

Appendix E
X-Ray Fluorescence

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Appendix E

X-Ray Fluorescence

The purpose of this appendix is to identify the parameters that must be considered when applying the x-ray fluorescence (XRF) analytical method at a field site to achieve the necessary quality of chemical data for soils and other heterogeneous solids to meet project objectives. This appendix presents information about the use of XRF based on two extremes: enforcement-quality on-site analysis and field screening analysis. It is a supplement to existing EPA guidance providing procedures for determining a quantifiable degree of certainty upon which to make site-specific decisions focusing on the use of the XRF method of analysis at the site.

E.1 Introduction

XRF technology has greatly expanded since Moseley discovered the importance of x-ray spectra in 1913. Instruments with reduced detection limits have been developed for a broad spectrum of elements and have become portable. XRF instruments can now be taken to the sample by a single individual and a screening analysis performed in less than a minute, with reasonable precision and accuracy.

XRF is being applied to Remedial Investigation/Feasibility Study (RI/FS) and cleanup sites to increase the representativeness of sampling, expedite the activity by performing real-time data analysis to support decisionmaking, and decrease both the time and cost of these activities. XRF analytical determinations are nondestructive and total analyses of chemical elements require minimal sample preparation. Consequently, XRF instruments are finding increased use in environmental studies.

Application of the XRF method depends on the project objectives and associated data quality objectives. The decision to use XRF at a site may occur during the first stage of developing the data quality objectives, but the application is generally defined in the second and third stages.¹ As with any method of analysis, precision and accuracy start with the sample collection and continue through each stage of the analysis until the chemical data are reported. Comparability of data produced by XRF with data from EPA's Contract Laboratory Program (CLP) has been established by field tests of XRF instruments. Representativeness and completeness are two of the major advantages of XRF use. On-site, real time chemical analysis can document representativeness and allows critical samples to be collected and analyzed, which typically ensures completeness.

E.2 Elements of Interest and Detection Limits

Radioisotope sources used in field-portable and semi-portable instruments include iron-55, cadmium-109, americium-241, and curium-244. Different sources are used for different elements of interest. For example, Cd109 and Cm244 are typically used for chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, and lead, and Am241 is typically used for silver, cadmium, antimony, and barium.

¹ U.S. Environmental Protection Agency, 1987, Data Quality Objectives for Remedial Response Activities, Development Process: EPA/540/g-87/004 (OSWER Directive 9355.07B).

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EPA's Environmental Monitoring Systems Laboratory (EMSL) has produced a sampling and analysis protocol for the use of a field portable XRF. Examples of the chemical analysis by a field portable instrument are documented to produce instrument detection limits of 15 to 90 milligrams per kilogram (mg/kg) for arsenic (two sites) and 30 to 140 mg/kg for lead, copper, zinc, and iron.² Typical method detection limits are not less than 50 mg/kg with a coefficient of variation between 5 and 10 percent but are often in the 100 to 200 mg/kg range with a coefficient of variation of 3 to 25 percent. The increase in detection limit is a result of using a lower x-ray source (radioisotopes) and a gas proportional detector in the field portable XRF instruments.

Prototype lithium drifted silicone (Si(Li)) probes are being developed that have the potential to lower the detection limit to less than 100 mg/kg for most heavy metals (copper, zinc, arsenic, lead, etc.).³ A semi-portable unit is currently available that uses sample cups for sample input rather than a surface probe. The semi-portable XRF instrument probably has an intermediate detection limit range between the field portable and the mobile unit. However, in selected instances, the semi-portable instrument may function almost as well as the mobile XRF instrument for selected elements. Similar to the field portable instrument, the semi-portable instrument uses a radioisotope as a source.

Mobile laboratory results have well-documented lower limits of detection of 4 mg/kg for cadmium, 7 for lead, 12 for arsenic, 19 for zinc and iron, 21 for manganese, and 26 for copper.⁴ In these tests, the samples were sieved and pulverized to a powder. A fundamental parameters model was used to calculate concentration from measured XRF intensity.

E.3 Equipment Options and Turnaround Times

Media that are commonly appropriate for XRF analysis include soils, in particular, but essentially all solids, as well as liquefied solids, such as sludges and slurries. Detection limits extend from mg/kg (parts per million) to the 100 percent range for mobile XRF instruments and from tens to hundreds of mg/kg to 100 percent for field portable instruments. These detection limits are not appropriate for typical surface and ground water; therefore, CLP laboratories are recommended for samples of these media. Samples analyzed by XRF, especially critical samples, are submitted to a CLP laboratory or equivalent laboratory for calibration and consultary chemical analysis.

