

Region 4
U.S. Environmental Protection Agency
Laboratory Services & Applied Science Division
Athens, Georgia

Operating Procedure

Title: Field X-Ray Fluorescence Measurement	ID: LSASDPROC-107-R6
Issuing Authority: Field Services Branch Supervisor	
Effective Date: April 22, 2023	Review Due Date: February 1, 2026
Method Reference: N/A	SOP Author: Kevin Simmons

Purpose

This document describes general and specific procedures, methods, and considerations to be used and observed when conducting field X-ray fluorescence (XRF) measurements of soil and sediment samples.

Scope/Application

The procedures contained in this document are to be used by field personnel when measuring metals concentrations in soil, sediment, or other solids in the field. On the occasion that LSASD field personnel determine that any of the procedures described in this procedure cannot be used to obtain metals analyses of the media being sampled, and that another method or XRF instrument must be used to obtain said measurements, the variant instrument and measurement procedure will be documented in the field logbook, along with a description of the circumstances requiring its use. While this SOP may be informative, it is not intended for and may not be directly applicable to operations in other organizations. Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

Note: LSB is currently migrating to a paperless laboratory. As a result, this SOP will allow for the creation of electronic tracking of standards and reagents in the LIMS to include stock material, intermediates and working material. Also permitted will be the use of electronic logbooks, checklists, and report forms as they are developed, which will also be housed in the LIMS and traceable to each sample and QC type within an analytical batch. LSB is committed to maintaining its quality system by continued traceability of reagents and standard material to NIST sources and the final reported results to the original samples as migration to an electronic system occurs.

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1. General Information

1.1. Documentation/Verification

1.1.1. This procedure was prepared by persons deemed technically competent by SESD management, based on their knowledge, skills and abilities and has been tested in practice and reviewed by a subject matter expert. The official copy of this procedure resides on the LSASD local area network (LAN). The Document Control Coordinator (DCC) is responsible for ensuring the most recent version of the procedure is placed on the LAN and for maintaining records of review conducted prior to its issuance.

2. General Precautions

2.1. Safety

2.1.1. Proper safety precautions must be observed when conducting field XRF measurements. Refer to the Region 4 Safety Manual and any pertinent site-specific Health and Safety Plans (HASPs) and/or Job Hazard Assessments (JHAs) for guidelines on safety precautions. It is recommended that users take the “Radiation Safety for Handheld XRF – X-Ray Tube” or other appropriate safety courses available on the Thermo Scientific™ website. These guidelines, however, should only be used to complement the judgment of an experienced professional. When using this procedure, minimize exposure to potential health hazards using protective clothing, eye wear and gloves. The operator should always be aware of the instrument’s orientation, the direction of its primary X-ray beam, when the primary beam is on or active, and the properties of the sample being analyzed. Address chemicals that pose specific toxicity or safety concerns and follow any other relevant requirements, as appropriate.

Number One Rule: The operator must **NEVER** aim the primary beam at themselves or others!

2.2. Procedural Precautions

2.2.1. All field XRF measurements pertinent to the sampling event are recorded in a bound field record logbook for the event. This record is created and maintained by the analyst providing the field XRF support. After the investigation is complete, the analyst will conduct post-processing of the field measurements and will enter final measurement data in the LSASD laboratory information management system and provide the LSASD project leader with a copy of the field measurement logbook. All other records and documentation of the investigation should be recorded according to the procedures outlined in the LSASD Operating Procedure for Logbooks (LSASDPROC-1002).

2.3. Limitations

2.3.1. There are three main sources of interference in XRF analysis that may impact data quality. They are sample preparation error, spectral interferences, and chemical matrix interferences.

- Preparation Error – The accuracy of the analysis is strongly impacted by sample homogenization. The more homogeneous the sample, typically analyzed by the cup method, the more accurate the results. There is no control of this limitation when conducting in situ analysis.
- Spectral Interference – Each element has a signature spectrum of energies and relative intensities. Many elements, however, produce X-rays of similar energy and discerning which element produced a detected X-ray is a factor of the detector's resolution capability and the software's ability to fit all of the data to the relative intensities produced by the various wavelengths.
- Chemical Matrix Interference – This refers to the effect that one element has on another in producing X-rays which reach the detector. Dominant elemental components of a sample, such as silicon in soils, vary in concentration from sample to sample and therefore so does that element's influence on the other elements in the sample.

