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REGION I, EPA-NEW ENGLAND

STANDARD OPERATING PROCEDURE FOR ELEMENTAL ANALYSIS USING THE X-MET 920 FIELD X-RAY FLUORESCENCE ANALYZER



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Standard Operating Procedure for Elemental Analysis
Using the X-MET 920 Field X-ray Fluorescence Analyzer

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Standard Operating Procedure for Elemental Analysis Using the X-MET 920 Field X-ray Fluorescence Analyzer

1.0 Scope and Application

The following Standard Operating Procedure (SOP) describes the procedures used to operate the EPA Region I X-MET 920 portable X-ray Fluorescence (XRF) analyzer for the analysis of metals in soils and sediments. The SOP describes two methods of calibration and analysis, quantitative analysis and semi-quantitative screening, to be used depending on the data quality objectives (DQOs) of the project. For example, projects involving comprehensive extent of contamination studies or site clean-up to a defined action level will require the quantitative technique of analysis, while the semi-quantitative screening technique would be more appropriate for site investigation work or initial delineation of site hot spots.

Whichever calibration technique is chosen, the analyst should always strive to prioritize the number of elements under investigation (typically 1 - 3 elements are recommended). This strategy will not only simplify instrument calibration, but will minimize the time, effort, and cost of the project. If the precision, accuracy, and detection limits of the field XRF analyzer meet the project DQOs, then XRF is a fast, powerful, cost effective technology for site characterization.

This SOP should be used in conjunction with the X-MET 920 Reference Manual supplied by the instrument manufacturer.

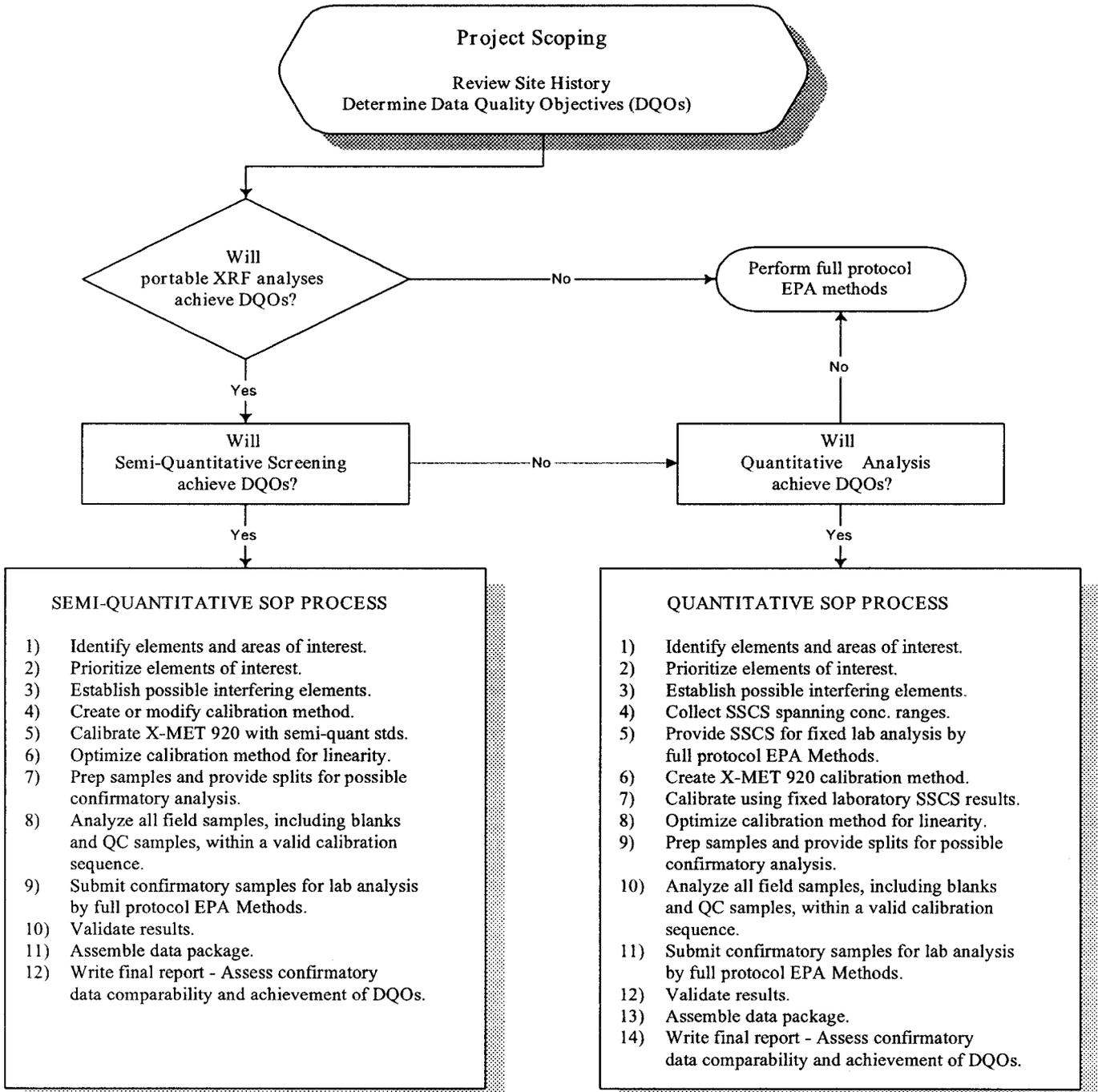
1.1 Practical Planning for Projects Using Field XRF

Figure 1 depicts a decision tree, which outlines the process that project planners should follow to plan environmental projects utilizing XRF. There are three basic steps which must be followed when planning projects that will utilize XRF analysis techniques:

1. Project scoping and determination of project DQOs
2. Ascertaining XRF needs
3. Developing the project Quality Assurance Project Plan/Sampling and Analysis Plan (QAPjP/SAP)

Performing these three steps prior to sample collection will enable the project planner to ensure that the XRF analyses are correctly executed on site and that the resultant XRF data are suitable for their intended use in site decision making.

Figure 1 Project Planning Decision Tree



1.1.1 Project Scoping and Determination of Project Data Quality Objectives

Before Field XRF analysis can be integrated into a project's sampling and analysis scheme, the project planner must establish the project DQOs. Prior to DQO development, the project planner should obtain and evaluate as much historical information as possible about the site conditions and history, including the results of any previous investigations at the site, so that the following questions can be answered:

- What and where is the contamination on the site?
- What is the source of contamination on the site?
- What is the purpose of sampling and analysis (data collection)?
- What are the target elements of interest?
- What are the Action Level concentrations for the elements of interest?
- What non-target metals or site conditions may be present that could create possible interference problems?
- What is the intended use of the data?

If the project planner can answer these questions completely, then the project DQOs have been developed properly and are understood. For assistance, refer to the Agency document Guidance for the Data Quality Objective Process, EPA QA/G-4, which describes the informational needs and critical decision processes that must be addressed during DQO development.

1.1.2 Ascertaining XRF Needs

Once the project target elements, action levels, and intended data uses have been established during DQO development, the project planner can proceed with ascertaining XRF needs for the project. The project planner should first determine whether the project DQOs can theoretically be met using XRF techniques. If the project planner decides that XRF techniques may be applicable to project DQOs, then the planner must answer the following questions:

- What type of XRF data are required: quantitative or semi-quantitative?
- What detection levels and/or action levels must be met for each target element?
- What full protocol EPA methods will be used for confirmatory and/or site-specific calibration standard (SSCS) analyses?
- Will the resultant XRF data meet project objectives?

Section 2.0 discusses the basic principles of XRF analysis so that project planners will be familiar with the technology.

1.1.3 Developing the QAPjP/SAP

The XRF project planner must develop a QAPjP/SAP that details the following:

- Project description and DQOs,
- Project personnel and their responsibilities,
- Sampling protocols; sampling locations and numbers of samples to be collected,
- Quality Assurance (QA) and Quality Control (QC) elements required, including frequency requirements, acceptance criteria, and corrective actions (refer to Section 8.0),

- SSCS analytical protocols for quantitative analysis, including frequency requirements, QC acceptance criteria, and corrective action measures,
- Confirmational analytical protocols with frequency requirements, QC acceptance criteria, and corrective action measures (note, these protocols should be the same as the SSCS protocol s when quantitative analysis is performed),
- Split sampling comparability acceptance criteria, and
- How the QC and field sample data will be used to determine whether project DQOs have been met (Data Quality Assessment).

The QAPjP/SAP should reflect the complexity of the XRF project. It must sufficiently address all of the relevant elements detailed in the Region I, EPA New England Quality Assurance Project Plan Guidance, Draft October 1996.

Detailed standard operating procedures (SOPs) for the sampling and analysis protocols can be referenced in the QAPjP/SAP as long as the applicable SOPs are appended to that QAPjP/SAP. All SOPs that are pertinent to project operations should be developed in accordance with EPA QA/G-6, Guidance for the Preparation of Standard Operating Procedures for Quality-related Operations.

The QAPjP/SAP must describe or reference documentation requirements for the resultant XRF and split sample confirmation data. Documentation that all key QC elements were performed and met project requirements is essential, regardless of intended data use. For XRF techniques, the preparation and analysis of each batch of samples, including related standards, QC samples and blanks, should be recorded in a field or laboratory notebook, run logs, and/or tabulated forms. Section 13.0 of this SOP offers a detailed reporting format for XRF projects. For conventional full protocol analytical methods, complete data packages should be produced in accordance with the Region I, EPA-NE specifications contained in the Training Manual for Reviewing Laboratory Data Package Completeness, dated June 1994.

Used properly, with the appropriate QC procedures and a definitive QA program, XRF can be a very effective tool. Used without regard to QC requirements and QA process controls, the resultant XRF data may be unusable or may not be able to be interpreted.

