USEPA Method 6200 and Field Portable X-ray Fluorescence

Overview:

These training notes provide a brief introduction to x-ray fluorescence (XRF) analysis of soils. XRF has been used to characterise a broad range of materials for over twenty years. Recent advances in digital electronics and semi-conductor technology has yielded very portable XRF analysers for field analysis of many sample types including soils. These notes will cover the following subjects:

1. Introduction to XRF, basic theory of operation

2. EPA Method 6200

3. Field use of XRF analysers for soil
   - In-situ testing
   - Prepared sample (or ex-situ) testing

4. Basic quality assurance and sample preparation strategies

During the training session, most of the time will be spent performing measurements on prepared and unprepared soil samples with XRF instruments provided.

1. Introduction to XRF

Basic Atomic Structure:

A model of an atom is shown in Figure 1. In this model, the atom consists of a nucleus occupied by protons and neutrons. Surrounding this nucleus are negatively charged particles called electrons. This is known as the Bohr model of the atom, because it assumes the electrons orbit around the nucleus of the atom in fixed orbits, much like the planets orbit the sun. While this model is not exactly correct, it is perfectly satisfactory to explain most of the principles encountered in x-ray fluorescence analysis. For an uncharged atom, the number of electrons equals the number of protons. For each element, the electrons are orbiting the nucleus at different energy levels. These "orbits" or "shells" each contain a specific number of electrons. The shells closest to the nucleus get filled first and the shells get filled from the inner-most to the outer-most shell. Shells are named with the inner-most being the K-shell, then L-shell, etc., alphabetically named. The K-shell electrons can be thought of as having the lowest level of stored energy. The further out the electron shells are, the higher the energy level they have stored (the L-shell electrons have more stored energy than the K-shell electrons, the M shell electrons have more stored than the L shell, etc.).

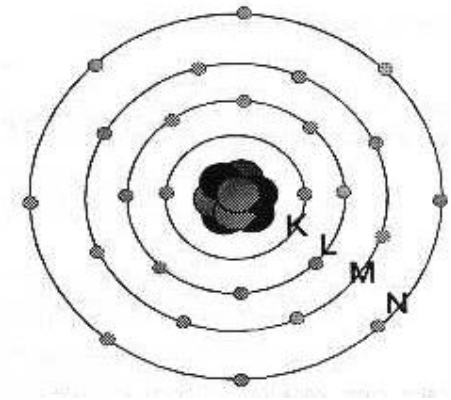

Figure 1. Bohr model of the atom, with nucleus of protons and neutrons.
Nucleus is surrounded by electrons in orbit, much like the planets orbit the sun.

What is X-ray Fluorescence?

X-ray fluorescence can be viewed as a three step process. In the first step, as shown in Figure 2, the atom is struck by an x-ray or gamma-ray (also called a photon) from a radioactive source.

In the second step, provided the x-ray or gamma-ray has sufficient energy either a K-shell or L-shell electron is knocked out of the atom, depending on the atom. For "light" atoms like chromium, arsenic, cadmium, a K-shell electron is knocked out. For "heavy" atoms like lead, mercury or uranium, an L-shell atom is removed. In the NITON XRF, the photons of energy that cause fluorescence is provided by either a cadmium-109 and/or an americium-241 radioactive source in the instrument. The cadmium-109 is a source of photons at 22.1 keV, 24.9 keV, and 88.0 keV. The americium-241 source provides 59.6 keV gamma-rays. For lead atoms, the 22.1 and 24.9 keV photons eliminate L-shell electrons, which cause L-shell fluorescence, which is used for soil analysis. The 88.0 keV gamma-rays eliminate k-shell electrons from lead atoms, which cause k-shell fluorescence, which is used for lead in paint measurements.

In the third and final step, the vacancy that is created from the electron being ejected is filled by a more outer shell electron. In dropping to the lower energy level, the electron gives off energy in the form of an x-ray. If a k-shell electron was ejected, the electron that jumps down to fill the vacancy emits a k-shell x-ray, if an L-shell electron was ejected, then the next highest electron in orbit emits an L-shell x-ray in order to jump down and fill the L-shell vacancy, etc.