2.3.2. There are several other limitations that the field investigator must be acutely aware of when conducting field analysis using XRF.

- Soil moisture – Excessive soil moisture biases the results low, i.e., the higher the soil moisture in a particular matrix, the lower the reported concentration relative to the actual concentration. This limitation may be overcome by drying the sample. Without sample drying, XRF measurement results for samples with typical soil moistures within the range of 15-25% are routinely reported at values less than laboratory confirmation analysis for the same samples. The actual difference may vary significantly for all samples from a site, but the XRF results reported by the instrument are typically on the order of 70-80% of the laboratory reported value for samples in this moisture range. This factor should be taken into consideration when making decisions based on XRF results.
- Lack of sensitivity with respect to certain analytes – Due to peak overlaps, some analytes may have problematically high detection limits, i.e., detection limits may be higher than project action levels for certain analytes, limiting its use for rapid field screening for certain elements. One of the most common examples of this phenomenon is the lead/arsenic analyte pair. When lead and arsenic are being analyzed, the peak overlap problem results in detection limits for arsenic that are several times higher than the typical action levels published for this analyte. It commonly is necessary to perform confirmatory

analysis in the laboratory to obtain analytical results for arsenic, or other analytes with high detection limits, to obtain data in the range necessary for making regulatory decisions.

2.4. Operational Checks and Quality Control

2.4.1. All XRF instruments shall be maintained and operated in accordance with the manufacturer's instructions, EPA Method 6200 and the LSASD Operating Procedure for Equipment Inventory and Management (LSASDPROC-1009). Prior to each operational period, the instrument is turned on and allowed to perform an internal calibration. Following this calibration, a performance check is conducted, using the appropriate National Institute of Standards and Technology (NIST)-traceable standard reference material for the analytes of concern, (i.e RCRApp 180-661). The value should be within +/- 20% of the stated value of the standard. Following this performance check, an instrument blank sample is analyzed to verify the instrument is not registering false positive results for the analytes of concern. After these checks, the instrument is ready for analysis.

2.4.2. The following operational and quality control requirements also apply to operation of the XRF instrument and should be followed and documented in the field logbook maintained by the analyst:

- During operations, the ambient air temperature will be recorded for each measurement and if the ambient temperature changes by more than 10°F, the instrument will be recalibrated.
- While the instrument is being used, the reference standards and the blank are run at the beginning of each workday, every 4 to 5 hours of analysis time, after the instrument has been off for 1 to 2 hours or if the battery has been changed, and also at the end of the period of operation, prior to turning the instrument off.
- For every twenty samples, or at least once per day, analyze a duplicate using the main sampling technique.
- Once per day, check the instrument's precision by analyzing one of the site samples at least seven times in replicate. This requirement should be done when possible, depending on field conditions and sample load.

2.4.3. EPA Method 6200 contains detailed instruction and guidance covering implementation of these procedures and any corrective actions that must be taken based on measured instrument behavior and performance. If at any time during a field investigation, it appears that the environmental conditions could jeopardize the quality of the measurement results, the measurements will be stopped. This will be documented in the field logbook.

2.4.4. In addition, the Region 4 Superfund X-Ray Fluorescence Field Operations Guide (XRF FOG), Most Recent Version, contains additional information, guidance, and QC procedures specific to analyzing soil samples by XRF.

3. Field X-Ray Fluorescence (XRF) Measurement Procedures

3.1. General

3.1.1. XRF is the property of a material to emit X-rays, with a characteristic energy, upon being irradiated by X-rays of a known source and energy. The emitted X-rays are detected by the particular XRF instrument as they impact a detector, which converts the energy of the emitted X-ray into electric current. The strength of the current is proportional to the energy of the X-ray. An onboard microprocessor counts how often an energy is detected, assigns the energy to a particular element and reports the calculated concentration for the element.

3.1.2. The XRF instrument available for use by LSASD field investigators is the Thermo Scientific™ Niton™ XL3t 955 Ultra Series Multi-element XRF Spectrum Analyzer. This instrument uses a miniaturized X-ray tube as its source rather than a radioactive isotope for X-ray generation for analysis.