2.0 Method Summary

2.1 Principles of Operation

XRF is a nondestructive qualitative and quantitative analytical technique used to determine the chemical composition of a sample. In an XRF analysis, primary X-rays emitted from an X-ray tube or a sealed radioisotope source are utilized to irradiate a sample. The primary X-rays incident on the sample cause the elements present in the sample to emit (that is, fluoresce) their characteristic X-ray line spectra. The elements may be identified by the energies of the wavelengths of their spectral lines. The unit of energy of an X-ray is the kilo electron volt (keV). The X-ray energy is proportional to the frequency of the X-ray waves and is inversely proportional to the wavelength. Since it is a fluorescent process, the energy of the fluorescent X-rays will always be of lower energy than the primary X-ray energy. In addition to the fluorescent X-rays, there will be a backscattering of the primary X-rays. Energies of the fluorescent and scattered X-rays are converted (within the detector) into a train of electric pulses, the amplitudes of which are linearly proportional to the energy. An electronic multichannel analyzer measures the pulses

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.

2.1.1 Fluorescent X-rays

During interaction of the primary source X-rays with samples, they may either undergo scattering or absorption by sample atoms in a process known as the photoelectric effect. This latter analytical phenomenon, illustrated in Figure 2, occurs when incident radiation knocks an electron from the inner most shells of an atom. The atom, now in an excited state, releases its surplus energy almost instantly by filling the vacancy created with an electron from one of the outer energy shells. This rearrangement of electrons is associated with the emission of an X-ray with a wavelength characteristic (in terms of energy) of the given atom.

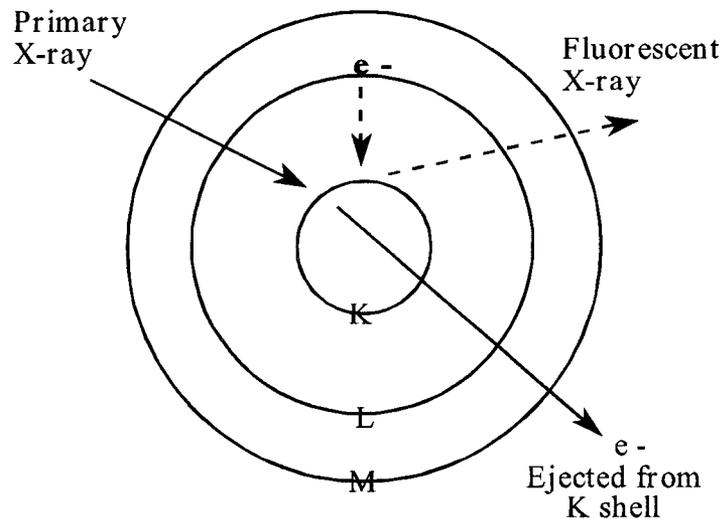
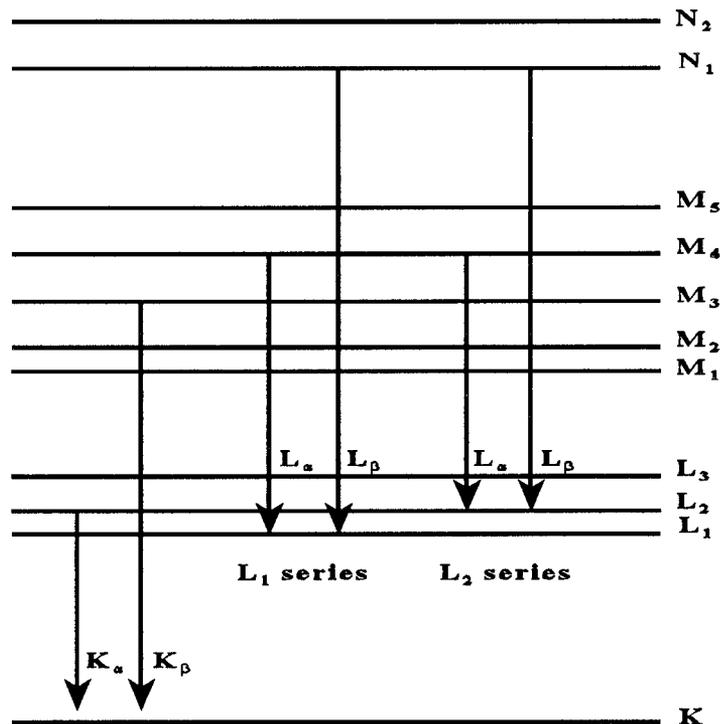


Figure 2 Electron rearrangement in an atom exposed to X-ray radiation generating a characteristic fluorescent X-ray.

X-rays are created in the inner most shells of an atom, the K, L, and M atomic shells. Each characteristic X-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α) or beta (β), which indicates the higher shell from which an electron 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. Figure 3 is a schematic which illustrates of the production of K and L X-rays. Since the electrons producing the fluorescent X-rays are not valence (outer) shell electrons, the X-ray energy is not affected by the chemical or physical form of the atom. Thus, elemental sulfur and CaSO_4 give the same sulfur X-ray. Since there are few allowed transitions, and thus relatively few X-ray lines, the X-rays for a specific element are well defined. K lines have the shortest wavelengths and ,

Figure 3 Production of K and L X-rays



therefore, the highest energies. L lines have longer wavelengths and thus lower energies and M lines have very long wavelengths and thus even lower energies.

An X-ray source can excite characteristic X-rays from an element only if the source energy is greater than a threshold energy associated with a particular line group (K, L, or M). This energy threshold, called the absorption edge (i.e., K absorption edge, L absorption edge, or M absorption edge) is greater than the corresponding line energy. (Actually, the K absorption edge energy is approximately equal to the sum of the K, L and M line energies. The L absorption

edge energy is approximately equal to the sum of the L and M line energies.) Also, the closer the absorption edge energy of an element is to the source energy (but not greater than the source energy), the more efficient is the excitation and the more sensitive is the element's detection. For example, if a source energy is sufficient enough to excite the K lines for both Zn (atomic number 30) and Ni (atomic number 28), then the Zn K lines will be more sensitive than the Ni K lines (i.e., the higher the atomic number, the higher the line energies, and the closer the line energy is to the source energy). If the source energy is sufficient to excite the K lines, then they will always be accompanied by the L and M lines of the same element. If there is insufficient energy to excite the K lines, but enough to excite the L line, then just the L and M lines will appear. XRF analyzers most commonly measure X-ray lines originating from the K and L shells; only elements with an atomic number greater than 57 have measurable M shell emissions.

2.1.2 Scattered X-rays

Scattered or backscattered radiation is simply the reflection of the primary X-rays off the sample. The source radiation is scattered from the sample by two physical reactions: coherent scattering (no energy loss) and incoherent or Compton scattering (small energy loss). Thus, for each line of primary radiation incident on the sample, two scattered X-ray lines close together are returned. The coherent scatter lines being equal to the source energy and the Compton scatter lines being slightly less than the source energy. The amount of scattering is due to the sample matrix. The two primary factors are particle size and average atomic number of the sample. Larger particle sizes and lighter matrices (lower average atomic number), produce more backscatter. The scattered X-rays have the highest energies in the spectrum.

2.2 X-MET 920 XRF Analyzer

The EPA Region I X-MET 920 XRF analyzer has two radioisotope sources, Cadmium-109 and Americium-241, available for the production of primary X-rays. Each source emits a specific energy range of primary X-rays that cause a corresponding range of elements in a sample to produce their fluorescent X-rays. Table 1 provides a listing of the recommended source and analysis line energies for typical environmental elements. The K_{α} or L_{α} line is always the most intense line in their respective line group and, for that reason, is usually the line of choice for analysis (note, the intensity ratio between K_{α} and K_{β} lines is approximately 7:1, respectively, while the ratio between L_{α} and L_{β} lines is approximately 3:2, respectively). When more than one source can excite the same element of interest, the appropriate source is selected according to the excitation efficiency of the elements of interest.

2.2.1 Sample Preparation Summary

Samples are prepared in one of two ways depending on the type of analysis. For semi-quantitative screening analysis, sticks, stones, and other matter that is non-representative of the sample are removed, the sample is then thoroughly homogenized, and an aliquot is placed directly in a plastic XRF sample cup. The sample cup is capped with a clear polypropylene film and the sample identification is clearly labeled prior to analysis.

For quantitative analysis, sticks, stones, and other matter that is non-representative of the sample are removed, and the sample is thoroughly homogenized. The sample is dried and then sieved through a No. 60 mesh sieve. The fraction of the sample that passes the No. 60 sieve is then re-homogenized and aliquoted into the XRF sample cup. The sample cup is capped with a clear polypropylene film and the sample identification is clearly labeled prior to analysis. Refer to section 11.0 for a complete discussion of sample preparation.

2.2.2 Sample Analysis Summary

For measurement, the cup is positioned in the sample holder and exposed to primary X-rays from the selected radiation source. The sample fluorescent and backscatter X-rays are detected and the results are recorded by the data system. Qualitative determinations of the elements present in the sample are based on the locations of characteristic peaks produced by individual

Table 1
 Recommended Source and X-ray Line Selection
 for Typical Elements of Environmental Concern

Isotope	Half Life	Primary Radiation	Element	Recommended Analysis Lines			
				K Line (keV)		L Lines (keV)	
				K _α	K _β	L _α	L _β
Cd-109	1.3 Years	Ag K X-ray, 22.1 keV	Cr	5.41	5.95		
			Mn	5.89	6.49		
			Fe	6.40	7.06		
			Co	6.92	7.65		
			Ni	7.47	8.30		
			Cu	8.04	8.94		
			Zn	8.63	9.61		
			As	10.5	11.8		
			Hg			9.98	11.9
			Tl			10.3	12.3
Pb			10.5	12.6			
Am-241	433 Years	Gamma Radiation, 59 keV	Mo	17.4	19.8		
			Ag	22.1	25.2		
			Cd	23.1	26.4		
			Sn	25.2	28.8		
			Sb	26.2	30.1		
			Ba	32.0	36.8		

elements in the energy spectra. Quantitative determination of an element present is made by comparing the intensity of a characteristic peak in the sample to a calibration curve of the same peak developed from standards of similar matrix and known concentrations.

