



Innovative X-ray Technologies

Metals in Soil Analysis Using Field Portable X-ray Fluorescence

A guideline to using portable XRF according to EPA Method 6200, basic overview of the technique of x-ray fluorescence (XRF), appropriate data quality assurance protocols and sample preparation steps for operators analyzing prepared soil samples.

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Section 1: Regulatory Status for Field Portable XRF

EPA Reference Method 6200 has been incorporated into SW486 under RCRA, and is now available for field portable XRF analysis of soils and sediments. Please call or email Innov-X Systems for a copy of Method 6200.

Method 6200: Field Portable XRF Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.

Features of this method:

1. It is a field screening method, for analysis of *in-situ* or bagged samples.
2. The method provides basic quality assurance methods, including calibration verification, determination of instrument precision, accuracy and limit of detection.
3. The method recognizes that some XRF instruments do not require site-specific calibrations by the operator, that is, the factory calibration provides appropriate data quality.
4. The method recommends that a minimum of 5-10% of samples tested by XRF be confirmed by an outside laboratory using a total-digestion EPA analytical reference method.

The purpose of EPA Method 6200 is NOT to replace laboratory analysis. There are two primary sources of error in assessing a site for metal concentration: **Analytical error** and **Sampling error**. Analytical error is the error in the analysis of any one sample by whatever technique is used, for example XRF, ICP, or AA. Sampling error arises when too few samples were collected and tested. In this case an incomplete picture of the extent of metals contamination may be obtained. Although any one sample may be analyzed very accurately (high analytical accuracy), if not enough samples are analyzed, contamination plumes may be mis-judged in size, depth into the soil, or even missed entirely.

EPA Method 6200 was developed to reduce Sampling Errors. Portable XRF is an ideal tool to make a large quantity of measurements in a short period of time. A large number of *in-situ* samples provides detailed data on contamination profiles, depth (provided surface soil is moved aside), and approximate contamination levels. This is because, in general, a large number of screening-level measurements provide a better characterization than a small number of measurements produced by sample removal and analytical analysis.

Portable XRF also can provide results with a high degree of analytical accuracy on any given sample. Please see Section 2 "Overview of Field Usage" for this discussion.

Section 2: Overview of Field Usage:

Field portable XRF is generally used in three ways to test for metals in soil:

- ❑ **In-situ soil testing:** Placing the XRF directly onto the ground to do soil testing. Operators remove any plant growth and foreign objects so that the analyzer probe is flush to the soil.
- ❑ **Bagged soil sample testing.** Collecting a soil sample in a thin plastic bag (i.e. a “Baggie”) and testing directly through the Baggie. Except for a few elements – namely Cr, V and Ba – testing through the thin plastic used for a plastic bag has little effect on the test result. Results for Cr, V and Ba will be lower by 20-30%.
- ❑ **Testing prepared soil samples.** Prepared sample testing assures the operator of the maximum possible accuracy. Prepared sample tests require a sample to be collected, dried if necessary, sieved and ground into a powder. The prepared sample is then placed into a baggie or XRF cup for analysis. **A complete Soil Preparation Guide is provided in Appendix 1.**

All analytical methods require a uniform, homogenous sample for the best results. **XRF is no different!** In-situ and bagged sample testing are considered field-screening methods. These are the methods described in EPA Method 6200. Although a field-screening method, in-situ testing is a valuable technique because it generates a great deal of data very quickly. Prepared soil samples generally offer the best accuracy, albeit with several minutes of sample preparation required per sample.



Figure 1. Use of a field portable XRF for in-situ soil testing.

Subsection 2-A: Data Quality Objectives.

The objectives of the testing generally determine the mixture of in-situ versus prepared sample testing. It is important to understand your data quality objectives (DQO) in order to determine the appropriate mix of field screening versus prepared sample testing.

In-situ testing usually only provides screening-level data quality. This is because analytical testing always requires a uniform, homogeneous sample matrix. A laboratory achieves this by digesting the sample into a hot acid before analysis. Testing directly on the ground does not ensure uniformity is met. Preparing a sample provides a uniform sample and likely better analytical data quality, although several minutes of testing time is required.