3.2. Mode of Operation

3.2.1. The instrument is typically used in one of two modes, either for taking in situ measurements or ex situ (measuring sample material that has been placed in a cup or bag for analysis in an instrument tray). The following is a brief description of these modes of operation.

3.3. In Situ Measurement

3.3.1. Prior to taking the in-situ measurement, the measurement location is cleared of any significant vegetation, such as large clumps of grass, and is scuffed or otherwise leveled to provide a flat surface on which to place the instrument window. A piece of thin Mylar® film is then placed on the measurement location. This protects the instrument window, preventing it from becoming damaged or contaminated by the media being tested. After the window is pressed to the Mylar® film, the window is opened for a nominal (i.e., programmed) sixty seconds.

3.3.2. Because of the shallow penetration of the X-rays in typical soils, the measured concentrations are representative of the concentrations present at the very surface of the material being measured. If conditions representing concentrations over a greater depth are required by the study data quality objectives (i.e., on the order of three to six inches), the cup method, described in Section 3.4, must be used.

3.4. Collected Sample (Ex-Situ) Measurement

- 3.4.1. This method is used to measure concentrations of metals in soil and sediment samples collected from a vertical interval, either as a grab or a composite sample. Typically, soil or sediment samples are collected as if the samples were being collected for routine chemical analyses LSASD Operating Procedure for Soil Sampling (LSASDPROC-300) and the LSASD Operating Procedure for Sediment Sampling (LSASDPROC-200). After mixing, the media being sampled may be placed in either an 8-ounce glass container or a clean, unused zip-closure plastic bag (or equivalent). The XRF analyst then takes an aliquot from the container and places it in a small plastic cup with a Mylar[®] covering. The cup containing the sample is then loaded into a tray for analysis by the XRF instrument. Alternatively, if project objectives allow, measurements may be obtained by reading directly through the plastic bag. Window opening time considerations are the same as for the in-situ measurement procedures described in Section 3.3.
- 3.4.2. The concentrations reported for the samples analyzed by the cup method are representative of the interval sampled, i.e., if the sampler collected the sample from the interval of 0 to 3 inches below ground surface, the reported concentration, assuming thorough homogenization, will be an average of the concentrations over that interval.
- 3.4.3. The Region 4 Superfund X-Ray Fluorescence Field Operations Guide (XRF FOG), Most Recent Version, contains additional information, guidance, and QC procedures, including spreadsheets available from the Region 4 Scientific Support Section, specific to ex-situ soil analysis by XRF. This XRF FOG should be consulted in addition to this SOP when planning and conducting XRF analysis.

4. Study Design

4.1. General

- 4.1.1. XRF instruments are typically used for two main purposes. First it may be used to rapidly assess site conditions to support a site reconnaissance. Secondly, it may be used to screen large numbers of soil or sediment samples to minimize the number of samples that are sent to a laboratory to provide detailed site characterization data. These uses are summarized in the following sections.

4.2. Reconnaissance

- 4.2.1. XRF may be used to obtain in situ measurements at a large number of locations in a short period of time to determine if a site warrants further attention with respect to characterization. When used in concert with GPS, and when observing the limitations described in Section 2.3, XRF can reveal, where present, contamination patterns at a site which can form the basis for development of a more detailed study

to provide definitive data for site characterization. Conversely, the reconnaissance results may form the basis for a “no further action” decision, providing a very cost-effective tool for the decision maker.