The analysis can either be performed in a quantitative or semi-quantitative fashion depending on the DQOs of the project. Quantitative analysis is performed by matching the matrix of the standards to that of the site. These standards, called "site specific calibration standards (SSCS)" are actual samples taken from the site that are representative of the matrix present and span the concentration range of the elements of interest. The samples are sent to a fixed laboratory, acid digested, and analyzed by AA or ICP in accordance with a full protocol EPA methods. It should be noted that confirmatory results will vary depending on whether a partial digestion procedure or a total digestion procedure is used. Confirmatory full protocol EPA methods should be chosen in the project scoping phase and meet the data quality objectives of the project. It is essential that all SSCS and confirmatory sample analyses be performed using the same EPA methods for sample preparation and analysis. These methods should be documented in the Quality Assurance Project Plan (QAPjP)/Sampling and Analysis Plan (SAP) and DQO Summary Form. Once the SSCS results are validated in accordance with Region I, EPA New England Data Validation Functional Guidelines for Evaluating Environmental Analyses and deemed usable, they are considered the true values of the SSCS and can be used in calibrating the XRF analyzer. SSCS are discussed in further detail in Section 7.1.

For semi-quantitative screening, standards used to calibrate the analyzer are obtained from sources other than the project site. These standards may be SSCS from another site, standards prepared in-house, or NIST certified standard reference materials. Screening standards are discussed further in Section 7.2.

3.0 Definitions

- 3.1 SSCS - Site Specific Calibration Standards
- 3.2 STCS - Site Typical Calibration Standards
- 3.3 LPCS - Laboratory Prepared Calibration Standards
- 3.4 SRM - Standard Reference Material

4.0 Health and Safety

The X-Met 920 Solid State Probe Set (SSPS) contains two nuclear radiation sources; cadmium 109 and Americium 241. During all measurements the sample lid on the probe must be closed over the sample to shield the user from exposure to nuclear radiation. The probe must not be opened except by authorized personnel.

Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to field operations. Radiation safety information for the X-MET 920 can be found in the operators manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local, state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with

which compliance is required. Licenses for radioactive materials are of two types; (1) general license which is usually provided by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) specific license which is issued to named persons for the operation of radioactive instruments as required by local state agencies. The radiation safety officer is responsible for properly instructing all personnel, maintaining inspection records and monitoring X-ray equipment at regular intervals. A copy of the radioactive material license and leak tests should be present with the instrument at all times and available to local and national authorities upon request.

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

5.0 Interferences and Potential Problems

Generally, the instrument precision is the least significant source of error in XRF analysis. User or application related error is more significant and will vary with each site and the completeness of instrument calibration. The components of user or application error are the following:

5.1 Sample Representativeness

To accurately characterize site conditions, samples collected must be representative of the site or area under investigation. Variables affecting sample representativeness include: geologic variability, contaminant concentration variability, and sample collection and preparation variability. Geologic variability can occur when more than one type of matrix exists on site (i.e., one part of the site is a rich organic soil while the other part of the site is a coarse sand). In this case, quantitative analysis may require two sets of site-specific calibration standards to minimize error.

Contaminant concentration variability is an issue that must be dealt with at each site. For example, if the contamination on site is due to a liquid waste dumped in the soil, the dispersion in the area of concern is more likely to be uniform, and thus the samples more likely to be representative of the area. If, however, the contamination is due to a solid waste of varying size and shape, the likelihood of samples being representative of the area is lower and thus the error in results is greater. In this latter case, the error can be minimized by homogenizing a large volume of sample prior to analyzing an aliquot, or by analyzing several samples at each sampling point and averaging the results.

Preparation and analytical variability are minimized by using consistency in technique and by matching standard and sample matrices.

5.2 Physical Matrix Effects

Physical matrix effects are the result of variations in the physical characteristics of the sample, including particle size, uniformity, homogeneity and surface condition. Thorough and consistent sample preparation is critical to minimizing these effects. For example, consider a sample composed of a mix of fine and coarse particles in which the element of interest is in the fine

particles. If two separate aliquots of the sample are prepared in such a manner that one sample receives a greater portion of the fine particles, then the relative volume of the element of interest in each sample will be different. Thus, when these samples are analyzed, a larger amount of the element of interest will be exposed to the source X-rays in the sample containing the larger volume of fine particles. This will then result in a higher intensity reading and a measured concentration in the sample that is biased high.

5.3 Chemical Matrix Effects

Chemical matrix effects result from differences in concentrations of interfering elements. These interelement effects appear as either X-ray absorption or enhancement phenomena. Both effects are common in soils contaminated with heavy metals. For example, consider a series of samples containing nickel (Ni) and chromium (Cr). Ni in the sample will absorb the fluorescent X-ray of Cr. If the concentration of Cr remained constant and the Ni concentration increased, then the detected signal for Cr would decrease. Thus, basing the concentration solely on the Cr signal, the Cr concentration would appear to decrease. In order to correct for this absorption effect on Cr, a term must be added to the regression equation for Ni. (Information on developing regression equations for instrument calibration is discussed at length in the X-MET 920 reference manual.) As a general guideline, elements that may cause chemical matrix effects are:

- 1) near the target element (± 4 or 5 atomic numbers),
- 2) excited by the source,
- 3) at a concentration greater than 10% of the target element's concentration, and
- 4) present in varying concentrations in the area under investigation.

It is essential to define the chemical matrix effects on the elements of interest prior to instrument calibration.

5.4 X-ray Spectrum Overlap

Certain emitted X-ray lines from different elements, when present in the sample, can be very close in energy and, therefore, interfere by producing an overlapping spectrum. Typical spectrum overlaps are caused by the K_{β} line of element $Z-1$ overlapping the K_{α} line of element Z , where Z = the atomic number of the element. (Note, in heavier elements, the K_{β} line of elements $Z-2$ or $Z-3$ may create the spectral overlap of the K_{α} line of element Z .) This is called the K_{α}/K_{β} interference. Since the $K_{\alpha}:K_{\beta}$ intensity ratio for a given element usually varies from 5:1 to 7:1, the interfering element must be present at a large concentration to disturb the measurement of element Z .

For example, a large concentration of vanadium ($Z = 23$) could interfere with chromium ($Z = 24$). Vanadium (V) has K_{α} and K_{β} energies equal to 4.951 and 5.427 keV, respectively. Chromium (Cr) has a K_{α} energy equal to 5.41 keV. Since the resolution of the Si(Li) detector in the X-MET 920 is approximately 0.170 keV, large amounts of vanadium in the sample will result in spectral overlap of the V K_{β} with the Cr K_{α} peak and the measured X-ray spectrum will include total counts for Cr plus V lines.

Other spectral interferences can occur between K/L, K/M, and L/M lines. An example is the As K_{α} /Pb L_{α} interference. In this case the lead can be measured from the Pb L_{β} line, and arsenic from either the As K_{α} or As K_{β} line; in this way the interference can be overcome. The X-MET 920 uses correction factors obtained from the analysis of single element standards to correct for spectrum

overlap. It is essential to define all possible spectral overlaps for the target elements and create and/or update the overlap correction factor table during instrument calibration (refer to Section 9.2.3 and the X-MET 920 reference manual for further details). Note, whenever spectral overlap is an issue, measurement sensitivity is reduced.

5.5 Moisture Content

Sample moisture content will affect the accuracy of the sample results. The measurement error may be minor when the moisture content is small (5-20 %), or it may be significant when measuring the surface of soils that are saturated with water. For quantitative analysis, moisture content will not be an issue because all samples are dried as part of the sample preparation. However, for semi-quantitative screening analysis, drying is not required, therefore, moisture content should be a practical concern in sample preparation. In general, air drying, oven drying, or some other mechanical technique of drying is recommended to reduce moisture content to within 5% of the calibration standard's moisture content. Microwave drying is not recommended.

6.0 Personnel Qualifications

Sample analysis must be performed by qualified personnel either experienced in the operation of the XRF analyzer and knowledgeable in X-ray fluorescence, or under the direct supervision of an experienced and knowledgeable individual. The analyst must be thoroughly familiar with this SOP and the X-Met 920 Reference Manual supplied by the instrument manufacturer.

7.0 Equipment and Supplies

7.1 Instrument Description

The X-Met 920 is a PC based energy dispersive X-ray analyzer which consists of three major units:

- 1.) Computer and Software
- 2.) X-Met PC Unit (XPCU)
- 3.) Solid State Probe Set (SSPS).

The X-MET 920 software (version 1.33), is MS-DOS based and provides total control of the instrument. The minimum computer configuration recommended for operation of the software is a 33 MHZ 486 DX computer with 2 MB RAM, 1 floppy drive, and an 80 MB hard drive. The XPCU board goes into an expansion slot inside the computer. It is the interface between the analysis probe and the computer and software. In addition to other electronic functions, this board contains a 2048 channel Multi Channel Analyzer (MCA) that records the spectra during measurements. The SSPS houses the sample holder, the Cd-109 and Am-241 radioisotope sources, and the Si(Li) detector. The Si(Li) detector is a silicon (drifted with lithium) semiconductor crystal diode which is reversely polarized and cooled by liquid nitrogen. The detector is capable of resolution equal to 0.170 keV.

7.1.1 Instrument Transport

The X-MET 920 (computer, monitor, probe etc.) MUST be handled with care during transport. The original shipping containers should be used at all times to avoid damage in transit. The shipping container for the SSPS must be properly labeled in accordance with regulations governing the shipment of radioactive materials.