Most portable XRF operators use a mixture of in-situ and prepared sample testing. Several examples are described below. The exact mixture of in-situ and prepared sample testing depends upon the goals of the soil testing. The examples below serve as guidelines. Please contact Innov-X (1-866-4 Innov-X or 866-446-6689) to discuss your specific testing requirements.

Example 1: Initial site investigation to provide detailed contamination data with efficient use of laboratory analysis costs.

Problem: Site needs to be assessed for metals contamination. Little information is available about what metals are present, likely contamination levels or geographic profile of contamination.

Goal of testing is to determine what metals are present at what levels, both in area and in depth into soil. Also locate possible contamination plumes and/or possible sources of contamination.

Recommended Testing Plan: This example uses predominately in-situ testing. Operator testing would be mainly in-situ testing, or gathering samples into plastic bags for XRF analysis. A testing grid can be established in two or three dimensions, every several feet. XRF tests can be taken at each location or bagged samples collected from each location for later analysis. The in-situ data for each element analyzed may be plotted in a 2-dimensional grid (X, Y coordinates versus elemental concentration) to profile a site. These concentration profiles are ideal for showing contamination patterns, boundaries and plumes. Combining this data with historical use data from the site often allows the operator to deduce sources of contamination. Obtaining this level of geographic data with purely laboratory analysis would produce excessive analytical costs.

Prepared sample analysis should also be done to confirm the regions where in-situ data indicates low or non-detected levels of metal contaminant. There is little need to prepare areas where in-situ testing indicates high concentration levels. Innov-X recommends the same procedure as EPA Method 6200. For locations where in-situ tested indicated low or non-detected concentrations, calculate the total number of in-situ tests, collect 5% of this number of tests from the various locations, and prepare these samples according to Appendix 1. Use these prepared samples to confirm the findings of the in-situ testing. Send a subset of these prepared samples to a laboratory for confirmatory results.

Cost Justification. To adequately characterize a site may require 100-200 samples/acre to be sure the contaminated areas are firmly established. This work may be done with in-situ testing to generate laboratory savings of \$5,000 - \$10,000/acre depending upon the number of elements being analyzed. The cost reduction in off-site analysis often justifies the price of the XRF.

Example 2: Monitor remediation efforts and assure site meets clearance levels before contractors leave the site.

Goal: Minimize remediation costs by only treating contaminated soil, and obtain immediate verification that various site locations meet clearance objectives.

Recommended Testing Plan: This type of project uses a lot of both in-situ and prepared sample testing. Use in-situ testing to thoroughly delineate contamination regions in both area and depth. To determine depth profiles, test surface soil, remove at least 1-2 inches, and retest. Repeat this step as necessary to profile contamination depth to guide remediation activities. (XRF is a surface technique and only analysis the first few mm of soil sample). As part of clearance, collect several samples from “cleared” area. Prepare samples according to Appendix 1 and test with portable XRF.

If XRF indicates that concentration levels are in excess of clearance requirements, then continue remediation efforts.

If XRF indicates concentration levels are below clearance requirements, then discontinue remediation efforts, send a subset of the samples to an analytical laboratory to confirm results. Most operators safely assume that the cleanup requirements have been met for the elements in question, but await final analysis from the laboratory.

If XRF lists concentration levels as non-detected, but the detection level reported exceeds clearance requirements, send samples to a laboratory for final results.

Cost Justification: In-situ results are used to guide remediation efforts, in order to obtain maximum efficiency. Efficiency is produced because contamination boundaries are firmly established, thus avoiding remediation efforts with “clean” soil. Prepared sample testing is used to assure that clearance requirements are met on-site in near real-time (pending laboratory confirmation). Costs savings are generated by avoiding clearance failures. The contractors can leave the site earlier thus reducing costs, and the contractor will not be called back to the site for additional cleanup.

Important Note: Never clear a site based solely on in-situ testing. Always use well-prepared samples to make a clearance decision.

Example 3: Minimize volume of hazardous waste for treatment or disposal.

Goal: For some cleanup projects, the cost of soil disposal in a hazardous waste landfill is much greater than disposal in a standard landfill. Testing soil samples with XRF may minimize the amount of “clean” soil that is inadvertently shipped to a hazardous-waste landfill.

Recommended Testing Plan: This example is almost entirely prepared sample testing. Representative samples are removed from the soil being hauled to landfill. Obtaining an accurate analysis of the samples is crucial for making a hazardous versus non-hazardous determination. For this reason, prepared sample testing is strongly recommended.

Important Note: These types of samples are subject to TCLP procedures for the landfill determination. In general, 20 times the XRF result should be less than the allowable limit for the metal in question. Please contact Innov-X Systems for more details on testing samples versus TCLP regulatory requirements.

Section 3: Quality Assurance.

Quality assurance is detailed for both the proper use of the analyzer (which is also provided in Method 6200) and for verifying the data quality of in-situ testing. All operators should perform the QC for the analyzer operation. This is required by Method 6200. For operators that are using in-situ testing data in guiding their reporting or remediation decisions, Innov-X recommends also verifying the data quality of in-situ test results. Procedures are listed below:

3.1: Proper verification of instrument operation

These procedures are taken from EPA Method 6200 and updated to be specific to the Innov-X analyzer. Quality assurance here constitutes testing of known standards to verify calibration, testing of blank standards determine limits of detection and to check for sample cross-contamination or instrument contamination. EPA Method 6200 provides a detailed procedure, which is provided here in abbreviated form. Components of instrument QC:

1. An energy calibration check sample at least twice daily
2. An instrument blank for every 20 environmental samples
3. A method blank for every 20 samples that are prepared.
4. A calibration verification check sample for every 20 samples
5. A precision sample at least one per day.
6. A confirmatory sample for every 10 environmental samples

Energy Calibration Check: The Innov-X analyzer performs this automatically, this is the purpose of the standardization check when the analyzer is started. The software does not allow the analyzer to be used if the standardization is not completed.

Instrument Blank: Operators should use the SiO₂ (silicon dioxide) blank provided with the analyzer. The purpose of this test is to verify there is no contamination on the analyzer window or other component that is “seen” by the x-rays. Method 6200 recommends an instrument blank at least once per day, preferably every 20 samples. For either in-situ or prepared-sample testing, the operator should just test the SiO₂ blank to be sure there are no reported contaminant metals.

Method Blank: Only used for prepared-sample testing. The purpose of the method blank is to verify cross-contamination is not introduced into samples during the sample preparation process. Method 6200 recommends following sample preparation procedures with clean SiO₂ once every 20 prepared samples. This QC step is not required if the operator is not preparing samples.

Calibration Verification. Perform upon instrument startup and periodically during testing. Note: Innov-X recommends a calibration check every 4 hours. EPA Method 6200 recommends a calibration check every 20 samples. Innov-X provides NIST standard reference samples are provided for calibration check by operator. Operator should place NIST standard to XRF and perform a 2-minute test. The difference between the XRF result for an element and the value of the standard should be 20% or less. NIST reference standards are generally applicable for Pb, As, Cr, Cu, Zn. Innov-X provides additional reference standards for other RCRA or Priority Pollutant metals including Cd, Se, Ag, Hg, Ag, Ba, Sn, Sb, Ni and Tl.

Precision Verification: Quoting from EPA “A minimum of one precision sample should be run per day by conducting from 7 to 10 replicate measurements of the sample. The precision is assessed by calculating a relative standard deviation (RSD) of the replicate measurements for the analyte. The RSD values should be less than 20 percent for most analytes, except chromium, for which the value should be less than 30 percent.

Confirmatory Sample: One confirmatory sample for every 10 samples collected. According to EPA Method 6200: “Confirmatory samples are collected from the same sample material that is analyzed on site, but are sent to an off-site laboratory for formal analysis. The purpose of a confirmatory sample is to judge the accuracy of the data obtained by analysis on site and to allow corrections, if necessary.”

Important Notes about confirmatory samples:

Innov-X always recommends that customers compare prepared-sample results to laboratory results. To do this, collect and prepare a sample following the protocols of Appendix 1. Take a subsample and submit to the laboratory for analysis. The single largest error in XRF analysis is lack of sample preparation. For the best comparison, always use prepared samples.

3.2: Determining data quality of in-situ testing:

For operators relying extensively on in-situ testing, it is important to determine the data quality of this testing at a given site. *This protocol is not intended for every sample, but rather for a small percentage of samples considered representative of the site.* If the operator can demonstrate that quantitative data is achieved with little or no sample preparation, then the site characterization will be completed much more quickly but correctly.

For example, an operator may be able to demonstrate that the XRF result changes considerably when samples are passed through a 2 mm sieve, but that XRF results do NOT change appreciably upon finer sieving. In this case the operator can conclude that good XRF data is achievable with only 2 mm sieving. Sieving only to this level requires far less time than a more robust sample preparation. A protocol to determine the appropriate level of sample preparation is the following:

1. Delineate a region of soil approximately 4" x 4".
2. Perform several in-situ tests in this area, or collect the top (approximately) quarter inch of soil from this region, bag the soil, test through the bag. In either case, average the results.
3. If you did not bag the in-situ test sample, collect the top (approximately) quarter inch of soil from this region and sieve through the 2 mm sieve provided. Otherwise sieve the bagged sample used for the in-situ test. Thoroughly mix the sieved sample, and place some of the sieved material into an XRF cup, and perform a test of this sample.
4. If the results of this prepared sample differ less than 20% with the average in-situ result, this indicates the soil in this region is reasonably homogeneous. The data quality in this case is probably at the semi-quantitative level, rather than just screening data.
5. If the results differ by more than 20%, this indicates the soil is not very homogeneous, and there are serious particle size effects affecting your in-situ measurements.
6. In this case, sieve the sample through the 250 ~m sieve. Mix this sample and place a subsample into an XRF cup for testing. If this result differs from the previous by less than 20% then this indicates that at a minimum the 2mm sieving is necessary to achieve higher data quality.

7. If this result differs by more than 20% from the sample sieved through 2 mm, then particle size effects are still affecting the XRF result. In this case samples should be sieved through 125 μm to assure data quality at the quantitative level.

Section 4: Calibration for Innov-X Portable XRF

The Innov-X analyzer may run three different calibration methods, described below. In nearly all cases, customers choose the Compton Normalization method. This method (recognized in EPA 6200) offers speed, ease of use, and generally good accuracy for concentration ranges from the ppm level up to 2-3% concentrations. Most field-testing is seeking to remediate or locate environmental contaminants, the upper limit of the calibration (2-3%) is generally not a limitation. If customers do require a calibration up to 100% concentration (i.e. a pure element) then Innov-X recommends they also include the Fundamental Parameters (FP) software module with the analyzer. The FP module may be added at time of purchase as an upgrade at any later date.

Note: In general customers do not need to calibrate the Innov-X analyzer for soil testing. The analyzer is delivered with a factory calibration, generally based upon the Compton Normalization (CN) method. The CN method has been proven over the past several years to provide a robust calibration generally independent of site-specific soil matrix chemistry. The operator may calibrate the Innov-X system if desired, but it is not required to use the analyzer effectively. All customers should follow the QC procedure described in Section 3, which includes a check of the calibration.

The final model is the empirical calibration. In this case, customers run standards to generate calibration curves for various elements in specific soil matrices. Provided the sample is well-prepared, the empirical method generally yields the most accurate result. In our experience, the accuracy gains going from Compton Normalization to Empirical Mode are small and not worth the extra effort in setting up calibration curves. (The greatest source of error for in-field XRF analysis of soil is lack of adequate sample preparation, thus there is little gained in developing a sophisticated empirical calibration if the operator is also not going to grind and homogenize the samples).

Calibration Requirements:

The concentration of an element in a soil sample is well-described by the formula:

$$w_i = \frac{k_i}{M(Z, i)} I_i$$

k_i = calibration constant for element "i"

w_i = concentration of element "i" – the quantity being measured.

I_i = measured x-ray intensity from element "i"

$M(Z, I)$ = Soil matrix value

The factory calibration determines the value of the calibration constants k_i for each element, and a typical value $M(Z,I)$. The calibration method – either CN, fundamental parameters, or empirical – performs the necessary corrections to the value $M(Z,I)$ that are important for the site-specific soil chemistry. The XRF analyzer uses the measured intensity of each element's fluorescence from the sample, and the calibration data, to produce elemental concentrations.

Compton Normalization:

The Compton Normalization method incorporates elements of both empirical and FP calibration. A single, well-characterized standard, such as an SRM or a SSCS, is analyzed, and the data are normalized for the Compton peak. The Compton peak is produced from incoherent backscattering of X-ray radiation from the excitation source and is present in the spectrum of every sample. The intensity of the Compton peak changes as various matrices affect the way in which source radiation is scattered. For that reason, normalizing to the Compton peak can reduce problems with matrix effects that vary among samples. Compton normalization is similar to the use of internal standards in analysis for organic analytes.

Fundamental Parameters Calibration:

The fundamental parameters (FP) calibration is a "standardless" calibration. Rather than calibrating a unit's calibration curve by measuring its response to standards that contain analytes of known concentrations, FP calibration relies on the known physics of the spectrometer's response to pure elements to set the calibration. Built-in mathematical algorithms are used to adjust the calibration for analysis of soil samples and to compensate for the effects of the soil matrix. The FP calibration is performed by the manufacturer, but the analyst can adjust the calibration curves (slope and y-intercept) on the bases of results of analyses of check samples, such as standard reference materials (SRM), which are analyzed in the field.

Empirical Calibration:

In performing an empirical calibration a number of actual samples, such as site-specific calibration standards (SSCS), are used, and the instrument's measurement of the concentrations of known analytes in the samples are measured. Empirical calibration is effective because the samples used closely match the sample matrix. SSCSs are well-prepared samples collected from the site of interest in which the concentrations of analytes have been determined by inductively coupled plasma (ICP), atomic absorption (AA), or other methods approved by the US Environmental Protection Agency (EPA). The standards should contain all the analytes of interest and interfering analytes. Manufacturers recommend that 10 to 20 calibration samples be used to generate a calibration curve. The empirical method is the least desirable calibration method as it requires new standards and curves be generated for each site that is analyzed.

Section 5: Effects of Moisture on XRF Results:

Sample moisture has two effects on XRF results:

- ❑ It alters the soil chemistry, since water is another chemical compound that comprises the soil matrix.
- ❑ Moisture impedes the ability to properly prepare samples.

- ❑ Laboratory results are provided on a “dry weight” basis.

Effect on Soil Chemistry:

While the presence of significant moisture does impact the soil chemistry, modern XRF analyzers all perform automatic corrections for variations in soil chemistry from site to site. Indeed, such variations are expected, and that is the reason analyzers use Compton Normalization or fundamental parameters, in order to correct for moisture content changes as well as other differences in soil geochemistry.

EPA Method 6200 states “Moisture content above 20 percent may cause problems, since moisture alters the soil matrix for which the FPXRF has been calibrated.” However, the Compton Normalization or fundamental parameters methods are implemented in order to automatically correct results for changes to the soil matrix. Thus, we believe that soil moisture is not a significant effect on accuracy due to effects of soil matrix.

Relation to sample preparation:

The inability to adequately prepare a wet sample, we believe, is the single biggest contributor to errors when testing wet samples. It is very difficult to grind or sieve a wet sample. The highest quality XRF results are generally obtained from prepared samples. If the operator is unwilling to dry the sample to prepare it, comparisons to the laboratory may yield poorer correlation since the samples are not homogeneous.

Laboratory Tests on Dry-Weigh Basis:

Laboratories always dry samples prior to analysis. They report percent weight content based upon a dry sample basis. Portable XRF may often be used to analyze wet samples in the field, and results are thus reported that include the moisture content. Thus, all other factors the same, the laboratory will report results higher than portable XRF. The results will be higher by the amount of moisture content in the sample. For example laboratory results will be 10% higher compared to XRF results, if the sample contained 10% by weight water when it was tested with XRF. Recall, this applies to samples where other possible sources of error are the same or negligible.

Section 6: Comparing XRF Results to Laboratory Results:

Innov-X strongly recommends that operators compare prepared sample results to laboratory results. This is because prepared-sample results yield the best possible accuracy with portable XRF. Moreover, the most common source of error is in non-uniform samples. The XRF technique, nor can any analytical technique, properly account for non-uniform sample types.

To perform a comparison between XRF results and laboratory:

1. Collect a sample and prepare it according to the sample preparation guide in Appendix 1.
2. Take a sub-sample (5-10 grams) of the fully-prepared sample, place it into an XRF cup and perform at least a one-minute test on that sample.

3. Send the same sample to the laboratory for wet chemistry analysis.
4. Require the laboratory to use a total-digestion method. If the laboratory does not use a total digestion method, they may not extract all of the elemental metal from the sample. In this case, the lab result will be lower than the XRF result. Incomplete sample digestion is one of the most common sources of laboratory error, thus it is very important to request a total digestion method.

Example of Error: Operator collects a bag of sample, performs XRF tests on one part of the bag, and sends the bag, or part of the bag of sample to a laboratory for analysis. The laboratory reports a very different value than the operator obtained with the XRF.

Problem: The sample is very non-homogeneous. The operator did not obtain a result that was representative of the entire bag of sample. Since the lab analyzed a different part of the sample they obtained a very different result because the sample was not uniform. The solution to this problem is, at a minimum, test several locations in the bag of sample and report the average value. Also note the differences between the tests, as this is indicative of the non-uniformity of the sample. Operator should send entire bag of sample to the lab, and instruct lab to prepare the sample before removing sub-sample for lab analysis. Best bet: Operator prepares bag of sample, collects sub-sample for XRF testing and sends same sample to lab.

Section 7: Common Interferences:

An interference occurs when the spectral peak from one element overlaps either partially or completely with the spectral peak of another. If the XRF is calibrated for both elements (CASE 1) i.e. the one causing the interference and the one being interfered with, it is generally capable of correctly handling the interference. In this case, the element being interfered with may be measured with a poorer detection limit or poorer precision, but the analytical results should still be acceptable for field-portable XRF. If the XRF is not calibrated for the element causing the interference (CASE 2), then the XRF may report the presence of elements not in the sample, or greatly elevated concentrations of elements in or not in the sample.

Example CASE 1: Lead and arsenic. Most XRFs are calibrated for lead and arsenic. Lead interferes with arsenic (not vice-versa though). The net effect is a worsened detection limit for arsenic, and poorer precision. The XRF handles the correction automatically, but the precision is affected. The loss of precision is also reported by the XRF. (Please refer to Innov-X Applications Sheet: *In-field Analysis of Lead and Arsenic in Soil Using Portable XRF* for more detail).

Example CASE 2: Bromine in the sample, but XRF is not calibrated for bromine. Bromine, as a fire retardant, is being seen more and more in soil and other sample types. For this reason, Innov-X analyzers include Br in the calibration data. If Br is not calibrated, but is present in the sample, the analyzer will report highly elevated levels of Pb, Hg and As. The levels will depend upon the concentration of Br in the sample.

Interferences between elements can be broadly categorized into a) Z, Z-1, Z+1 interferences, and b) K/L interferences. Interference type “a” occurs when high levels of an element of atomic

number Z are present. This can cause elevated levels of elements with atomic number $Z-1$ or $Z+1$. Generally, portable XRFs have good correction methods, so this interference only causes problems with very high levels of the element in question. Example: High concentrations of Fe ($Z=26$) in excess of 10% may cause elevated levels of Mn or Co ($Z=25$ or $Z=27$ respectively).

The type “b” interference occurs when the L-shell line of one element overlaps with the K-shell spectral line of another element. The most common example is the lead/arsenic interference where the L-alpha line of lead is in nearly the exact same location as the K-alpha line of arsenic.

Sample preparation protocol provided in Appendix 1