The choice of radioactive source depends on what elements you are trying to measure. Cadmium-109 sources are suitable for excitation of the K-shell or L-shell energies of many other elements. Examples include five of the eight RCRA metals - arsenic, chromium, selenium via their K-shell x-rays and lead and mercury via their L-shells and K-shells. Other elements often tested with a cadmium-109 source include zinc, copper, nickel, iron via the K-shell x-rays and gold, uranium via the L-shell x-rays and K-shell x-rays. Americium-241 is used for K-shell fluorescence of cadmium, silver, barium, tin and antimony, but other elements are possible. For environmental purposes, XRF instruments with both sources - cadmium and americium - are ideal since they produce x-rays from all eight RCRA metals.

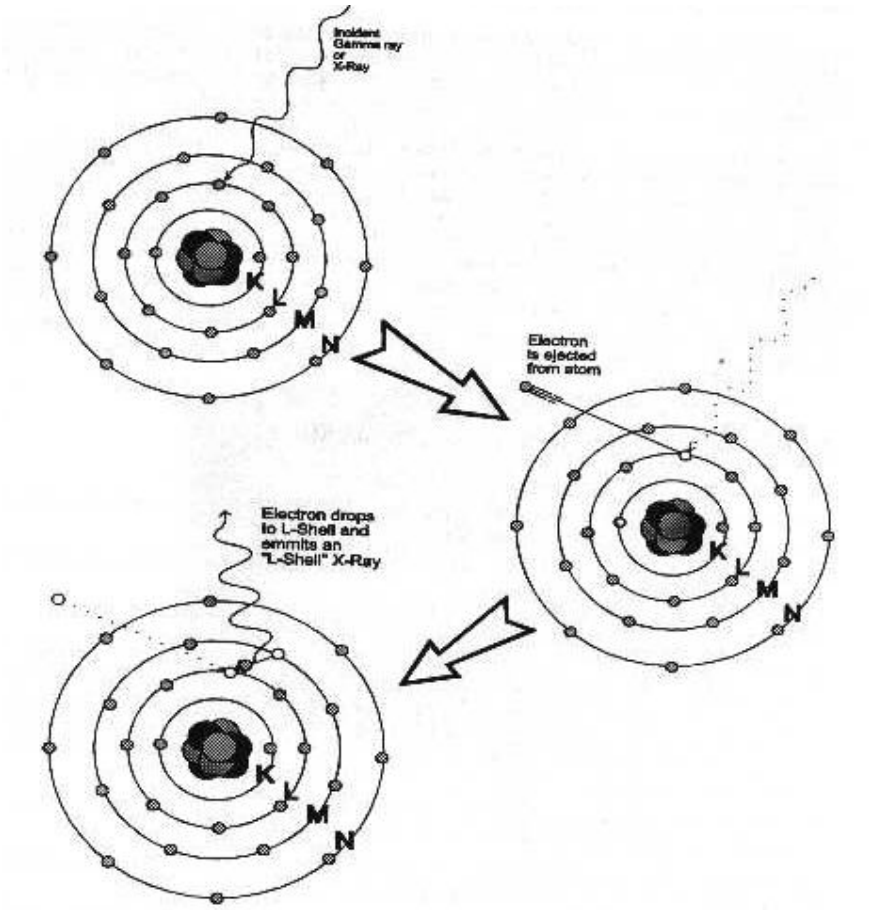

Figure 2. The three step process describing x-ray fluorescence.

Turning the x-ray fluorescence into something useful:
During testing, all the various metals within a soil sample are fluorescing. The XRF instrument must use this fluorescence to identify what elements are present and their concentrations in the sample.

XRF analysers use x-ray detectors, electronics, and on-board microprocessors to quantify various levels of elements in a sample. Remember, each element produces a fluorescence x-ray at a unique frequency (or energy). Detectors respond differently to different frequencies of x-rays. The electronics connected to the detector use this differing response to determine the frequency of every x-ray that enters the detector, and how many x-rays at each frequency strike the detector. By determining the frequency, the XRF device knows what element emitted the x-ray since elements all have unique x-ray emission frequencies. By determining the total number of x-rays at a particular frequency during a given amount of time, the device can determine the concentration of that particular element in the sample.

2. Regulatory Status - USEPA Method 6200

A USEPA Reference Method, incorporated into SW486 under RCRA, is now available for field portable XRF analysis of soils and sediments:

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

Features of this method:

- It is a field screening method, for analysis of in-situ or bagged samples. Developers of the method cite field studies indicating that variability in contaminate concentrations over small distances greatly exceeds instrument measurement variability. Thus, the method is used to thoroughly characterise a site. A large number of screening-level measurements provide a better characterisation than a small number of measurements produced by sample removal and analytical analysis.

- The method provides basic quality assurance methods, including calibration verification, determination of instrument precision, accuracy and limit of detection.

- The method recognises the some XRF instruments do not require site-specific calibrations by the operator, that is, the factory calibration provides appropriate data quality.

- The method recommends that a minimum of 5% of all samples tested by XRF be confirmed by an outside laboratory using a total-digestion USEPA analytical reference method.

- The method **does not** provide a technique for sample preparation (NITON Corporation is authoring an ASTM Method for sample preparation), or a method to determine data quality of in-situ testing results. Refer to section 4 of this paper or the NITON Manual for more detail.

3. Field Use of XRF Analysers for Soil:

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

- In-situ soil testing,
- Bagged soil sample testing
- Testing prepared soil samples

In general, in-situ and bagged sample testing are considered field screening methods. *In-situ testing is still a very valuable technique because it is a very rapid testing method and screening methods can generate a great deal of data very quickly.* Common usage and benefits of in-situ testing are provided on the next page, in **Advantages of Field Screening with XRF.**

To achieve analytical-grade data quality operators usually (but not always) must prepare the sample by sieving and perhaps grinding it. It is important to understand your data quality objectives (DQO) in order to determine the appropriate mix of field screening versus prepared sample testing. Illustrations of in-situ and prepared sample testing are shown in Figures 3 and 4.

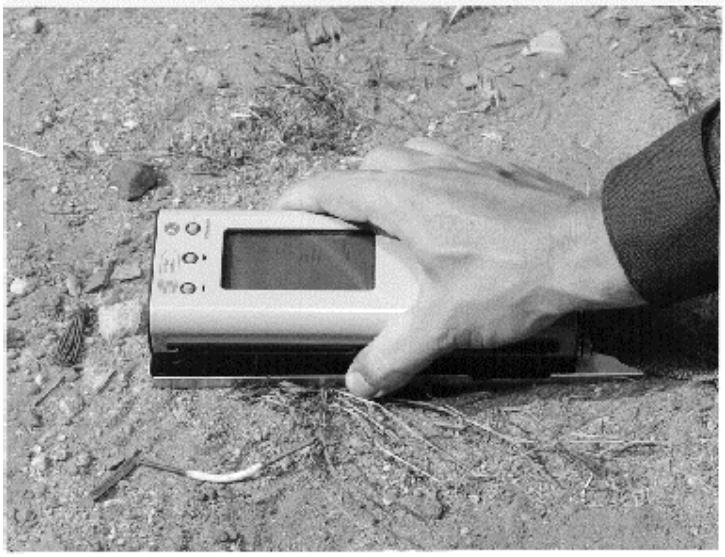

Figure 3. In-situ testing of soil by placing XRF directly onto the ground. This type of testing is generally screening level data quality.

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. Two methods often used to determine the data quality of in-situ testing, relative to well-prepared samples, is given in the section titled **Basic Quality Assurance.**

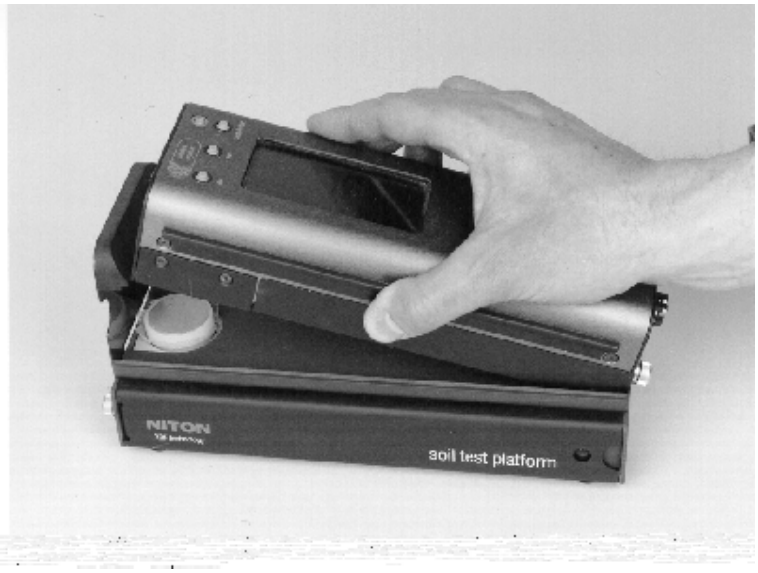

Figure 4. Prepared sample testing using XRF.
With proper sample homogenisation, analytical grade testing data is usually achieved.

Advantages of Field Screening with XRF

1. Focus sampling for laboratory analysis.

Operators can profile a site with in-situ testing in order to determine a sampling plan. Sources of contamination can be located very quickly. Contamination boundaries can be established. Regions of low and high contamination can be delineated. Even main analytes of interest can be determined. Sample collection can then be concentrated in regions where contaminants are below or near clean-up levels. There is little need for off-site analysis of samples that the XRF reports as being above the clean-up levels. The cost reduction in off- site analysis easily justifies the up-front price of the XRF.

2. Assure site meets clearance levels before contractors leave the site.
By combining in-situ and prepared-sample XRF testing, you can eliminate failed clearance tests. Before samples are sent to the lab for final clearance, XRF operators can prepare and test the same samples on-site because XRF is non-destructive. Provided the XRF reports levels below clean-up standards, operators can be assured that the lab will concur. XRF operators should always use prepared samples for this analysis. This procedure virtually guarantees clearance criteria will be met. Benefits include:

- The contractors can leave the site earlier thus reducing costs.

- Pre-testing prepared samples with XRF has assured that the lab will report levels below clean-up criteria, which reduces cost since the contractor will not be called back to the site for additional clean-up.

3. Minimise volume of hazardous waste for treatment or disposal.
Samples can be constantly evaluated on-site with field portable XRF to be sure only soils with contaminant levels in excess of clean-up levels are being treated or removed. Also, samples can be analysed on-site to determine if waste will pass/fail TCLP testing. Soils that pass this procedure can be disposed at a non-hazardous waste landfill, generating enormous savings.

4. Basic Quality Assurance and Sample Preparation Strategies

This section is intended to provide basic quality assurance steps for XRF testing. This is mainly on overview. The NITON manual covers these topics in depth.

Two Important Rules of Thumb:

- Never report XRF results as being below clean-up levels based solely on in-situ XRF test results. Always perform some sample preparation to support these results. It is a good idea to confirm at least 5% of results via laboratory testing. In general in-situ XRF results will be lower than results from prepared samples, or from laboratory results. EPA Method 6200 recommends a minimum of 5% confirmatory analysis.

- Always evaluate the data quality of in-situ testing results using one of the methods described in detail below.

Quality assurance can be broken into three main areas:

1. Proper verification of instrument operation

2. Determining data quality of in-situ testing, and amount of sample preparation required to achieve analytical data quality.

3. Proper sample preparation and testing for comparison to reference laboratory analysis.

1. Instrument verification:
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.

2. Determining data quality of in-situ testing:
For operators relying extensively on in-situ testing, it is extremely important to determine the data quality of this testing at a given site. XRF operators generally follow one of two procedures to determine data quality of in-situ testing:

- Direct comparison of in-situ test results to laboratory results to determine correlation curve.

- For subset of samples perform stepwise sample preparation to determine the effect of sample preparation on XRF testing results, and compare XRF test of fully prepared sample to laboratory analysis of the same sample.

Method (1) for determining data quality of in-situ test results:

Direct comparison of in-situ testing to laboratory testing
Operators will pick a number of testing locations and take several in-situ XRF measurements in that location. Or a sample can be collected and bagged, with several XRF tests performed directly into the bag. A sample is then collected from the testing region and sent to a laboratory for homogenisation and analysis. (Or the bagged sample is sent). The average result from this series of XRF tests is plotted against the laboratory result. A correlation curve is determined, and this curve is used to "correct" future in-situ testing results from the site in question. The correlation curve developed from this analysis incorporates bias in the XRF result due to the lack of sample preparation. In this way, the bias from in-situ testing is removed, on average, from the in-situ test results.

As an example, in-situ testing data for zinc in soil is shown in Figure 5. A direct comparison of the in-situ XRF results to the laboratory results reveals a consistent bias in the XRF data. Based on the least squares fit shown in the graph, the laboratory result is on average about 35% greater than the XRF result. This bias exists because the soil was not prepared before XRF testing, and particles like small pebbles in the soil surface "shielded" the zinc x-rays from reaching the detector. However, the comparison reveals a well-behaved correspondence between XRF and laboratory results. For this site, operators relied on extensive in-situ XRF analysis, but used the correction factor of 1.35 to correct in-situ results. This is a good example of using a direct comparison between initial in-situ XRF data and laboratory analysis to then gather a large amount of in-situ XRF data for off-line correction.

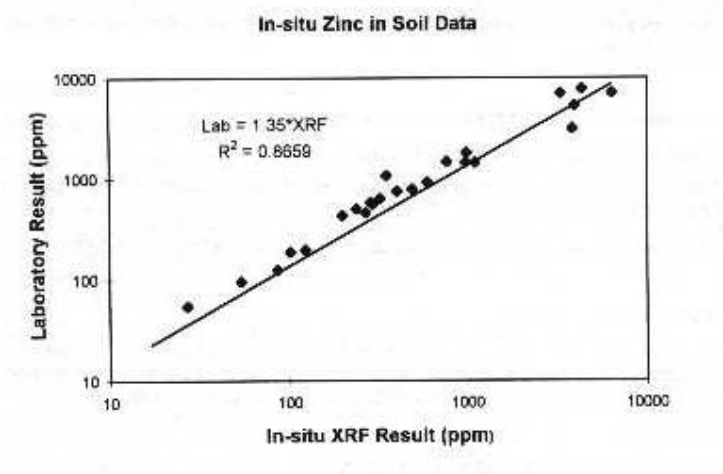

Figure 5. Comparison of in-situ XRF results for zinc in soil to laboratory results.

Method (2) for determining data quality of in-situ test results:

Stepwise sample preparation to determine data quality of in-situ testing.
The purpose of this protocol is to determine the amount of sample preparation required to get quantitative, as opposed to screening level, data quality. The basic strategy is to perform increasingly rigorous levels of sample preparation, followed by XRF analysis each time, until the XRF result stops changing. *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 characterisation 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 10 cm x 10 cm.

2. Perform several in-situ tests in this area, or collect the top (approximately) 25 mm 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 sub-sample 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, and then particle size effects are still affecting the XRF result. In this case samples should be sieved through 125 ∝m to assure data quality at the quantitative level. In our experience, sieving through 125 ∝m is always adequate to assure a quantitative data quality level.

Comparison of prepared XRF samples to laboratory analysis.

As shown in Figure 6, comparison of XRF analysis of prepared soil samples generally yields very good agreement with laboratory analysis, provided proper sample preparation and handling is performed. The data shown is from a NITON 700Series XRF used within the USEPA lead laboratory accreditation program (ELPAT). In this program participant laboratories (including field operators) receive quarterly samples for analysis. Results are reported, and compared to reference laboratory results as a means for laboratories to gauge their measurement accuracy.

The data shown below are several rounds of analysis where NITON operators participated in this program, to demonstrate that field portable XRF can routinely meet USEPA lead laboratory accreditation requirements for prepared samples. It is important to note that samples sent to participant laboratories are homogenised and ground to 125 ∝m particle sizes or less.

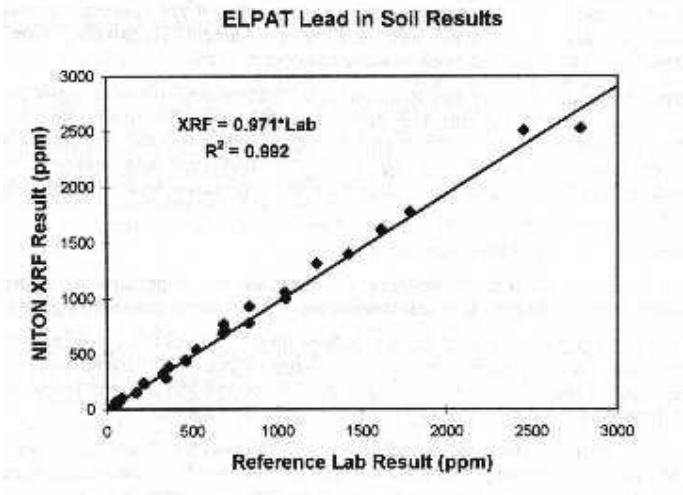

Figure 6. Comparison of XRF results to laboratory results for prepared soil samples.

Some XRF operators compare prepared XRF analysis to laboratory analysis to demonstrate the accuracy of XRF analysis. This is most often done to satisfy regulatory or client demands for defensible data. Please note this is different than the previous comparison of in-situ results to lab results. In that case it is expected that the results will differ, and the goal is to determine an overall correction factor. For prepared samples the operator is attempting to make a direct comparison of the absolute XRF result to the laboratory result to show no further corrections to the data are required.

JBS Environmental has showed the same strong performance in the Quality Control Technology (QCT) Soils, Dusts and Sediments program and the findings form the primary evidence demonstrated to NATA registration due later this year (Figures 7 & 8). Soils, dusts and sediments collected from a range of "real life" environmental sources then homogenised and two samples are distributed to each participant at the beginning of each month. QCT programs are recognised by National Association of Testing Authorities, Australia (NATA).

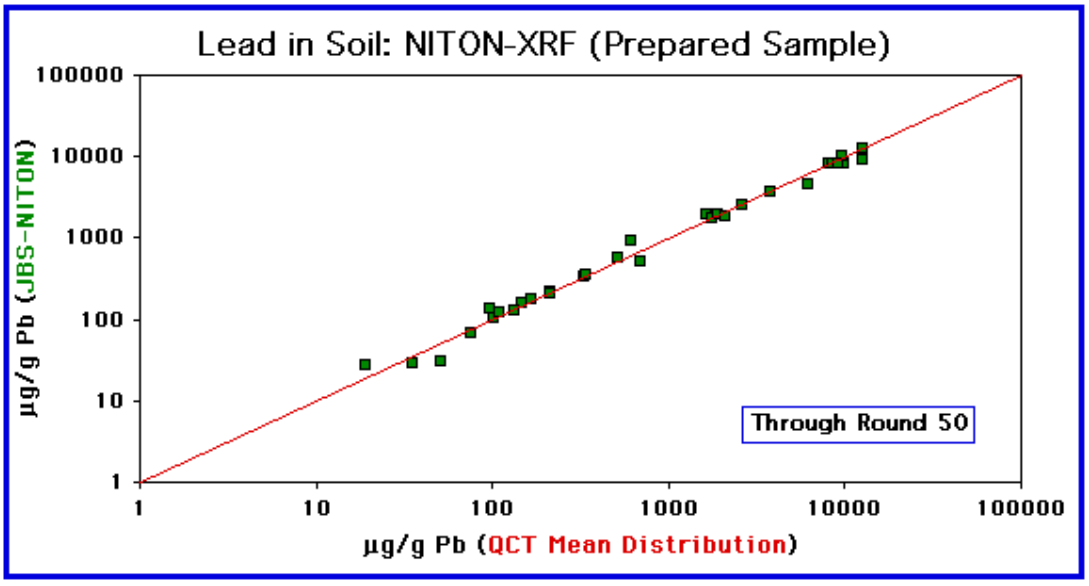

Figure 7 Comparison of XRF results to laboratory results for prepared samples (r^2=0.997)