Field portable instruments are more useful than mobile instruments in a site investigation. Field-portable instruments are those equipped with radioisotope source(s), generally gas proportional tube detectors, usually weighing less than 20 pounds (including batteries) and can be carried in one hand to the sample location. Semi-portable instruments are those instruments

² Chappell, R.W., Davis, A.O., and Olsen, R.L., 1986, Portable X-Ray Fluorescence as a Screening Tool for Analysis of Heavy Metals in Soils and Mine Wastes: Proc. Natl. Conf. on Management of Uncontrolled Hazardous Waste Sites, Washington, DC, pp. 115-119.

³ Piorek, S., and Pasmore, J.R., 1991, A Si(Li) Based High Resolution Portable X-Ray Analyzer for Field Screening of Hazardous Waste: Second Intl. Symposium, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, EMSL, Las Vegas, NV, 5p.

⁴ Harding, A.R., 1991, Low Concentration Soil Contaminant Characterization Using EDXRF Analysis: Second Intl. Symposium, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, EMSL, Las Vegas, NV, 7p.

that may be equipped with radioisotopes but are equipped with a Si(Li) detector, weighing more than 20 pounds (including batteries) but can still be carried by one person to a site, and samples are placed in a cup for analysis by the instrument. Mobile instruments use an x-ray-tube for the x-ray source and, therefore, require line voltage, and are usually placed within a specific building near or at the site to generate enforcement quality data. Instruments can also be installed in a van. They can be moved from site to site but normally would be retained at a site until analytical data are no longer necessary (potentially months).

An initial field investigation using a field portable XRF involves gridding the site and determining relative concentrations for a suite of elements at all points in the grid. Hot spots are identified and their nature and extent characterized before leaving the field. A suite of representative samples are collected and sent to a CLP laboratory for a "broad spectrum analysis" that documents the concentrations of hot spot and peripheral elements for the site. Contaminated areas of concern within the site are thereby documented from the initial XRF work by converting field readings to absolute concentrations with a known, documented accuracy and precision.

Mobile XRF instruments are more appropriate for sites undergoing cleanup activities. A mobile XRF instrument can be installed in a section of a typical room near the site. Samples can be collected, prepared, brought to the instrument, and analyzed in a matter of a few hours. Analytical quality can be comparable to a CLP or equivalent laboratory. Comparability is documented by split samples sent to a CLP laboratory. Decisions concerning the attainment of an action level can be made quickly at the site. Coupling the use of a field portable and mobile laboratory instruments at a site would allow almost immediate decisions to be made concerning an action level in the field that can be confirmed by the mobile laboratory doing routine remedial action samples. Ultimately, a representative composite sample from the site area under remedial action is sent to the CLP or equivalent laboratory for final documentation of the clean up level.

E.4 Special Considerations When Using XRF

All XRF instruments begin with the total counts received by the detector for an energy that is specific for each element. The detection limit, accuracy, and precision of the measurement is directly determined by the magnitude of the total counts and resolution width of the peak. The total counts are expressed as intensity in counts per second.

The analytical capability of an XRF instrument depends on excitation source, source-to-sample geometry, instrument stability, counting time, and sample matrix. Commercial instruments are available for both enforcement and screening analysis. Analysis for enforcement data requiring low concentrations of a broad spectrum of selected elements (on the order of 10 mg/kg) uses semi-mobile, x-ray-tube-sourced instruments equipped with crystal detectors (for example, Si(Li) detectors). Analysis for screening data allows a broad spectrum of elements to be semiquantitatively determined using radioactive sources that are limited by safety regulations to 5 and 6 orders of magnitude lower x-ray emission than x-ray tubes. This limitation is partially compensated for by the nearly monochromatic x-ray source with closer source-to-sample geometry that allows a reasonably low detection limit for many elements. High resolution gas--proportional tubes are the most common detectors but Si(Li) detectors are available for both semi-portable and most recently for portable instrumentation.

E.4.1 Site-Specific Calibration Samples

An initial set of site samples is required for calibration purposes. The samples should cover the matrices and concentration range of elements of concern as determined by a total metals (hydrofluoric acid digestion) analysis by a CLP or equivalent laboratory. The samples should be prepared by the laboratory using the same protocol that will be used at the site. This initial set of samples is best collected using the field screening instrument to determine that samples are representative of media (potential for stratification), elements of concern, and concentration ranges. Similarly, preparation of samples for XRF analysis by the field preparation facility is preferable to preparation by a fixed laboratory using other equipment and protocols. EMSL has protocols for the collection, preparation, and analysis of a suite of site-specific calibration standards.

E.4.2 Sample Preparation

At the sample location, a field-portable instrument is equipped with a probe that allows considerable flexibility in how a sample is presented to the source. It may be pressed against the media of interest (soils, tailings, walls, etc.) or a sample cup of material (soil, slurry, sludge, etc.) can be placed on top of the source. Samples may be sieved or pulverized but sample preparation is typically minimal. Field-portable instruments are versatile but have the highest detection limits of the three types of instruments. Typical detection limits with little to no sample preparation are in the 100 mg/kg range, depending on sample matrix. Instruments vary in the amount of data processing that they provide. Some give minimal processing, reporting in intensity (total counts or total counts divided by backscatter). Others are capable of processing the data to report in mg/kg concentration units.

The semi-portable instruments have a potential detection limit equal to that of the larger mobile instruments. The semi-portable instrument requires the use of a sample cup, therefore, some preparation may be necessary unless the sample particle size is small enough to be placed in a sample cup (soils, slurries, liquids, etc.).

For mobile instruments, sample preparation is part of the analytical schedule and includes sieving and pulverizing. A CLP level of quality control is used and data are typically processed through a computer for conversion to mg/kg concentration units. Fundamental parameter computer models are commonly used. A typical detection limit will range from 5 to 30 mg/kg, depending on the sample matrix. Sample preparation may include making pressed powder briquettes for analysis, but does not typically extend to fusing or dissolution. If these more aggressive techniques are required to achieve enforcement quality data, commercial laboratories are better equipped to prepare and analyze the samples.

E.4.3 Interferences

The overlap of fluorescence peaks must be corrected for in both screening and quantitative XRF analytical work. This effect is responsible for more errors in reporting analytical results than all the other effects combined. Comparing the peak energy levels of the element of interest with other peaks for the same or nearly the same energy level is a trivial but extremely important aspect of using the XRF for the analytical determination of any element.

One of the most commonly encountered peak overlaps is that between the k-alpha peak for arsenic (10.5 keV) with the l-alpha peak of lead (also 10.5 keV). The overlapping peaks for both elements are the peaks contributing the highest primary fluorescence. If both arsenic and

lead are present in variably high concentrations at a site, the k-beta peak for arsenic (11.8 keV) and the l-beta peak for lead (12.6 keV) are used or the overlap peak is separated by mathematically subtracting the lead contribution to the overlapped peak intensity. The arsenic k-beta peak has only about 15 percent of the k-alpha peak intensity. The lead l-beta peak has about two-thirds of the l-alpha peak. Therefore, even though the l-level peaks are lower in intensity than that of k-level peaks, the detection limit for lead is less affected by the lower energy peak than the arsenic. Other elements will involve peak overlap and can usually be handled in a similar fashion.

E.4.4 Sample Variance Calibration

Sample preparation and particle size variance are major potential sources of error. If enough of the original suite of calibration samples has been collected, they are the preferred suite for determining potential sources of error in sample preparation. If volatile elements are involved (or mercury and arsenic to a lesser extent) sample drying should be performed at approximately 85 degrees celsius or less). Air drying versus any other method of drying should be investigated. If samples are to be split, stored for long periods of time, or transported from one point to another, they should be homogenized before any other preparation procedure. Complete mixing is imperative if a representative sample is to be prepared or analyzed.

Particle size variance is a two part problem. The first part concerns the field particle size that potentially contains most of the elements of concern. The second concerns the pulverized particle size. To determine the field particle size distribution, a suite of approximately 10 samples should be selected that cover the media, elements, and concentration ranges of a primary metal of concern. Each of the samples should be wet sieved through a minimum of three sieve sizes. For example, 8, 80, and 200 mesh sieves could be selected. A sample of the unsieved material (with root mat, pebbles, and extraneous material removed) and each size fraction is pulverized using the design protocol for pulverization. A split should be analyzed by both the XRF and a CLP laboratory (using the hydrofluoric acid digestion method for total metals). In some instances, sieving is preferable to pulverizing.

Particle size is one of the operator-controlled heterogeneity effects that is the most difficult to deal with without resorting to fusion or dissolution, both of which are time-consuming laboratory procedures. Particle size effects are minimized by using a rigidly consistent procedure for both sample preparation (drying, disaggregating, pulverizing, etc.) and pelletizing a constant volume of sample. In most instances, pelletizing is necessary for defensible quantitative chemical analyses. Liquids and properly prepared soils are potential exceptions. Site-specific samples should be used for the determination of potential particle size effects.

E.4.5 Counting Time

There are two methods of controlling the coefficient of variation or relative percent difference (RPD) of the analytical results generated by an XRF instrument: fixed count time or fixed count. Most operators of XRF instruments use a fixed counting time instead of a fixed count because fixed count may require very long counting times. The fixed count time allows a known RPD to be calculated and sample turn-around time to be managed. The statistical error is equal to the inverse of the square root of the total counts. For example, a total count of 1,000 would produce a relative standard deviation of approximately 3 percent; 100 counts, 10 percent, and 10,000 counts, 1 percent.

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X-ray tubes, with their higher x-ray flux can produce much higher counts than radioisotope sources, and therefore, the detection limit, precision, and accuracy of instruments equipped with these sources are, accordingly, comparably higher. Typically, 200 second counting times are used for enforcement analysis using mobile instruments. On the other hand, screening analysis using field portable instruments rarely uses counting-times of more than 100 seconds to make effective use of field time. In addition to the other factors described in this section, the counting time is one of the major reasons for differences in the quality of analytical data.

E.5 Quality Control

Exceptionally high expectations and indiscriminate use of the instruments outside the design limits has sometimes led to discouragement in the application of field-portable XRF instruments. Litigation-defensible quantitation limits are possible for selected elements using properly applied field-portable instruments. Although a particularly low detection limit may not be achievable in some cases, the instrumentation will usually determine hot spot areas, document that representative sampling has been accomplished, and determine that an action-level for a particular element has been reached in real time at the location.

Confirmatory analyses are performed by a CLP or comparable fixed analytical laboratory. A comparable metals analysis would require the addition of hydrofluoric acid to the normal CLP digestion. Typically, there are no differences between the methods for most metals but some metals (for example, chromium) can occur as a refractory phase that is fully digested by the normal CLP analysis.

Commercial laboratories are an integral part of the use of any of the sampling instruments. The calibration and verification of analytical data generated by the use of the XRF instruments depend on laboratory determination of the same elements. Samples sent to the laboratory for these purposes must be the same samples analyzed by the XRF. Sample splits are acceptable but duplicate samples should not be used for these purposes without the support of splits. Homogenization at the laboratory is even more important than for the XRF because a smaller sample is typically used at the laboratory than for the XRF sample. A total digestion of the sample is necessary, involving hydrofluoric acid in the digestion process. EMSL has an excellent protocol for the preparation of samples for both XRF and specifications for the laboratory. The laboratory should also analyze a subset of approximately 20 samples covering the range of elemental concentrations of concern to determine if a difference exists between normal CLP total metals analysis and hydrofluoric acid digested total metals.

E.6 Examples of Site Projects Using XRF

The total extent of XRF application to abandoned mine sites is undoubtedly larger than the published accounts of such applications. Documented use of field-portable XRF instruments start in 1985 with the Smuggler Mountain Site near Aspen, Colorado.⁵ The instrument was used to determine action-level boundaries of 1,000 mg/kg lead and 10 mg/kg cadmium in soils and mine waste. The same site was used for the evaluation of a prototype field-portable XRF

⁵ Mernitz, S., Olsen, R., and Staible, T., 1985, Use of Portable X-Ray Analyzer and Geostatistical Methods to Detect and Evaluate Hazardous Materials in Mine/Mill Tailings: Proc. Natl. Conf. on Management of Uncontrolled Hazardous Waste Sites, Washington, DC, pp. 107-111.

instrument specifically for hazardous waste screening⁶. Field-portable instruments have also been used at the California Gulch Site, Leadville, Colorado; Silver Bow Creek and other sites near Butte, Montana; Bunker Hill Site, near Kellogg, Idaho; and the Cherokee County Site, Tri-State Mining District, Kansas for screening purposes during nature and extent RI/Fs.

A field-portable instrument has been used to screen a large area (21 square miles) to select large, homogeneous volumes of heavily contaminated soils for treatability studies and for Site Comparison Samples at the Bunker Hill Site.⁷ Portability and "real-time" basis data were necessary prerequisites.

A mobile XRF instrument was used for multi-element analysis of lead, arsenic, chromium, and copper in soils.⁸ Detection limits with the x-ray-tube-source and Si(Li) detector were as low as 10 mg/kg. The data were used to map the extent of contamination within a superfund site.

Detection limits for field-portable instruments are not low enough to determine cadmium concentrations as low as 10 mg/kg in some areas/matrices, but zinc was found to be a good surrogate indicator element for cadmium in Cherokee County, Kansas. Unlike anthropogenic organic solvents that can occur as discrete species (with degradation even organics have multiple compounds), inorganics, particularly metals, share interrelated characteristics of migration that allow detection through other associated elements that occur at higher, detectable concentrations.

⁶ Raab, G.A., Cardenas, D., Simon, S.J., and Eccles, L.A., 1987, Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening: EMSL, EPA 600/4-87/021, U.S. Environmental Protection Agency, Washington, DC, 33 p.

⁷ Barich, III, J.J., Jones, R.R., Raab, G.A., and Pasmore, J.R., 1988, The Application of X-Ray Fluorescence Technology in the Creation of Site Comparison Samples and in the Design of Hazardous Waste Treatment Studies: First Intl. Symposium, Field Screening Methods for Hazardous Waste Site Investigations, EMSL, Las Vegas, NV, pp. 75-80.

⁸ Perlis, R., and Chapin, M., 1988, Low Level XRF Screening Analysis of Hazardous Waste Sites: First Intl. Symposium, Field Screening Methods for Hazardous Waste Site Investigations, EMSL, Las Vegas, NV, p. 81-94.

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