

Ozarks Environmental and Water Resources Institute (OEWRI)
Missouri State University (MSU)

Standard Operating Procedure for:

Niton XL3t-500 Series Handheld XRF Analyzer

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Identification of the Test Method

Operation of the Niton XL3t 500 series handheld elemental analyzer for heavy metal screening and measurement of contaminated soil. The instrument is classified as a portable hand-held high performance thermoelectrically cooled detector with open-beam X-ray tube based analytical X-ray device.

Applicable Matrix or Matrices

This instrument can be used for natural soil samples.

Detection Limit

For an element to be detected by your analyzer in a given sample, the measured concentration of the sample must be at least three times the standard deviation of the measurement. This detection limit will depend on the composition of the sample.

An element is classified as “detected” if the measured concentration (in ppm) is at least 1.5 times the measurement error of the analyzer, or three standard deviations. Detected elements are displayed in ppm, followed by the measurement 95% confidence interval (two standard deviations). Non-detected elements are shown as < the detection limit (<LOD) for that sample. The detection limit for a given element varies depending on the other elements in the matrix.

Scope of the Test Method

1. This procedure will be used as a field and laboratory reference guide for the collection of heavy metal data from soil samples in both the laboratory and field.
2. The instrument is capable of measuring Fe, Mo, Zr, Sr, U, Rb, Th, Pb, Au, Se, As, Hg, Zn, W, Cu, Ni, Co, Fe, Mn, Cr, V, Ti, Sc, Ca, K, S, Ba, Cs, Te, Sb, Sn, Cd, Ag, Pd, Nb, and Bi concentrations in natural soil sediments from cutbank profiles, soil cores, floodplain and channel sediments, or prepared sediment samples in a laboratory setting.
3. The procedures described here present principal components of the instrument, pre-operating instruction, actual sample analyses, instrument settings, safety components associated with ionizing radiation, and reporting procedures. The user should review the instrument manuals for further information about the instrument.

Summary of Test Method

The Thermo Scientific Niton XL3t 500 Series handheld elemental analyzer uses energy-dispersive X-ray fluorescence (EDXRF) technology to rapidly determine elemental concentrations in soil and sediment samples. The analyzer contains an X-ray tube that emits primary X-rays into the sample. These X-rays excite atoms within the sample, causing them to emit secondary (fluorescent) X-rays with energies characteristic of the elements present. The detector measures the intensity and energy of the emitted X-rays, and the instrument calculates elemental concentrations using manufacturer calibrations based on Certified Reference Materials and internal algorithms.

Definitions

1. Analytical batch: The set of samples processed at the same time.
2. Blank: The plastic film used to cover the sample analysis divot during field determinations or the exact brand of plastic freezer bag containing the samples during laboratory analysis. Only the plastic film or plastic bag is measured to determine additions or interferences

present from field procedures, storage procedures, apparatus, or the laboratory environment.

3. **Backscattering**: Deflection of radiation in a scattering process through an angle greater than 90°. X-rays that reflect back to the detector and scatter in the direction of the instrument operator.
4. **Chain of Custody (COC)**: Used to describe the written record of the collection, possession, and handling of samples. Chain of custody forms should be completed as described in the Chain of Custody SOP-001. Chain of custody (COC) forms are located on a board in Blunt Hall 125.
5. **Characteristic X-rays**: A form of ionizing electromagnetic radiation with wavelengths ranging from 10 to 0.01 nanometers, corresponding to frequencies between 30 PHz to 30 EH. X-rays, which have no mass or electrical charge, are emitted when electrons undergo transitions between energy levels in an atom's electron shells. These X-rays can travel several hundred feet through the air and have the highest penetrating power among ionizing radiation types. They are best shielded with materials such as concrete, lead, or steel.
6. **Check Standard**: Standard sediment sample of known concentration and purity that produces consistent concentrations of analytes. These standards are used to check instrument performance.
7. **Controlled Area**: An area where access, occupancy, and working conditions are monitored by the responsible person to control radiation exposure to personnel.
8. **Fundamental Parameters (FP)**: An Assay & Grade method used for analyses performed using this SOP that measures the elemental concentrations of unknown samples. Specifically, "Soil FP" will be used for analyzing heavy element concentrations in soil.
9. **Ionizing Radiation**: Energy in the form of waves or moving subatomic particles that has enough energy to remove electrons from neutral atoms or molecules. Ionizing radiation has the potential to alter the chemical structure of living cells.
10. **Laboratory Duplicate (LD)**: Two samples taken at the same time and placed under identical circumstances and that are treated identically throughout field and laboratory procedures. Analysis of laboratory duplicates indicates the precision associated with sample collection, preservation, and storage as well as laboratory procedures.
11. **Method detection limit (MDL)**: The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.
12. **Minimum Quantification Interval**: The lowest level that can be quantitated accurately. This is generally defined as four times the method detection limit = 4(MDL).
13. **Primary Beam**: Ionizing radiation from an X-ray tube that is directed through an aperture in the radiation source housing for use in conducting X-ray fluorescence measurements.
14. **Radiation**: Energy in the form of waves or moving subatomic particles that is classified as non-ionizing and ionizing.
15. **Relative Percent Difference (RPD)**: calculated as the difference between a sample and duplicate results, divided by the average of the sample and duplicate results, multiplied by 100%.
16. **System Barrier**: The portion of an area that clearly defines the transition from a controlled area to a radiation area that provides the necessary shielding to limit the dose rate in the controlled area during normal operation.

Interferences

A. Measurement Geometry

1. Elemental concentrations are affected by the distance and orientation between the analyzer and the sample surface. To obtain consistent results, the measurement window shall remain in direct contact with the sample (or sample bag), and the analyzer shall be positioned perpendicular (90°) to the sample surface throughout the analysis.
2. Penetration depth may also influence elemental determinations. For example, accurate measurement of cadmium requires a minimum sample thickness of approximately 6 mm.

B. Sample Characteristics

1. The sample should be as smooth and clean as possible. Rust, oil, and dust buildup in and around the analysis window will interfere with element analyses.
2. Samples containing particles larger than 2 mm should be sieved prior to analysis when project objectives require quantitative measurements.
3. Soil moisture attenuates X-rays and may reduce analytical accuracy. Field measurements of moist soils should be considered less accurate than laboratory analyses. Laboratory samples shall be oven dried prior to analysis. Moisture content should generally not exceed 10–20%.

C. Sample Homogeneity

1. Coarse sand and gravel may reduce sample homogeneity and affect elemental determinations. Sample homogeneity should be evaluated by drying the sample and analyzing it at least three times. The average concentration for each element shall be reported.
2. If particles larger than 2 mm are removed, the sample shall be reanalyzed at least three additional times and the elemental concentrations averaged.
 - i. If the average concentrations obtained before and after sieving differ by less than 20%, the sample is considered sufficiently homogeneous for semi-quantitative analysis.
 - ii. Differences greater than 20% indicate that particle size is affecting elemental determinations. Additional sample preparation or sieving may be required, as determined by the Project Manager and Laboratory Supervisor.

D. Spectral Interferences

1. Some elements emit fluorescent X-rays with similar energies, producing overlapping spectral peaks that can interfere with elemental identification and quantification. Manufacturer calibration standards and the Niton spectral deconvolution algorithms compensate for many of these interferences by applying matrix-specific correction factors based on the measured X-ray intensities.
2. Compton and backscatter peaks may also interfere with elemental measurements. The laboratory sample holder and the field background plate should be used whenever practical to minimize these effects.

Health and Safety

- A. Authorized Personnel: Operation of the Thermo Scientific Niton XL3t 500 Series analyzer is limited to personnel who have completed the required instrument and

radiation safety training and are familiar with this SOP. The Director of OEWRI is responsible for overall oversight of the instrument.

- B. **Instrument Safety Features:** The Thermo Scientific Niton XL3t is designed to comply with ANSI N43.2-2001, 19 CSR 20-10., and 29 CFR §1910.1096 safety requirements for analytical X-ray equipment. The analyzer incorporates multiple engineering controls to minimize radiation exposure, including:
1. Password-protected operation (OEWRI QA/QC Manager holds password)
 2. Trigger-activated X-ray generation
 3. Infrared safety sensor that prevents X-ray production unless the measurement window is covered by a sample
 4. LED lights that illuminate when X-rays are being generated
 5. A sealed X-ray tube and high-voltage power supply enclosed within multiple layers of shielding and tamper-resistant housing
- C. **Radiation Hazards:** The analyzer produces ionizing radiation during operation. Exposure to ionizing radiation can damage living tissue and increase the risk of cancer. Radiation dose is measured in sieverts (Sv), with 1 millisievert (mSv) equal to 1/1,000 of a sievert. Occupational radiation exposure shall not exceed an annual average of 20 mSv over five years, consistent with recommendations of the International Commission on Radiological Protection (ICRP), BEIR Committee, U.S. Environmental Protection Agency (EPA), and National Council on Radiation Protection and Measurements (NCRP) (ICRP-1990).
- D. **Radiation Safety Practices:** All operators shall follow the As Low As Reasonably Achievable (ALARA) principle by minimizing exposure time, maximizing distance from the radiation source, and using appropriate shielding. During instrument operation:
1. Non-operators shall remain at least 3 feet (1 m) from the analyzer (Figure 1a).
 2. ***Never point the analyzer at any person or body part.***
 3. Never place fingers or any body part in front of the measurement window during an analysis (Figure 1b). Always use the background plate or sample holder to position samples.
 4. When analyzing samples that do not completely cover the measurement window, install the safety shield to prevent unattenuated X-rays from exiting the instrument.
 5. Use the laboratory sample holder whenever practical to reduce unnecessary radiation exposure to nearby personnel.
 6. Radiation may scatter from surrounding surfaces; therefore, walls or partitions shall not be relied upon as the sole means of shielding.
 7. Because bone absorbs X-rays more readily than soft tissue, direct exposure of the hands to the primary beam shall be avoided at all times.
 8. The primary X-ray beam exits the analyzer at approximately a 45° angle to the left of the instrument (Table 1; Figure 1c). Operators should remain aware of the beam direction when positioning themselves and nearby personnel during analyses.
 9. Proper use of the instrument is shown in Figure 1d.
- E. **Instrument Handling:** To maintain the integrity of the analyzer and its safety systems:

1. Never remove safety labels or tamper with the instrument housing. This poses a risk of voiding the warranty and leading to potentially unsafe use.
2. Never bypass or disable any safety feature.
3. Report any damage to the instrument or shielding immediately to the QA/QC Manager.
4. ***In an emergency, immediately terminate X-ray production by powering off the instrument and removing the battery pack.***
5. Dosimeters are available for students operating the analyzer or working in the laboratory during analyses.

Instrument Security and Maintenance

A. Instrument Storage & Security:

- a. Never leave the instrument unattended. It must always be in the operator's possession or stored securely.
- b. The analyzer shall remain under the direct control of the primary operator whenever it is removed from storage.
- c. When not in use, the analyzer shall be stored in its locked carrying case within the designated laboratory cabinet.

B. Maintenance and Records

- a. The analyzer shall undergo functional testing at least every six months to verify proper operation of the ON/OFF mechanism and safety systems.
- b. Instrument use, maintenance, calibration, and service records shall be maintained for a minimum of two years or until ownership of the instrument is transferred or the analyzer is decommissioned.
- c. Any damage or concerns will be reported to the OEWRI QA/QC Manager immediately.

Emergency Procedures and Call List

1. The first action to take in the event of an accident involving the instrument is to stop all X-ray production by turning the instrument off and removing the battery pack or unplugging the instrument.
2. If any hardware item is damaged, even if the instrument remains operable, contact the OEWRI QA/QC manager. Use of a damaged instrument may lead to unnecessary radiation exposure and inaccurate analyses.
3. Questions and additional instruction should be directed to the OEWRI QA/QC manager.
 - a. The QA/QC manager will contact university emergency personnel or off-campus contacts as necessary.
 - b. The Missouri State University Radiation Safety Office can be reached at 417-836-3737.

Personnel Qualifications

Soil parameters will be collected by Missouri State University (MSU) graduate assistants who have received appropriate training, prior coursework, and field experience regarding the collection of soil parameter data, and who are familiar with all MSU's sample handling and

labeling procedures. All operators of the Niton XL3t will be trained and will know all safety and operation procedures before using the instrument.

Equipment and Supplies

- Niton XL3t 500 series Handheld Elemental Analyzer, Thermo Fisher Scientific, 2 Radcliff Rd Tewksbury, Massachusetts, 01876.
- Power Supply:
 - Field - Two batteries charged as indicated by a green status light while plugged into the charger
 - Laboratory - power cord
- XRF Stand
- Lead-free bags
- Safety shield for small samples
- Field or Laboratory Book, Pen
- Instrument Use Record

Reagents and Standards

- Soil Check Sample: NIST SRF 2709a (sample stored in XRF case)
- Blank: SiO₂ (sample stored in XRF case)

Sample Collection, Preservation, Shipment, and Storage

The analyses are conducted *in situ* and only samples containing a predetermined level of contaminants will be collected and transferred to the laboratory. Samples will be placed into plastic bags and labeled. There are no special provisions for shipment. Sample bags should be opened and placed into 60° C oven immediately upon return to laboratory and left in the oven until dried.

Quality Control

A. Initial Precision and Recovery

1. To establish the ability to generate acceptably precise and accurate results, the manufacturer performed an extensive calibration of the instrument using various masses of solids which illustrate the instrument's response to analyte concentration. The instrument calibration should remain stable for the life of the instrument.

B. Quality Control Program

1. The minimum requirements of the quality control program for this analysis consist of an initial demonstration of laboratory capability and the periodic analysis of blanks and standard check samples as a continuing check on performance.
2. Soil Check Standard "NIST 2709a" and SiO₂ Blank will be measured at the start of the analytical cycle and after every 10 samples or at least twice during a batch analysis.
 - a. Certified values for elements in the NIST Standard Reference Material 2709a Soil Standard (NIST, 2018) are found in Table 3 & Appendix B.
3. A laboratory duplicate (LD) will be analyzed after every twenty samples or will be analyzed at least twice during a batch analysis. The criteria for these checks are noted in Table 2. The laboratory must maintain performance records that define the quality of the data that is generated.

4. Analyses of laboratory blanks are required to demonstrate freedom from contamination.
5. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.
6. The laboratory should maintain records to define the quality of data that is generated.
7. Method performance has been evaluated through comparison of XRF measurements with aqua regia digestion results. Results of this comparison are provided in Appendix A and demonstrate the comparability of XRF-derived elemental concentrations with aqua regia-based measurements.

C. Initial Demonstration of Performance

The following must be satisfied before the analytical procedure may be used for samples and before a new analyst may analyze samples:

1. **Demonstration of capability**
 - a. Read this standard operating procedure
 - b. Demonstrate to a previously trained analyst that the procedures outlined in this document are being followed, and
 - c. Successfully complete a report using data collected with these procedures
2. **Instrument Detection Limit (LOD)**
 - a. The instrument LOD for each element was determined by repeated analysis of a SiO₂ blank using the XRF analyzer. The LOD values reported by the instrument for each element were recorded for each blank measurement.
 - b. The mean of the reported LOD values for each element was calculated to establish the instrument LOD. The resulting LOD values are provided in Table 4.
 - c. The instrument LOD represents the detection capability of the XRF under the analytical conditions used for this determination. The method detection limit for a given soil sample may differ due to matrix effects and other sample-specific factors.

Calibration and Standardization

1. The instrument comes pre-calibrated from the manufacturer, Thermo Scientific, using the Universal Soils Fundamental Parameters calibration for the assay of 33 common alloying elements for soils analysis and 32 common alloying elements for mining analysis. This calibration, based on Certified Reference Materials and Reference Materials, is documented in a calibration certificate kept with the original operating and safety manuals in the OEWRI Lab (ThermoScientific, n.d.).
2. To ensure accurate and precise results, blanks and standards are regularly analyzed alongside test samples. Errors are inherent in the measurement of X-rays due to the nature of radioactive disintegration of the ray source.
3. Randomness of the emission of X-rays from the sample is random but predictable.
4. The background plate will be used to minimize accuracy errors and reduce backscattering.

5. Any damage to the instrument will be reported to the QA/QC manager. The instrument will be maintained as defined in the user manual (ThermoScientific, n.d.)

Field Procedure

A. Field Preparation

1. Prior to field deployment, coordinate instrument use with the OEWRI QA/QC Manager and/or Director. Verify that all required training has been completed and that the analyzer and associated materials are available.
2. Recharge both XRF batteries prior to field activities. Plug each battery into the charger located in the OEWRI Laboratory (Blunt 305).
 - a. *Each battery may require up to 2 hours to fully recharge. A fully charged battery will operate the analyzer for approximately 4–6 hours.*
3. Install one fully charged battery into the analyzer by inserting the battery into the handle until it clicks into place.
4. Place the analyzer, spare battery, and associated materials into the XRF carrying case. Arrange attachments and supplemental materials to prevent movement during transport. Close and lock the case.
 - a. *The analyzer shall remain protected from excessive heat, moisture, and physical damage during transport.*
 - b. *The analyzer shall remain under the control of the primary operator during field activities and shall not be left unattended unless secured in an appropriate location.*

B. Field Instrument Setup

1. Upon arrival at the sampling location, unlock the carrying case and secure the lock inside the case to prevent loss.
2. Turn on the analyzer by holding down the power button. The display will illuminate. Allow the X-ray tube to stabilize before proceeding.
3. Press anywhere on the screen to access the login menu. When the radiation warning screen appears, select 'Yes' and enter the instrument password.
4. Perform a System Check: Select Perform System Check > Yes. If system is ok > Close.
5. Click System > Date and Time to make sure it is accurate > Save. Next, click Specs to verify date and time are the same > Return. Note: The current year may not be available for selection.
6. To enable the Easy Trigger: Select Advanced > Start/Stop setup > select Easy Trigger > Save > Return.
7. To Measure Field Samples: Select Sample Type > Soils and Minerals > Test All Geo. Confirm that 'Test All Geo' and 'Easy Trigger' are displayed in the upper-left portion of the camera window. See Table 5 for mode descriptions.
8. Name the sample and project by Data Entry > type in sample name > Return > ↑ > Info. Enter operator initials in the inspector field.

C. Field Sample Analysis

1. Prepare the sample measurement area by removing leaves, vegetation, rocks, or other materials that may interfere with analysis.
2. Position the analyzer measurement window directly against the sample surface, sample bag, or core material.
3. Initiate analysis by pulling and releasing the trigger.
 - a. Indicator lights will illuminate while X-rays are being generated.
 - b. Ensure that the operator and any other personnel remain a minimum safe distance from the analyzer during analysis.
 - c. Three sets of beeps will indicate completion of the measurement sequence.
 - d. Once the four indicator lights located on the front and sides of the analyzer turn off, the analysis is complete and it is safe to proceed to the next sample.
4. Perform Quality Control analyses through analyzing the NIST 2709a Standard, SiO₂ blank, and duplicate measurements every 10 samples as outlined in the Quality Control section of this SOP.
5. Continue analyzing samples by entering the appropriate sample names. Samples may be analyzed in situ, from cores, or from sample bags depending on project requirements.
6. Record sample analyses and locations in the field notebook in addition to the analyzer data. Record GPS coordinates in the field notebook or incorporate location information into the sample identifier when multiple locations are analyzed.
7. The analyzer may remain powered on between analyses or while moving between sampling locations. Transport the analyzer using either the carrying case or holster.

D. Field Shutdown

1. When all analyses are complete, turn off the XRF by holding down the power button. Return the XRF to the carrying case. The data will not be erased.
2. Verify that all standards, blanks, holster, and other accessories are present before closing and locking the case.
3. Upon returning to the OEWRI lab, return the batteries to the charging area near the XRF storage location. Return the analyzer to its designated locked storage location.
4. Notify the QA/QC Manager of any damage, missing components, or instrument issues.

Laboratory Procedure

A. Laboratory Instrument Setup

1. Prior to laboratory analysis, coordinate instrument use with the OEWRI QA/QC Manager and/or Director.
2. Unlock the XRF case and position the analyzer in the benchtop stand as shown in Figure 2.
 - a. Align the grooves on the side of the analyzer body and handle with the stand. Press the analyzer into the stand until it is securely seated. The display should face away from the stand.

3. Remove the battery from the XRF (if installed) and connect the auxiliary power supply cord to the analyzer. The cord used for the battery charging station is the auxiliary power supply cord.
 - a. The electrical outlet is located above the XRF workstation. The auxiliary power supply cord shall remain connected to the laboratory workstation and should not be removed from the bench.
4. Turn on the analyzer by holding down the power button. The display will illuminate. Allow the X-ray tube to stabilize before proceeding.
5. Press anywhere on the screen to access the login menu. When the radiation warning screen appears, select 'Yes' and enter the instrument password.
6. Perform a System Check: Select Perform System Check > Yes. If system is ok > Close.
7. