analyzer conducted five replicate measurements of the in situ field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 5 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square,

measurements of different soil samples were actually taking place within the square. Table 5 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five instead of ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy measurements -- Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 6 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 6 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 6. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 6.

Table 7 provides a more detailed summary of accuracy data for one particular FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. These data are provided for guidance purposes only. Table 7 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

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

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 8. Similar trends in the data were seen for all instruments. These data are provided for guidance purposes only.

Table 8 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. These data are provided for guidance purposes only. The soil types are as follows: soil 1--sand; soil 2--loam; and soil 3--silty clay. The preparation methods are as follows: preparation 1--in situ in the field; preparation 2--intrusive, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not

ground; and preparation 4–intrusive, with sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

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

Table 8 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 8 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

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

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

13.8.1 A. D. Hewitt, "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_α Peak Normalization Analysis," American Environmental Laboratory, pp 24-32, 1994.

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

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

14.0 POLLUTION PREVENTION

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

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

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

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

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

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

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

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

TABLE 1

EXAMPLE INTERFERENCE FREE LOWER LIMITS OF DETECTION

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

Source: Refs. 1, 2, and 3
These data are provided for guidance purposes only.

TABLE 2

SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS

Source	Activity (mCi)	Half-Life (Years)	Excitation Energy (keV)	Elemental Analysis Range	
Fe-55	20-50	2.7	5.9	Sulfur to Chromium 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	432	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: Refs. 1, 2, and 3

TABLE 3

SUMMARY OF X-RAY TUBE SOURCE CHARACTERISTICS

Anode Material	Recommended Voltage Range (kV)	K-alpha Emission (keV)	Elemental Analysis Range	
Cu	18-22	8.04	Potassium to Cobalt 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: Ref. 4

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

TABLE 4

EXAMPLE PRECISION VALUES

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

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

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

NR Not reported.

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

TABLE 5

EXAMPLES OF PRECISION AS AFFECTED BY SAMPLE PREPARATION

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

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

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

ND Not detected.

NR Not reported.

TABLE 6

EXAMPLE ACCURACY VALUES

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

Source: Ref. 4. These data are provided for guidance purposes only.
n: Number of samples that contained a certified value for the analyte and produced a detectable concentration from the FPXRF instrument.
SD: Standard deviation; NA: Not applicable; only two data points, therefore, a SD was not calculated.
%Rec.: Percent recovery.
-- No data.

TABLE 7

EXAMPLE ACCURACY FOR TN 9000[a]

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

Source: Ref. 4. These data are provided for guidance purposes only.
[a] All concentrations in milligrams per kilogram.
%Rec.: Percent recovery; ND: Not detected; NA: Not applicable.
-- No data.

TABLE 8

EXAMPLE REGRESSION PARAMETERS FOR COMPARABILITY[1]

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

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

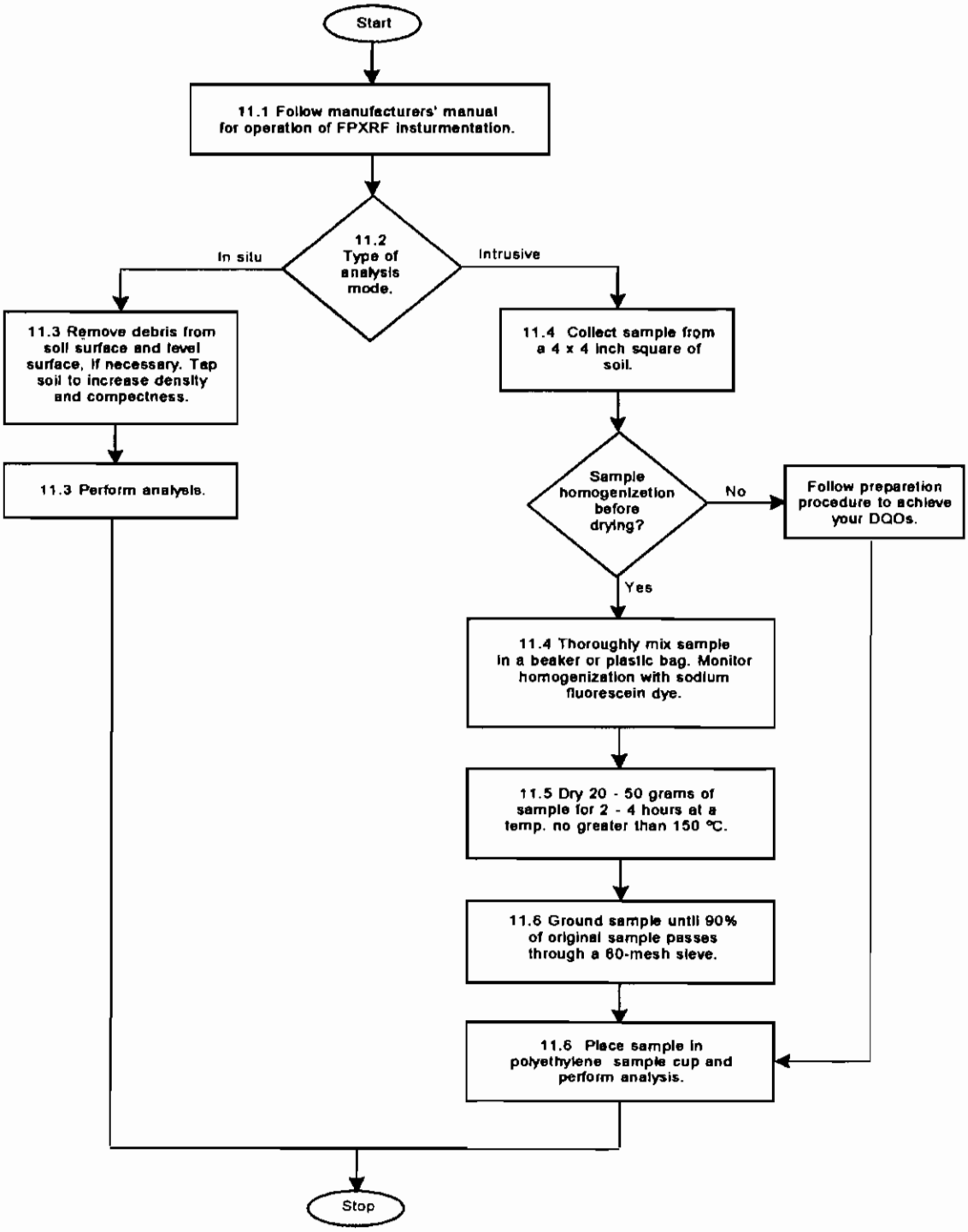
Source: Ref. 4. These data are provided for guidance purposes only.

[1] Log-transformed data

n: Number of data points; r^2: Coefficient of determination; Int.: Y-intercept

— No applicable data

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



ATTACHMENT B

INNOV-X USER Manual for Alpha Series XRF

THE USER MANUAL CAN BE FOUND WITH THE INSTRUMENT IN ITS CASE, OR ON LINE AT INNOV-X.COM

ATTACHMENT C

MEDEP SOP FOR COLLECTION OF DUST WIPE SAMPLES

Part #7	**Section #3**	**Data Quality Assurance**
Description:	Settled Dust Sampling for Lead	
Type:	Lead Sampling	
Date Issued:	April 20, 2004	

1.0 Scope

1.1 This section establishes sampling procedures and protocols for collecting settled dust samples.

2.0 Policy

2.1 Unit staff shall use these procedures for collecting paint chip samples of building components suspected of containing lead-based paint. Unit staff may deviate from these procedures with warranted justification and shall note deviations on the inspection report.

3.0 General Information

Wipe Sampling for Settled Lead-Contaminated Dust. Wipe samples for settled leaded dust can be collected from floors (both carpeted and uncarpeted), interior and sash/sill contact areas, and other reasonably smooth surfaces. Wherever possible, hard surfaces should be sampled. Wipe media should be sufficiently durable so that it is not easily torn, but can be easily digested in the laboratory. Recovery rates of between 80-120% of the true value should be obtained for all media used for wipe sampling. Blank media should contain no more than 25 ug/wipe (the detection limit using Flame Atomic Absorption)

4.0 Sampling Tools and Materials

4.1 **Type of disposable wipe:** Any wipe material that meets the following criteria may be used:

Contains low background lead levels,
Is a single thickness,
Is durable and does not tear easily (do not use Whatman™ filters),
Does not contain aloe,
Can be digested in the laboratory,
Has been shown to yield 80-120% recovery rates from samples spiked with leaded dust (not lead in solution), and
Must remain moist during the wipe sampling process (wipes containing alcohol may be used as long as they do not dry out).

4.2 **Non-sterilized non-powdered disposable gloves.** Disposable gloves are required to prevent cross-sample contamination from hands.

4.3 Non-sterilized polyethylene centrifuge tubes (50 ml size) or equivalent hard-shell container that can be rinsed quantitatively in the laboratory.

4.4 Dust sample collection forms.

4.5 Camera & film to document exact locations (Optional).

4.6 **Template Options.** Masking tape or hard, smooth, reusable templates may be used to define the area to be wiped. Periodic wipe samples should be taken from the templates to determine if the template is contaminated. Disposal templates are also permitted so long as they are not used for more than a single surface. Templates must be larger than $0.1ft^2$, but smaller than $2ft^2$. Templates for floors are typically $1ft^2$. Templates are usually not used for windows due to the variability in size and shape (use masking tape instead).

Note:	Masking tape may damage the painted surface.

4.7 Container labels or permanent marker.

4.8 Trash bag or other receptacle (do not use pockets or trash containers at the residence).

4.9 Rack, bag, or box to carry tubes (optional).

4.10 Measuring tape.

4.11 Disposable shoe coverings (optional).

5.0 Single Surface Wipe Sampling Procedure

5.1 Outline Wipe Area:

5.1.1 Floors: Identify the area to be wiped. Do not walk on or touch the surface to be sampled (the wipe area). Apply masking tape to perimeter of the wipe area to form a square or rectangle of about one square foot. No measurement is required at this time. The tape should be positioned in a straight line and corners should be nominally perpendicular. When putting down any template, do not touch the interior wipe area.

5.1.2 Window sills and other rectangular surfaces: Identify the area to be wiped. Do not touch the wipe area. Apply two strips of masking tape across the sill to define a wipe area at least 0.1 square foot in size (approx. 4 inches x 4 inches).

5.2 **Preliminary inspection of the disposable wipes.** Inspect the wipes to determine if they are moist. If they have dried out, do not use them. When using

a container that dispenses wipes through a "pop-up" lid, the first wipe in the dispenser at the beginning of the day should be thrown away. The first wipe may be contaminated by the lid and is likely to have dried to some extent. Rotate the container prior to each use to ensure liquid inside the container contacts the wipes.

5.3 **Gloves.** Don a disposable glove on one hand; use a new glove for each sample collected. If two hands are necessary to handle the sample, use new gloves, one for each hand. It is not necessary to wipe the gloved hand before sampling.

5.4 **Collection of sample.** Place the wipe at one corner of the surface to be wiped with wipe fully opened and flat on the surface. For square sample areas, complete a first wipe pass side-to-side as follows. With the fingers together, grasp the wipe between the thumb and the palm. Press down firmly, but not excessively with both the palm and fingers (Do not use only the fingertips or the heel of the hand to hold down the wipe, because there will not be complete contact with the surface and some dust may be missed.) Do not touch the surface with the thumb. Proceed to wipe side-to-side with as many "S"-like motions as are necessary to completely cover the entire wipe area. Exerting excessive pressure on the wipe will cause it to curl. Exerting too little pressure will result in poor collection of dust. Attempt to remove all visible dust from the wipe area.

5.4.1 Next, fold the wipe in half with the contaminated side facing inward. (The wipe can be straightened out by laying it on the wipe area, contaminated side up, and folding it over.) Once folded, place in the top corner of the wipe area and press down firmly with the palm and fingers. Complete a second wipe pass moving from top-to-bottom and wiping the area with "S"-like motions. Attempt to remove all visible dust. Do not touch the contaminated side of the wipe with the hand or fingers. Do not shake the wipe in an attempt to straighten it out, since dust may be lost during shaking.

5.5 For rectangular sample areas: two side-to-side passes must be made over half of this surface, the second pass with the wipe folded so that the contaminated side faces inward. For a window sill, do not attempt to wipe the irregular edges presented by the contour of the window channel. Avoid touching other portions of the window with the wipe. If there are paint chips or gross debris in the window sill, attempt to include as much of it as possible on the wipe. If all of the material cannot be picked up with one wipe, field personnel may use a second wipe at their discretion and insert it in the same container. Consult with the analytical laboratory to determine if they can perform analysis of two wipes as a single sample. When performing single-surface sampling, do not use more than two single surface wipes for each container. If heavily dust-laden, a smaller area should be wiped. It is not necessary to wipe the entire window well but do not wipe less than 0.10 ft^2 (approx. 4" x 4").

6.0 **Packaging the Wipe.** After wiping, fold the wipe with the contaminated side facing inward again, and insert aseptically (without touching anything else) into the centrifuge tube or other hard-shelled container. If gross debris is present, such as paint chips in a

window well, make every attempt to include as much of the debris as possible in the wipe.

6.1 **Seal the tube and label with the appropriate identifier.** Record the laboratory submittal sample number on the field sampling form.

7.0 **Area Measurement.** After sampling, measure the surface area wiped to the nearest eighth of an inch using a tape measure or a ruler. The size of the area wiped must be at least 0.10 ft^2 in order to obtain an adequate limit of quantitation. No more than 2 square feet should be wiped with the same wipe or else the wipe may fall apart. Record specific measurements for each area wiped on the field sampling form.

8.0 **Form completion.** Fill out the appropriate field sampling forms completely. Collect and maintain any field notes regarding type of wipe used, lot number, collection protocol, etc.

9.0 **Trash Disposal.** After sampling, remove the masking tape and throw it away in a trash bag. Remove the glove; put all contaminated gloves and sampling debris used for the sampling period into a trash bag. Remove the trash bag when leaving the dwelling. Do not throw away gloves or wipes inside the dwelling unit where they could be accessible to young children, resulting in a suffocation hazard.

10.0 **Blank Preparation.** After sampling the final dwelling unit of the day, but before decontamination, field blank samples should be obtained. Analysis of the field blank samples determines if the sample media is contaminated. Each field blank should be labeled with a unique identifier similar to the others but that identifies the sample as a field blank.

10.1 Blank wipes are collected by removing a wipe from the container with a new glove, shaking the wipe open, refolding as it occurs during the actual sampling procedure, and then inserting it into the centrifuge tube without touching any surface or other object. One blank wipe is collected for each dwelling unit sampled or, if more than one dwelling unit is sampled per day, one blank for every 50 field samples, whichever is less. Also, collect one blank for every lot used. Record the lot number.

11.0 **Lead Inspector Decontamination.** After sampling, wash hands thoroughly with plenty of soap and water. A bathroom in the dwelling unit may be used for this purpose, with the owner's or resident's permission. If there is not running water in the dwelling unit, use wet wipes to clean the hands. During sampling, inspector must not eat, drink, smoke, or otherwise cause hand to mouth contact.

12.0. **Laboratory Submittal.** Submittal Form Preparation. The sample numbers on the sample container must be the same as those on the field sampling form and must also be used on the laboratory submittal form. Confirm that all samples recorded are in fact present on the laboratory submittal form. Chain of custody requirements should be followed.

13.0. **Laboratory Analytical Procedure.** Laboratories analyzing dust samples must participate in the Environmental Lead Laboratory Proficiency Testing Program or equivalent and be an EPA-NLLAP Accredited Laboratory and certified for environmental

lead analysis in accordance with the Maine Department of Human Services Chapter 263, "Maine Comprehensive and Limited Environmental Laboratory Certification Rules". The Maine Health and Environmental Testing Laboratory (HETL) currently meets these standards.