7.2 Supplies

7.2.1 Sieve: No. 60 (250 μ m) stainless steel, Nylon, or equivalent mesh sieve

7.2.2 Polyethylene XRF sample cups

7.2.3 Film for sample containment: Mylar, Kapton, Spectrolene, polypropylene or equivalent; 2.5 or 6.0 μ m thick

7.2.4 Stainless steel spoons

7.2.5 Mortar and pestle: glass, agate, or aluminum oxide

7.2.6 Aluminum drying pans

7.2.7 Drying oven

8.0 Calibration Standards

The appropriate choice of calibration standards is made based on the project DQOs. When definitive quantitation is required, site-specific calibration standards must be used (refer to Section 7.1). When semi-quantitative results are required, the choice of the appropriate semi-quantitative calibration standards is made (refer to Section 7.2).

The first step in selecting the calibration standards is to determine the target elements of interest. The basic rule is to prioritize the target elements and then reduce the number of elements to be analyzed in the field to the minimum amount required to perform the task. For example, suppose the site requiring cleanup was a metals plating facility which contained a waste lagoon known to be contaminated with high concentration of several metals, and cadmium was the element present with the highest risk (i.e., lowest action level). In this case, the amount of target elements required to monitor the cleanup could be reduced to 1 element, cadmium. Here, by simplifying the calibration procedures and using only one radioisotope source, sample throughput for the project can be maximized. Note, confirmatory samples taken throughout the cleanup and a final round of confirmatory sampling following completion of the project will help ensure that cleanup action levels for all target elements of interest were obtained.

Another reason to reduce the number of target elements to be analyzed in the field applies directly to quantitative analysis using site-specific calibration standards (SSCS). In order to properly model the regression equation for an element, additional SSCS must be included for each element that may cause possible chemical matrix effects (approximately five per interfering element). Thus, by reducing the number of target elements, the number of required SSCS can be significantly reduced, the complexity of the calibration can be simplified, and a large cost savings can be

realized by reducing the number of samples that require fixed laboratory analysis using full protocol EPA methods.

Note, the X-MET 920 can only analyzed ten (10) elements at one time in a calibration method. Of those 10 elements, only 6 elements may be reported quantitatively and of the remaining four elements, one must always be the backscatter peak (the Compton K_{α} peak from the source radiation).

Figure 1 (Section 1.1) illustrates the typical sampling and an alysis scheme for both quantitative and semi-quantitative analyses.

8.1 Quantitative Analysis Using Site-Specific Calibration Standards

Site-specific calibration standards (SSCS) are actual samples from the site under investigation that span the range of concentrations found on site for the elements of interest. Elements of interest not only include the target elements under investigation, but also those elements present that may create possible interference effects. SSCS must be representative of the matrix under investigation (refer to Section 5.1). If there are distinctly different matrices on site that require analysis, separate SSCS must be sampled for each matrix.

The concentration of all target elements, and any elements present that may cause chemical matrix effects (refer to Section 5.3), must be determined by independent AA or ICP analysis in accordance with the full protocol EPA methods specified in the QAPjP/SAP. (The same method must be used to perform all confirmatory analyses to ensure data comparability.) Independent SSCS analyses must be performed in triplicate and the average result for each element is to be used in the instrument calibration. SSCS data must be validated in accordance with the most recent version of the Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses prior to use and all raw data and information must be provided with the data package to ensure the scientific defensibility of the calibration standards.

The X-MET 920 reference manual uses the term "modeling" to describe the process of modifying the regression equation of an element's calibration curve to correct for chemical matrix effects and backscatter from the X-ray source. To properly model a regression equation and compensate for these effects, a series of SSCS, containing both interfering and target elements at known and varying concentrations, are required. The total number of SSCS required increases significantly with each target and interfering element. (Again, by reducing the number of target elements in the analysis, the number of SSCS required may be greatly reduced.)

8.1.1 Site-Specific Calibration Standard Sampling

Collect sufficient SSCS to generate a minimum 5-point calibration curve for each target element, that spans the range of concentrations found in the area under investigation. The high and low SSCS for each target element will determine that element's linear calibration range. The remaining standard concentrations should be roughly distributed throughout this range. Note, additional SSCS near the concentration range of interest or site action level will improve the accuracy of the calibration at that level. For each interfering element present, increase the number of SSCS for the element being interfered with, by 5.

For example, consider an analysis in which Pb and Cr are the target elements. To develop the two 5-point calibration curves, it required a combination of 7 SSCS to span the range of

concentrations found on site. Unfortunately, Ni was also present in high enough concentrations to cause a chemical matrix effect with the Cr X-ray. In order to improve the calibration model and reduce the chemical matrix effects, 5 more Cr SSCS which contain Ni, are added to the Cr calibration curve. Thus, a total of 12 SSCS are now needed to calibrate the instrument for the two target elements.

SSCS collected for an interfering element should reflect the variability of that element's concentration found in relation to the concentration of the target element. (Note, mixing of high and low concentration soils to provide a full range of target element concentrations is not recommended because the ratio of the interfering element to the target element will remain the same and the interelement effect in the calibration will be skewed in one direction.) All target and interfering element concentrations, in each of the SSCS collected, should be included as calibration points. Outliers can later be eliminated when the regression equations are being developed (refer to "developing regression equations" in the reference manual).

To assist in determining appropriate SSCS for laboratory analysis, sample points may be pre-screened with the instrument calibrated using semi-quantitative calibration standards (refer to Section 7.2).

8.1.2 Site-Specific Calibration Standard Preparation

The SSCS samples collected in the field must be oven-dried at $< 150^{\circ}\text{C}$ for 2 to 4 hours to remove moisture. The entire sample should be spread out in a drying pan and clumps broken up with a stainless steel spoon. If mercury is to be analyzed, a separate sample must be air dried until the moisture content is $< 20\%$, as heating may volatilize the mercury. After drying, all large organic debris and non-representative material (sticks, twigs, leaves, roots, insects, asphalt, rocks, etc.) are removed and the sample is transferred to a mortar and ground with a pestle to a uniform consistency.

The dried and ground sample is then sieved through a No. 60 ($250\ \mu\text{m}$) mesh stainless steel sieve. At no time should the material be forced through the sieve. Pebbles and organic matter remaining on the sieve should be discarded. The under-sieve fraction of the material constitutes the sample. (Although a maximum final particle size of 60-mesh is normally recommended, a smaller sieve size may be used if the physical characteristics of the sample or DQOs of the project dictate. Note, the identical sieve size must be used to prepare all SSCS and samples. Deviations in the sieve size and the reason for the change should be documented in an amendment to the QAPjP/SAP and must be recorded in the sample preparation log and noted in the final report.)

Homogenize the sieved sample by placing 150 - 200 grams of 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.

Fill one or more XRF sample cups approximately 3/4 full with sample. Cut and tension (wrinkle-free) a piece of polypropylene film over the top of the cup and seal using the plastic film securing ring. Label the sample cups appropriately. The remainder of the sample is then split into two portions and placed in clean labeled glass or plastic containers. One portion of the sample is submitted to the approved laboratory for analysis of the requested element(s) by

the full protocol EPA methods, and the other portion is archived for possible future use. The stainless steel sieve and spoons must be decontaminated between samples by washing with soap and water and drying.

8.2 Semi-Quantitative Calibration Standards

When the site objectives require semi-quantitative measurements, the choice of an appropriate calibration standard must be determined (Sections 7.2.1 - 7.2.3). Depending on the relative accuracy of the screening desired, one or more calibration standards may be used. Note, due to the differences in representativeness between standards and samples, as well as the other interference factors described in Section 6.0, semi-quantitative calibrations may generate false positive and/or negative results.

8.2.1 Site Typical Calibration Standards (STCS)

STCS are SSCS from a different site that contain the target elements of interest in the approximate range and matrix as the site under investigation. If possible, STCS should be chosen to reflect any chemical matrix effects that may be present in the samples on site. A new instrument calibration must be performed in accordance with Section 9.1 each time STCS are employed. STCS data must be validated in accordance with the most recent version of the Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses prior to use and all raw data and information must be provided with the data package to ensure the scientific defensibility of the calibration standards.

8.2.2 Laboratory Prepared Calibration Standards (LPCS)

If satisfactory STCS are not available for all elements at appropriate concentrations, it may be necessary to prepare quantitative standards from laboratory stock chemicals. Such standards may be prepared by mixing finely ground dry chemicals or liquid standards with a clean soil, silica sand or other inert material (e.g. Somar Mix, from Somar Laboratories, NY, NY, or equivalent).

8.2.2.1 Solid Chemical Prepared LPCS

Prepare the high LPCS first, by adding a known weight of dry chemical(s) to a known weight of clean dry soil or inert material. The clean soil or inert material must first be pre-dried and sieved through a No. 60 (250 μ m) sieve. Following the addition of the dry chemical, the combined mixture must be ground in a mortar and pestle to thoroughly homogenize the standard to a uniform consistency and particle size. Serial dilutions of the high standard may then be prepared to establish the calibration range for the analysis. All serial dilutions must be mixed in the identical manner as the initial standard.

For example, to prepare a 10,000 mg/kg antimony standard, add 0.60 g of Sb_2O_3 to 49.4 g of dry clean soil and mix/grind thoroughly.

$$\frac{(600 \text{ mg } \text{Sb}_2\text{O}_3) (83.5 \% \text{ Sb})}{(0.050 \text{ kg})} = 10,000 \text{ mg/kg Sb}$$

Note, if the purity of the dry chemical is < 97%, then the amount of chemical added or final concentration must be adjusted to reflect this.

The clean soil or inert material used in LPCS preparation must be analyzed as a control blank, following instrument calibration, to verify that the elements of interest are not present. If the soil or inert matrix contains an element of interest, its concentration must be determined by the method of standard addition and the actual LPCS concentrations must be corrected for this amount. A minimum of 3 LPCS and the unspiked matrix are required to perform the method of standards addition. Once the base level concentration of the soil or inert matrix is determined, the instrument must be recalibrated using the unspike d matrix as an additional calibration point along with the corrected LPCS concentrations.

8.2.2.2 Liquid Chemical Prepared LPCS

Alternatively, a standard may be prepared by adding a known amount of an aqueous standard to a known amount of clean soil or inert material. The clean soil or inert material must first be pre-dried and sieved through a No. 60 (250 µm) sieve. The volume of aqueous metals standard used must be sufficient to create a standard/soil slurry where all parts of the soil come in contact with the liquid standard. The slurry is then thoroughly mixed and dried at ≤ 105°C. The dried standard must be ground in a mortar and pestle to thoroughly homogenize the standard to a uniform consistency and particle size. To establish a calibration range for the analysis, additional standards may be prepared from aqueous standards of different concentrations, or by preparing serial dilutions of the first standard. All serial dilutions must mixed in the identical manner as described in Section 7.2.2.1.

For example, to prepare a 10,000 mg/kg antimony standard, pipet 10 mL of a 10,000 mg/L antimony AA/ICP standard into a beaker containing 10 g of dry clean soil or inert material. Mix to a uniform slurry, dry in an oven at ≤ 105°C, and re-mix/grind until the standard is thoroughly homogenized.

$$\frac{(10,000 \text{ mg/L Sb}) (0.010 \text{ L})}{(0.010 \text{ kg})} = 10,000 \text{ mg/kg Sb}$$

The clean soil or inert material used in LPCS preparation must be analyzed as a control blank, following instrument calibration, to verify that the elements of interest are not present. If the soil or inert matrix contains an element of interest, its concentration must be determined by the method of standard addition and the actual LPCS concentrations must be corrected for this amount. A minimum of 3 LPCS and the unspiked matrix are required to perform the method of standards addition. Once the base level concentration of the soil or inert matrix is determined, the instrument must be recalibrated using the unspike d matrix as an additional calibration point along with the corrected LPCS concentrations.

8.2.3 Standard Reference Material (SRM)

NIST or other commercially available certified standard reference materials may be used. A copy of the certified results must be included in the final data package.

9.0 Calibration and Operation

9.1 Instrument Calibration

The X-MET 920 may be calibrated using one of several techniques available depending on the data quality objectives of the project.

- For quantitative field analysis, empirical calibration procedures must be used that incorporate site-specific calibration standards.
- For semi-quantitative screening, one of three calibration procedures, empirical calibration, fundamental parameters calibration, or Compton peak normalization calibration, may be used to calibrate the instrument depending on the standards and instrument software available.

Empirical Calibration - The standard software package supplied with the X-MET 920 supports the empirical calibration technique. This calibration technique is used for all quantitative analyses and for semi-quantitative analysis using a series of either site-typical calibration standards, laboratory prepared calibration standards, or standard reference materials. Refer to Instrument Operation, Section 9.2 of this SOP, and X-MET reference manual for information on performing an empirical calibration.

Fundamental Parameters - Alternatively, an optional software package called ACES (Automated Contaminant Evaluation Software), is available which uses a modified fundamental parameter approach to generate a calibration. This calibration technique may only be used for semi-quantitative screening analyses. This calibration relies on the ability of the liquid nitrogen cooled, Li(Si) solid state detector to separate the coherent (Rayleigh) backscatter peaks from the incoherent (Compton) 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 ACES user's manual. The ACES program is not presently available on the Region I X-MET 920, and thus, the fundamental parameters calibration procedure is beyond the scope of this SOP and will not be addressed further.

Compton Peak Normalization - The last calibration technique, Compton peak normalization, is a manual calibration technique used for semi-quantitative screening analyses. It is based on the analysis of one or more certified standards, where the intensities of the lines of interest (i.e., target elements) in the sample are ratioed against those in the standard, following normalization of the Compton peaks. 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 is similar to using internal standard calibration and can reduce the problems associated with varying sample matrices. Use Equation 5 to calculate Compton peak normalized sample results.

Equation 5

$$\text{Sample Concentration (mg/Kg)} = \frac{(A_p) (S_k) (S_c)}{(A_k) (S_p)}$$

Where:

- A_I = Baseline corrected sample intensity
- A_K = Baseline corrected sample Compton K_{α} intensity
- S_K = Baseline corrected standard Compton K_{α} intensity
- S_I = Baseline corrected standard intensity
- S_C = Standard concentration (mg/Kg)

Certified standards, used in Compton peak normalization calibrations, may include either SSCS, STCS, LPCS, or SRM. For optimum results, the certified reference standards should be of similar matrix as the samples and should contain the elements of interest at concentrations near those expected in the samples. Although the X-MET 920 software can be adapted to supply the line intensities to manually calculate Compton peak normalized results, it is not a routine procedure accommodated by this instrument and will thus not be addressed further in this SOP.

9.1.1 Instrument Performance Check

Prior to the analysis of any standards or samples, the peak calibration of the X-MET 920 must be verified. The channel for the Pb L_{β} line (on the multi-channel analyzer of the XPCU board) must be verified at the beginning of the day (prior to the initial calibration) and at the end of the analysis sequence or every 8 hours, whichever is more frequent. If the initial peak calibration check at the beginning of the day for the Pb L_{β} line is not at 990 ± 2 channels, re-set the peak calibration, verify that it is correct, and perform an initial calibration. If the peak calibration check performed at the end of the analytical sequence (or after eight hours) does not meet the above criteria, then re-set the peak calibration, re-perform the initial calibration and re-analyze all samples since the last compliant peak calibration check. All samples must be analyzed within a valid analytical sequence.

9.1.2 Initial Calibration (ICAL)

This SOP is specific to the use of empirical calibration. The other calibration techniques for semi-quantitative analysis, fundamental parameters and Compton peak normalization, are acceptable for use, but will require modifications to this SOP (Sections 9.1.2 and 9.2.3) and documentation of these changes in the QAPjP/SAP. All other procedures discussed in this SOP are valid for these other calibration techniques and should remain implemented.

After the peak calibration check criteria are met, and prior to the analysis of any samples, the X-MET 920 must be calibrated empirically for quantitative or semi-quantitative analysis. The instrument must be calibrated at a minimum of once every seven (7) days for the Cd-109 source, once every thirty (30) days for the Am-241 source, and any time the continuing calibration verification criteria below are not met. The correlation coefficient of the calibration curve for each target element must be ≥ 0.98 . If the correlation coefficient is less than 0.98, the problem must be identified and corrected prior to sample analysis. If a correlation coefficient of ≥ 0.98 is unattainable due to the chemical matrix effects, the best possible calibration must be established for analysis and the problems associated with the calibration documented in the report narrative.

9.1.3 Initial Calibration Verification (ICV)

The ICV is an independent standard (or standards), from a source other than that used in the initial calibration, that contains all the target elements of interest. The ICV may be an STCS, LPCS, or SRM, or for quantitative analysis using SSCS, an additional SSCS not used in the ICAL may be used for the ICV. The ICV must be analyzed immediately after the initial calibration is completed. ICV target element concentrations should be near the site action levels, or if no action level has been determined, they should be near the level of interest or the mid-point of the initial calibration. Calculate the percent recovery for each target element in the ICV using Equation 6.

Equation 6

$$\text{Percent Recovery (\%)} = \frac{\text{Found Value}}{\text{True Value}} \times 100$$

The percent recovery for each element in the ICV must be 50 - 150 %, inclusive. If the true value of an ICV element is < 2 times the MDL, then the control limit is the true value \pm MDL. If the ICV does not meet the control limits, then the analysis must be terminated, and the problem must be identified and corrected. An acceptable ICV must be obtained prior to sample analysis.

9.1.4 Continuing Calibration Verification (CCV)

A CCV standard(s) must be analyzed at the beginning and end of an analysis sequence and after every 10 samples. The CCV standard(s) is an ICAL standard that contains all of the target elements. The concentration of the CCV should be near the site action level, or if no action level has been determined, the concentration should be near the level of interest or the mid-point of the initial calibration.

Calculate the percent recovery for each target element in the CCV using Equation 6. The percent recovery for each target element in the CCV must be 80 - 120 %, inclusive. If the true value of the CCV is \geq MDL and < PQL, then the control limit is the true value \pm MDL. If the CCV does not meet the control limits, then the analysis must be terminated, the problem must be corrected, and the CCV must be reanalyzed. If the CCV reanalysis yields a result within the acceptance criteria, then the analysis may continue and all samples analyzed since the last compliant CCV must be re-analyzed. If the reanalysis of the CCV still does not meet the acceptance criteria, then the instrument must be recalibrated, the ICV verified and all affected samples reanalyzed within a valid analytical sequence.

9.2 Instrument Operation

9.2.1 Filling the Probe Dewar with Liquid Nitrogen

To operate the Solid State Probe Set (SSPS), the Si(Li) detector must be cooled with liquid nitrogen.

1. Place the probe on its side on a flat surface. Unscrew the dewar plug (brass screw) from the filling port.
2. Slide the L-shaped outlet tube of the funnel all the way into the filling port and hand tighten the brass knurled nut on top the filling port thread. Arrange the funnel so that its cone faces upward.
3. Pour liquid nitrogen slowly into a funnel and let it flow into the probe dewar. It usually takes approximately three funnel volumes of liquid N₂ to fill the probe dewar (0.45 liter capacity). The dewar is filled when you see a cone-like spray of liquid nitrogen from around the brass nut of the funnel connector.
4. After the probe dewar is filled, carefully unscrew the funnel nut (holding the insulated sleeve) and withdraw the funnel from the dewar port. Quickly screw back in the dewar plug and hand tighten. In a few seconds the pressure of the liquid nitrogen will build up inside the probe dewar and "hissing" sounds of escaping gas through relief valves will be heard. Press the green switch on the probe to secure the radioactive sources from use until the probe reaches the proper operating temperature.
5. Wait approximately thirty minutes for the probe to cool down before operating.

NOTE: The threads on the dewar filling port will require periodic lubrication on a semi-annual basis or as needed. Lubricate with DOW Corning 33 Lubricant, or equivalent.

While the Si(Li) Solid State Probe is cooling, turn on the computer and monitor. Type either SSPSA for the Cd-109 Source, or SSPSB for the AM-241 source. Follow the prompts and press ENTER. After thirty minutes the instrumentation is ready for use.

9.2.2 Instrument Performance Check

The Lead (Pb) L_β peak optimum must be checked before instrument calibration or analysis is performed, and at the end of the analytical sequence, or every eight hours, whichever is more frequent.

To assure proper peak assignment and identifications, you must check to make sure the Pb L_β peak (right side large Pb peak) is at channel 990 ± two channels. To do this, place the pure element Pb standard into the SSPS probe sample holder.

The Main Menu for X-Met 920 Software (Version 1.33, November 1994) consists of:

- 1.) ANALYSIS
- 2.) CALIBRATION
- 3.) MAINTENANCE

From the main menu of the computer, arrow down to MAINTENANCE and press ENTER.

Press F3 for Instrument

Press F3 for Test Measurement

Press F3 for Time

When in Time, type 30 (for 30 second analysis time) and press "ENTER".

The screen message says "Probe in Reference position. Press Start to begin"

On the base of the SSPS probe, push the red start button, and then Press F1 on the keyboard to start acquisition. When acquisition is complete, check to see that Pb L_β peak is at channel 990 ± two channels. To do this, move the yellow cursor to the Pb L_β peak (second large peak on screen which is shaded) and read the channel number where the area count is at the maximum. If the Pb L_β peak is at 990 ± two channels, press F8 to quit. If not, press F8 again and type the letter "O" to optimize. After optimization, repeat the above procedure to make sure the Pb L_β peak assignment is proper.

The Instrument is now ready for use. In order to perform sample analysis using empirical calibration, a new calibration method must be developed or an existing calibration method must be updated.

9.2.3 Empirical Calibration and Method Development

Refer to the reference manual for more complete information on software operation. Particular attention must be given to the calibration sections in the manual describing the setting of regression terms to establish the best possible instrument calibration for analyzing field samples.

NOTE: Since sources decay, net count rates for elements will vary as time passes. Therefore, calibration standards must be analyzed and the calibration updated at a minimum of once every seven (7) days for the Cd-109 source and once every thirty (30) days for the Am-241 source. Calibration records must be maintained during an ongoing project to insure that the X-MET 920 is calibrated at the proper frequency.

To perform an empirical calibration for either quantitative analysis or semi-quantitative screening, follow the steps below:

Screen 1: To begin a new calibration, follow the prompts:

1. At the Main Menu arrow down to CALIBRATION and press "ENTER"
2. Press "F1" for New Method

Screen 2: Answer the questions at the prompt which are as follows:

Method Name : (Up to 8 alphanumeric characters) "ENTER"

Calibration Date : (Computer fills this in for you) "ENTER"

Operator : (Type the two initials of your name) "ENTER"

Number of Measurement Windows : (Type the number of elements you will be analyzing for in this method and ADD one for the backscatter peak. For example, if you were analyzing Pb and Cr, you would type 3) "ENTER"

Number of Standards: (Number of standards to be used in the calibration) "ENTER"

Probe: (Arrow down to SSPS) "ENTER"

Window 1: (Computer automatically puts in BS [Backscatter] for you)

Window 2: (Type in one element symbol for an analyte of interest, i.e., Pb). "ENTER" Continue entering the remaining elements of interest, both target elements and matrix elements, in the additional window slots (up to 10 total).

Window Time: 60 (Leave at 60) "ENTER" This is the default analysis time used to measure single element standards for setting each element's measurement window. From this information the software automatically calculates the overlap correction factors.

Standard Time: 120 "ENTER" The default time for standard analysis is 120 seconds.

Analysis Time: 120 "ENTER" The default time for sample analysis is 120 seconds. This time may be altered depending on the DQOs of the project. Analysis times generally range from 60 - 300 seconds. Longer count times improve the precision or reproducibility of the measurement, however increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing returns. Increasing the count time also decreases the detection limit, and decreases sample throughput. Standard and sample analysis times should be identical.

If you are satisfied with all entries press F7 to continue. If you need to make changes to any entries, press F1 and arrow key down to the entries you need to change. When you are satisfied, press F7 to continue.

Screen 3: Analytes selection. Move the highlight bar with the arrow keys onto the elements you wish to analyze and press "ENTER" each time. After the analytes are chosen press F7.

Screen 4: Units and standard concentrations. Enter the concentration units for each element selected. Then enter the high and low standard concentrations for each element. When completed, press F7.

Screen 5: The next step in the calibration sets the measurement windows for each element in the method using single element samples. The windows are set for target and matrix elements as well as for backscatter. The measurement windows identify areas in the spectrum where analytical signals are measured for each element. (Note, the spectra of the single element standards are also used to determine the interelement correction factors that are used to correct for spectral overlap. The X-MET 920 software automatically calculates these factors.) On the screen, you are asked if you want to use the spectra in memory. Press F1 for yes (you will see the location of the analytes) and then select the single element spectra. If all spectra needed for calibration are not selected or present in memory, the X-MET 920 will then list the elements that need to be measured. By pressing F1, the software will prompt for measurement of each single element standard. Based on the element measured, the software automatically selects the peak location (K_{α} , L_{α} , etc.) and the measurement window to the peak width at half height. (Refer to the reference manual for instructions on manually selecting the window location and limits, if required.) When measured, the spectra from the single element samples are automatically stored to disk for use at a later time. If the measured spectrum is already in the library, the new spectrum will replace the old. X-ray emission on the energy scale is in kilo electron Volts (keV). Press F7 to continue.

Screen 6: The next screen prompts you to enter the assay value for each element for your first calibration standard. Type this information and press "ENTER". Press F1 to accept this information.

Screen 7: The next screen asks to place standard #1 in the SSPS and press "Start". To do this, take the standard #1 XRF cup, wipe the bottom of the cup with a dry tissue, and place it over measurement window. Close the cover (radiation shield) and press the small RED button at the base of the SSPS probe unit. This will start the analysis of standard #1. Repeat this for each standard in the method.

Screen 8: After running all standards in the calibration curve, the screen shows "Selection of Regression Term(s) for Analytes". Choose regression terms using the arrow keys and press "ENTER" on the chosen terms. Press F1 to perform the regression. You MUST press F4 (Residuals) to view and save calibration curve. If you need to, you can delete outlying points when viewing a calibration curve by pressing F1. Ideally, the regression term chosen will give a linear regression with a correlation coefficient (R) close to 1.00, a standard error of fit (S) which is very low, and a Fisher's factor (F) which is maximized. (Refer to reference manual for the discussion on choosing regression terms and establishing the best possible assay method.) When complete, print out the calibration curve by pressing F3. Press F7 to continue.

If satisfied with the calibration curve for an analyte, press F2 to move on to the "Next Analyte". Continue defining the regression terms for each target element's calibration. After the calibration of the last element is set, press F2 to save it to memory and move onto the next screen.

Screen 9: The final element screen will prompt you to "Insert check sample number." Choose a standard at the action level (if possible), or a mid-point standard from

the calibration curve and following the prompts. Analyze this standard. Note which standard is used. This check sample (standard) can be used later to manually update a calibration curve for source decay. After running the check standard, the screen will show "Calibration Finished". Press F8 to quit calibration mode.

9.2.4 Checking and Updating an Existing Method

Although the X-Met 920 automatically updates calibration curves for source decay, there are times when manual normalization may be needed. This could be the case if unexpected results are obtained on a known sample used to measure the reliability of the instrument. To do this, go to the X-Met 920 Main Menu, arrow down to Maintenance, and hit Enter. Hit F2 for Method Update and arrow key down to the method to be checked/updated. Hit F7 for Check Standard and follow the screen prompts. Place the Check Standard for the specific method into the probe, hit F1 and the red button on the probe to run the check analysis. At the end of the analysis a table of assay values and deviations will be displayed. If the difference in the results is within 3 standard deviations, no correction is required. If the difference in results is within the range of greater than 3 but less than 20 standard deviations, the regression equation is corrected. If the difference in results is off by more than 20 standard deviations, the instrument must be recalibrated.

10.0 Quality Assurance and Quality Control

10.1 Instrument Performance Check

The instrument peak calibration must be verified at the beginning of the day (prior to the initial calibration) and at the end of the analysis sequence or every 8 hours, whichever is more frequent. If the initial peak calibration check at the beginning of the day for the $Pb\ L_{\beta}$ line is not at 990 ± 2 channels, re-set the peak calibration, verify that it is correct, and perform an initial calibration. If the peak calibration check performed at the end of the analytical sequence (or after eight hours) does not meet the above criteria, then re-set the peak calibration, perform an initial calibration and re-analyze all samples since the last compliant peak calibration check within a valid analytical sequence.

10.2 Sensitivity - Method Detection Limit and Practical Quantitation Limit

The site-specific method and quantitation limits must be determined for each target element during the initial stages of a project. Site-specific method detection limits (MDLs) and practical detection limits (PQLs) must be determined for each project, and on long term projects, must be repeated quarterly thereafter. If there are distinctly different matrices on site, MDLs and PQLs must be determined for each matrix. For quantitative analysis, the MDLs are generated by preparing and analyzing a minimum of seven aliquots (i.e., sample cups) of the lowest SSCS for each target element in accordance with 40 CFR Part 136, Appendix B. For semi-quantitative screening, a low concentration sample, STCS, LPCS, or SRM may be used. Element concentrations should be approximately 3 - 5 times the expected MDL to generate accurate MDLs and PQLs. Calculate the MDL using Equation 1.

Equation 1

$$MDL = t_{(n-1, 1-\alpha = 0.99)} (S)$$

Where:

$t_{(n-1, 1-\alpha = 0.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table 2.

S = standard deviation of the replicate analyses.

Table 2 - Students' t Values at the 99 Percent Confidence Level

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, 1-\alpha = 0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602

Calculate the PQL for each element by multiplying the MDL by 3.

10.3 Precision

10.3.1 Analytical Precision Test

The precision of the analytical method is determined by performing multiple analyses on a field sample with low, moderate, or high concentrations of target elements. The frequency of precision measurements will depend on the DQOs of the project. At a minimum, one analytical precision test must be performed per day. The sample chosen for testing should be analyzed a minimum of 7 times in replicate (same sample cup 7 times). It is extremely important if the site action level(s) are known, that the sample used to determine method precision be at concentrations near the site action levels. If several precision measurements will be made over time, it is recommended that samples with varying concentration ranges be used to assess the effect of concentration on method precision. Samples at the site's action levels should, however, dominate the precision measurement process. Precision measurements must be made using the same analysis time as that used to analyze the other project samples.

To assess analytical precision, calculate the relative standard deviation (RSD) of the replicate analyses using Equation 2. Field XRF data, to be considered adequately precise, should be $\leq 20\%$ with the exception of chromium. RSD values for chromium should be $\leq 30\%$.

Equation 2

$$RSD = \frac{S}{\text{Mean}} \times 100$$

Where:

S = Standard deviation of the analyte concentration with n-1 degrees of freedom
Mean = Mean concentration of the analyte

10.3.2 Laboratory Duplicates

The precision of the sample preparation and analytical methods is determined by performing a laboratory duplicate analysis. Laboratory duplicates must be prepared and analyzed at a frequency of 1 per 20 samples or 1 per sample matrix, whichever is greater. Laboratory duplicates are two aliquots of the same sample that are prepared, homogenized and analyzed in the same manner. Note, proper sample homogenization is critical in producing meaningful results. Calculate the RPD between the sample and its duplicate using Equation 3.

Equation 3

$$RPD = \frac{|(S - D)|}{\frac{(S + D)}{2}} \times 100$$

Where:

S = Original sample result
D = Duplicate sample result

Laboratory duplicates must meet the following criteria.

- If both the original and laboratory duplicate values are \geq PQL, then the control limit for RPD is $\leq 35\%$,
- If one or both values are $<$ PQL, then do not assess the RPD.

If duplicate criteria are not met, then re-prepare and reanalyze both the original and laboratory duplicate samples. If duplicate criteria are still not met, then flag that target element with an "*" on the final report for both the original and duplicate samples. Note, report both the original and duplicate analyses; do not report the average. The sample ID for laboratory duplicate samples shall contain the suffix "LD".

10.3.3 Field Duplicates

Field duplicates measure cumulative effects of both the field and method precision and hence provide an indicator of overall precision. Sample field duplicates must be prepared and analyzed at a frequency of 1 per 20 samples or 1 per sample matrix, whichever is greater. Field duplicates are samples collected adjacent to each other at the same sample location (not

two aliquots of the same sample). Calculate the Relative Percent Difference (RPD) between the sample and its duplicate using Equation 3.

If the field duplicate criteria specified below are not met, then flag that target element with an “*” on the final report for both the original and field duplicate samples. Note, report both the original and field duplicate analyses; do not report the average. The sample ID for field duplicate samples shall contain the suffix “FD”.

- If both the original and field duplicate values are \geq PQL, then the control limit for RPD is $\leq 50\%$,
- If one or both values are $<$ PQL, then do not assess the RPD.

If more rigorous field duplicate criteria are needed to achieve the project DQOs, then the criteria should be documented in the QAPjP/SAP.

10.4 Blanks

Two types of blank samples, instrument blanks and method blanks, must be analyzed with every XRF analysis. A third type of blank, the control blank used in the preparation of laboratory prepared calibration standards (LPCS), must be analyzed whenever LPCS are used in instrument calibration.

10.4.1 Instrument blank

The 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 Teflon block, a quartz block, “clean” sand, or lithium carbonate. This instrument must be analyzed on each working day before and after analyses are conducted and once per 20 samples. In addition, an instrument blank should be analyzed whenever contamination is suspected by the analyst. The analysis time must match that of the other project samples. Element concentrations must be below their respective MDLs. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not the problem, then the instrument must be “zeroed” by following the manufacturer’s instructions. The instrument blank analyses must meet criteria in order for the analysis to continue. All samples analyzed since the last compliant instrument blank must be re-analyzed in an analysis sequence which meets blank criteria.

10.4.2 Method blank

A method blank is used to monitor for sample preparation-induced contaminants or interferences. The method blank can be “clean” silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. Method blanks must be prepared at a frequency of 1 per group of samples prepared or 1 per 20 samples, whichever is more frequent. The method blank must not contain element concentrations greater than their respective MDLs. If concentrations exceed these limits, then the cause of the problem must be determined and corrected, and all samples associated with that method blank must be re-prepared and reanalyzed.

10.4.3 Control Blank

The clean soil or inert material used in LPCS preparation must be analyzed as a control blank, in accordance with Sections 8.2.2.1 and/or 8.2.2.2, immediately after the initial calibration.

10.5 Confirmatory Sample Analyses

Confirmation of XRF sample results using standard EPA method protocols is required and should support the project's data quality objectives. Confirmatory samples are splits of the thoroughly homogenized material obtained following sample preparation. In general, a frequency of a minimum of 1 per 20 samples or 1 per sample matrix, whichever is more frequent, is recommended. The confirmatory samples should be selected to include samples with element concentrations at or near site action levels. The choice of digestion and analysis methods, the frequency of confirmation sampling, and the comparability criteria for confirmatory analyses should be established at the scoping phase of the sampling and analysis event. Confirmation results should be validated in accordance with the most recent revision of the Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses and accompany the XRF final report upon their completion.

XRF field data shall be compared to the confirmatory results using Equation 4.

Equation 4 Confirmatory Analyses

$$\% \text{ Difference} = \frac{|C_1 - C_2|}{C_1} \times 100$$

Where:

C_1 = Concentration determined by full protocol confirmatory analysis

C_2 = Concentration determined by XRF analysis

Comparability criteria for confirmatory analysis must be established and documented in the QAPJP or SAP. Samples that exceed the criteria should be discussed in the final report.

10.6 Performance Evaluation Samples

Performance evaluation (PE) samples should be submitted for analysis on the X-MET 920 and to the fixed laboratory performing the full protocol EPA methods to provide information on the quality of the individual data packages in accordance with the EPA Region I Performance Evaluation Program Guidance. PE samples are certified standard reference materials (SRMs) from a source other than that used to calibrate the instrument. At least one PE sample should undergo both XRF analysis and confirmatory full protocol EPA method analysis to facilitate data comparability. A copy of the certified values for the SRM must be submitted with the final data packages to facilitate data evaluation.

10.7 Data Verification and Validation

Data should be verified daily, by a person other than that performing the work, to check for calculation and transcription errors and to ensure that all QC samples meet acceptance criteria.

All data must be validated in accordance with the Region I, EPA New England Data Validation Functional Guidelines for Evaluating Environmental Analyses.

10.8 Audits

10.8.1 Internal Audits

As part of the Quality Assurance/Quality Control Program for an XRF project, a series of internal audit checks should be instituted to monitor and maintain the integrity of the data. A daily QC review will insure that all QC samples met acceptance criteria and monitor any corrective actions taken and/or institute corrective action that should have been taken and were not. All corrective actions taken as part of an internal audit must be documented in the appropriate logbooks, and if these corrective actions impact the final data reported, then they must also be documented in the final report narrative.

10.8.2 External Audits

The Agency reserves the right to perform periodic field audits to ensure compliance with this SOP.

11.0 Sample Collection, Preservation, and Storage

Soil and sediment samples may be collected in either glass or plastic containers, or plastic zip-lock bags. Approximately 8 ounces of sample volume should be collected. This is equivalent to a sampling area approximately 4 inches by 4 inches square by 1 inch deep in size. Initial homogenization of the sample and removal of non-representative material should take place at the time of sampling.

To maintain sample integrity, chain-of-custody procedures must be implemented at the time of sampling to 1) document all sample locations and associated field sample identification numbers, 2) document all quality control samples taken, including field duplicates, split samples for confirmatory analyses, and PE samples, and 3) document the transfer of field samples from field sampler to field chemist and from field chemist to the fixed laboratory.

Samples may be stored at room temperature and have an indefinite shelf life. Mercury analysis has a six month holding time.

12.0 Sample Preparation and Analysis

12.1 Sample Preparation

12.1.1 Quantitative Analysis Preparation

Samples for quantitative analysis must be prepared in the identical manner as the SSCS. Field samples are spread out in a drying pan, clumps are broken up with a stainless steel spoon, and the sample is oven-dried at $< 150^{\circ}\text{C}$ for 2 to 4 hours to remove moisture. If mercury is to be analyzed, a separate sample must be air dried until the moisture content is $< 20\%$, as heating may volatilize the mercury. After drying, all large organic debris and non-representative material (sticks, twigs, leaves, roots, insects, asphalt, rocks, etc.) are removed and the sample is transferred to a mortar and pestle and ground to a uniform consistency.

The dried and ground sample is then sieved through a No. 60 (250 μm) mesh stainless steel sieve. At no time should the material be forced through the sieve. Pebbles and organic matter remaining on the sieve should be discarded. The under-sieve fraction of the material constitutes the sample. (Although a maximum final particle size of 60-mesh is normally recommended, a smaller sieve size may be used if the DQOs of the project dictate. Note, the identical sieve size must be used to prepare all samples and standards. Deviations in the sieve size and the reason for the change must be recorded in the sample preparation log and noted in the final report.)