4.3. Screening Support for Definitive Level Site Characterization

- 4.3.1. XRF may be used to supplement laboratory analyses to allow for the collection of large numbers of samples to provide a detailed characterization of a site. A high sample density grid or sampling pattern is created to provide adequate detail to meet the data quality objectives of the study or investigation. This sampling pattern may also involve the collection of significant numbers of subsurface soil samples to characterize any contamination present in the subsurface.
- 4.3.2. All samples, collected according to procedures found in LSASD Operating Procedure for Soil Sampling (LSASDPROC-300) and LSASD Operating Procedure for Sediment Sampling (LSASDPROC-200), are delivered to the XRF analyst on site. The analysis of these samples is conducted according to the method described in Section 3.4 of this procedure.
- 4.3.3. Based on the limiting factors described in Section 2.3, a confirmatory analytical scheme can be developed which minimizes the numbers of samples that must undergo laboratory analyses, yet provides definitive level data, with a high degree of confidence, to the project leader and other decision makers. Using the moisture limiting factor, there is usually a high degree of confidence that samples screened at concentrations less than 70-80% of the site action level will not exceed the action level. Of the samples that screen at or within 20-30% of the action level, most all, with a high degree of confidence, exceed the action level. If a reconnaissance is conducted prior to the full-scale site investigation, in addition to the in-situ analysis, it is advisable to collect and analyze a small subset of the screened locations to generate site-specific moisture limiting factors. This correlation factor can be used to develop a sampling scheme with more confidence.
- 4.3.4. Using these relationships, the following scheme may be implemented:
- Ten percent of the samples that screen at concentrations less than approximately 70-80% (or other correlation factor developed on actual data) of the site action levels are submitted for confirmation analyses to confirm that concentrations are, in fact, below the site action levels.
 - All of the samples that screen at concentrations of 70-80% (or other correlation factor developed on actual data) of the action level up to the action level value are submitted for confirmation analyses to confirm that concentrations are, in fact, equal to or greater than the site action levels.

- Ten percent of the samples that screen at concentrations exceeding the action levels are submitted for confirmation analyses to confirm that concentrations are, in fact, greater than the site action levels.

References

LSASD Operating Procedure for Equipment Inventory and Management, SESDPROC-108, Most Recent Version

LSASD Operating Procedure for Logbooks, LSASDPROC-1002, Most Recent Version

LSASD Operating Procedure for Sediment Sampling, LSASDPROC-200, Most Recent Version

LSASD Operating Procedure for Soil Sampling, LSASDPROC-300, Most Recent Version

United States Environmental Protection Agency (US EPA). Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment, Method 6200, Revision 0, February 2007.

Quality System and Technical Procedures for LSASD Field Branches. US-EPA Region 4 Laboratory Services & Applied Science Division (LSASD), Athens, GA. Most Recent Versions.

US EPA. Region 4 Safety Manual. Region 4 LSASD, Athens, GA, Most Recent Version.

Region 4 Superfund X-Ray Fluorescence Field Operations Guide (XRF FOG), Most Recent Version.

Thermo Scientific™ Safety Training found at:

<https://www.thermofisher.com/us/en/home/industrial/spectroscopy-elemental-isotope-analysis/portable-analysis-material-id/xrf-radiation-safety-training.html>

Revision History

History	Effective Date
Replaced Chief with Supervisor; General formatting revisions.	April 22, 2023
<p>LSASDPROC-107-R5, Field X-Ray Fluorescence Measurement, replaces SESDPROC-107-R4</p> <p>General: Corrected any typographical, grammatical and/or editorial errors. SOP Title block and document formatted into the new SOP format. Throughout the document SESD was changed to LSASD. Left justified text to make document easier to read.</p>	February 2, 2022
<p>SESDPROC-107-R4, Field X-Ray Fluorescence Measurement, replaces SESDPROC-107-R3</p> <p>General: Corrected any typographical, grammatical and/or editorial errors. Throughout the document references were added to reference the Region 4 Superfund X-Ray Fluorescence Field Operations Guide (XRF FOG).</p> <p>Section 2: Omitted second bullet. Revised third bullet to up update the frequency that reference standards and blanks are run.</p> <p>Section 3.2: Added “or bag” to first sentence of paragraph.</p> <p>Section 3.2.2: Added “(Ex-Situ)” into Section title.</p>	September 8, 2017
SESDPROC-107-R3, Field X-Ray Fluorescence Measurement, replaces SESDPROC-107-R2	December 18, 2015
SESDPROC-107-R2, Field X-Ray Fluorescence Measurement, replaces SESDPROC-107-R1	December 20, 2011
SESDPROC-107-R1, Field X-Ray Fluorescence Measurement, replaces SESDPROC-107-R0	November 1, 2007
SESDPROC-107-R0, Field X-Ray Fluorescence, Original Issue	February 05, 2007

Note: SOP section references prior to the February 2, 2022, update are from the old SOP form.