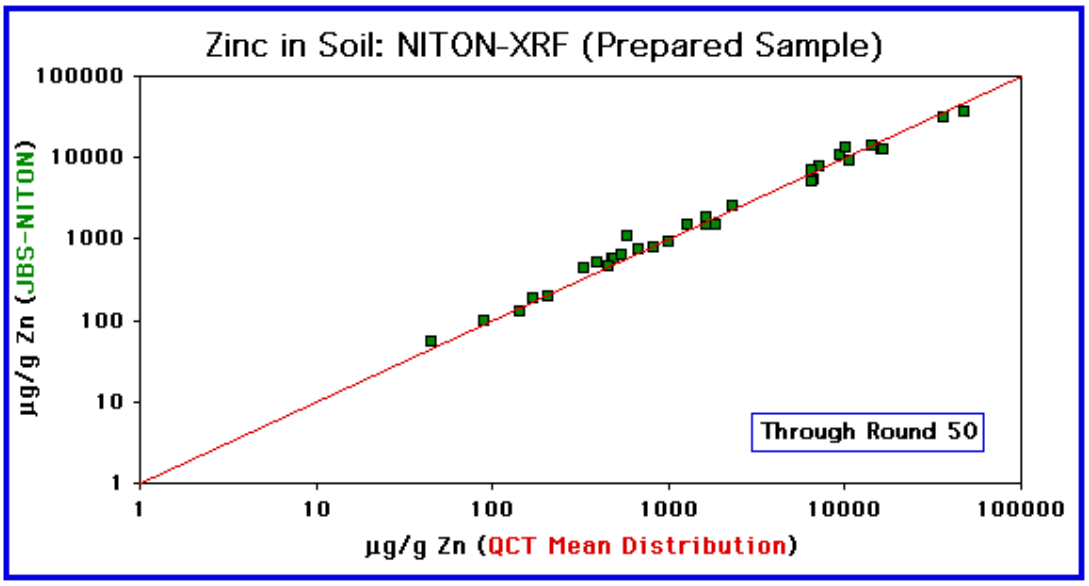

Figure 8 Comparison of XRF results to laboratory results for prepared samples (r^2=0.994)

Sample preparation protocol.
When comparing XRF results to laboratory performance always use thoroughly prepared samples before XRF testing. One possible sample preparation protocol is described in Figure 9. This protocol guarantees that the test results are being compared properly. Without such a preparation protocol there is no way to assure that the samples being compared are identical. Use of this protocol for prepared-sample XRF analysis generally provides analytical-level data quality.

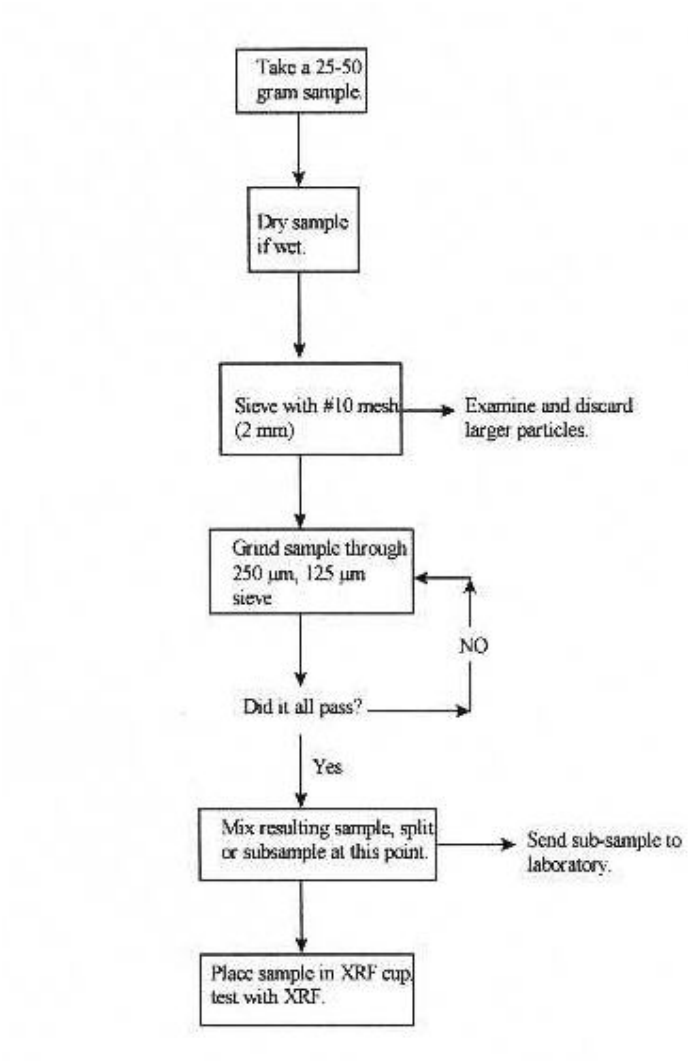

Figure 9 Detailed soil preparation procedure