Homogenize the sieved sample by placing 150 - 200 grams of 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.

Fill one or more XRF sample cups approximately 3/4 full with sample. Cut and tension (wrinkle-free) a piece of polypropylene film over the top of the cup and seal using the plastic film securing ring. Label the sample cups appropriately. Place the remaining sample in a clean labeled glass or plastic container for archival and possible confirmation analysis. The stainless steel sieve and spoons must be decontaminated between samples by washing with soap and water and drying.

12.1.2 Semi-Quantitative Screening Preparation

For semi-quantitative screening analysis, the collected sample is spread out in a pan, clumps are broken up with a stainless steel spoon, and sticks, stones, and other matter non-representative matter are removed from the sample. The sample is then thoroughly homogenized in the pan by dividing it into quarters and physically mixing opposite quarters with a clean stainless steel spoon. Re-composite and repeat the quartering process three times.

Fill one or more XRF sample cups approximately 3/4 full with sample. Cut and tension (wrinkle-free) a piece of polypropylene film over the top of the cup and seal using the plastic film securing ring. Label the sample cups appropriately. The remaining sample may be placed in a clean labeled glass or plastic container to be archived or submitted for confirmatory

analysis. The stainless steel sieve and spoons must be decontaminated between samples by washing with soap and water and drying.

12.2 Sample Analysis

From the main menu, arrow up to ANALYSIS and press "ENTER". Arrow down to the method you wish to use. Press F5 to toggle the printer on. Press "ENTER" to chose the method.

On the top of the screen you will see NAME >. Near the bottom of the screen is the method name chosen, the probe type, the analysis time, and "print" if the printer is activated. At the very bottom of the screen there are numbers 1-8 with soft key functions.

To analyze the sample, after NAME > type the sample name and then "ENTER". Wipe the bottom of the sample cup to be analyzed with a tissue to remove any dirt, dust or moisture and place cleaned sample cup into SSPS probe sample holder. Close the sample holder protective cover.

On the computer, press F1 to start (screen says set probe in measurement position), then press the red start button on the base of the probe. This starts the acquisition. The screen show s "measurement in progress" and in the top right corner is the analysis time countdown. When sample acquisition is complete, assay results and standard deviations are shown on the screen.

12.3 Analysis sequence

1. Verify instrument peak calibration by checking the Pb L_β line (Section 9.2.2)
2. Perform initial calibration using either quantitative or semi-quantitative calibration standards (Section 9.1).
3. Analyze the initial calibration verification (ICV) standard(s) (Section 9.1.2).
4. Analyze continuing calibration verification (CCV) standard(s) (Section 9.1.3).
5. Analyze 10 samples maximum. (Note, control blanks used in preparing LPCS, Section 7.2.2, should be analyzed at the beginning of the run sequence prior to sample analysis.)
6. Analyze CCV (continue 10 samples/CCV sequence)
7. Analyze last sample.
8. Analyze CCV
9. Verify instrument peak calibration by checking the Pb L_β line.

13.0 Documentation, Reporting Results, and the Final Report

13.1 Field XRF Final Report

13.1.1 Report Narrative

The final XRF data package must contain a report narrative that includes the following:

- The narrative must list all the sample numbers for the sample results being reported and include any pertinent information related to their sampling location (sampling map or written description).
- The narrative must identify the SSCS and field samples sent to the fixed laboratory for confirmation analysis and must reference the full protocol EPA digestion and analysis methods.
- The narrative must also include any comments related to problems encountered in sample preparation or analysis, any technical or administrative problems, and the corrective actions taken and/or the resolution of the problem.
- Discuss precision in terms of the daily precision tests performed and field duplicate analyses. Evaluate the impact on sample results.
- Discuss accuracy in terms of PE samples analyzed and confirmatory analysis results.
- Discuss sensitivity in terms of calibration response and evaluate the impact on sample results.
- Discuss data completeness in terms of the number of samples analyzed and successfully analyzed. Evaluate the impact on sample results.
- Discuss contamination in terms of blank contamination and evaluate the impact on sample results.

13.1.2 Sample Results

Tabulate all sample results. Quantitative results shall be reported in mg/Kg dry weight, and semi-quantitative results shall be reported in mg/Kg wet weight. Results < 1000 mg/Kg are reported to two significant figures and results \geq 1000 mg/Kg are reported to three significant figures.

- All values < MDL shall be reported as the MDL and flagged with the letter "U".
- All values \geq MDL and < PQL shall be reported as is and flagged with the letter "B".

13.1.3 Quality Control Results

- 13.1.3.1 Tabulate the initial calibration data for each target element, including the linear regression data indicating the correlation coefficient, standard error of fit, and the F-test value.
- 13.1.3.2 Tabulate all ICV and CCV percent recovery data. Include the true value, found value, % recovery, and control limits.
- 13.1.3.3 Tabulate all instrument and method blank results.
- 13.1.3.4 Tabulate all field and laboratory duplicate results. Include the original result, the duplicate result, the mean, the relative percent difference (RPD), the control limits, and the flag qualifier "*" for those results not meeting the control limits. Note, report duplicate results as separate field samples. The sample ID for the duplicate samples shall contain the suffix "FD" or "LD" for field duplicate or laboratory duplicate, respectively. Element results not meeting the control limits for duplicate analyses shall be flagged in the tabulated sample results, but only for the original and duplicate data result.
- 13.1.3.5 Tabulate all PE sample results. Include the true value, found value, % recovery, and control limits.

13.1.4 Raw Data

All raw data associated with the preparation and analysis of standards, QC samples, and field samples analyzed on the X-MET 920 must be submitted with the final report. The raw data shall include:

- 13.1.4.1 Instrument printouts from all standards, QC samples, blanks, and field samples analyzed. Instrument printouts shall include:
 - 1. Energy Spectra. The energy spectra must be labeled with the appropriate standard or sample ID and be scaled appropriately such that the energy peaks of interest are easily visible.
 - 2. Data. The data printout must indicate the standard or sample ID, the analysis date, and the peak energy information, including the associated target elements and intensity and/or concentration readouts.
- 13.1.4.2 Copies of all relevant standard, QC, and field sample Preparation Logbook pages. The logbook must include:
 - 1. Site name, CERCLIS number (if available), and EPA Site Manager
 - 2. Name and affiliation (EPA, Contractor company name, etc.) of analyst preparing the samples,
 - 3. Preparation date,
 - 4. IDs of all standards, QC samples, and field samples prepared (correlating to field location),
 - 5. IDs of SSCS and field samples sent to a fixed laboratory for confirmation analysis, and

6. Pertinent comments. Comments shall include a description of the samples (color, particle size: course/fine/clay, organic vs. sand/sediment, etc.), any problems encountered in preparation, the resolution of those problems, any deviations from the methodology and the reasons why, and all pertinent information related to the preparation of Laboratory Prepared Calibration Standards.

13.1.4.3 Copies of all relevant Analysis Logbook pages. The Analysis Logbook must detail the exact sequence in which all standards, QC samples, blanks, and field samples were analyzed. The logbook must include:

1. Site name, CERCLIS number (if available), and EPA Site Manager,
2. Name and affiliation (EPA, Contractor company name, etc.) of analyst preparing the samples,
3. Analysis date,
4. Radioisotope source used,
5. Report peak calibration results for the Pb L_β line. Indicate the peak energy reading and any recalibration steps taken, including a list of any samples requiring reanalysis.
6. IDs of all standards, QC samples, and field samples analyzed (include pertinent concentrations of standards and QC samples),
7. Data file IDs (if different than samples IDs) and any data disk storage identification, and
8. Pertinent comments related to the analysis. Comments shall include any problems encountered during the analysis, the resolution of those problems, any deviations from the methodology and the reasons why, and all pertinent information related to analysis decisions made during the run sequence.

13.1.4.4 Copies of all other relevant Field Logbook pages,

13.2 ICP/AA Confirmatory Data Package and Data Validation Report for SSCS

For full protocol EPA method analyses, complete data packages should be provided in accordance with the Region I, EPA-NE specifications contained in the Training Manual for Reviewing Laboratory Data Package Completeness, dated June 1994. Confirmation results should be validated in accordance with the most recent revision of the Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses. The complete confirmatory data package and validation report should accompany the XRF final report.

13.3 ICP/AA Confirmatory Data Package and Data Validation Report for Field Samples

Confirmation results should be provided and validated as specified in Section 12.4. In addition, confirmation results should be compared in tabular format against the XRF results as specified in Section 8.7 and these results checked against the comparability criteria established during the DQO phase of the project. The complete confirmatory data package, validation report and tabulated comparability results should accompany the XRF final report upon their completion.

14.0 References

- 1) Test Methods for Evaluating Solid Waste, Physical/Chemical Properties, SW-846, Method 6200, Draft Revision, March 1996.
- 2) X-MET 920 User's Manual, Metorex.
- 3) X-MET 880 Field Portable X-Ray Fluorescence Operating Procedures, U.S. EPA Environmental Response Team, SOP # 1707, Rev. 0.0, December 1994.
- 4) McGraw Hill Encyclopedia of Science and Technology, X-ray Fluorescence Analysis, Volume 14, 1971.
- 5) Guidance for the Data Quality Objective Process, QA/G-4, EPA/600/R-96/055, September 1994.
- 6) Region I, EPA New England Quality Assurance Project Plan Guidance, Draft October 1996.
- 7) Guidance for the Preparation of Standard Operating Procedures for Quality-related Operations, QA/G-6, EPA/600/R-96/027, November 1995.
- 8) Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses, July 1996.
- 9) Training Manual for Reviewing Laboratory Data Package Completeness, June 1994.
- 10) EPA Region I Performance Evaluation Program Guidance, July 1996.
- 11) U.S. EPA Code of Federal Regulations, 40 CFR, Part 136, Appendix B, Revised as of July 1995.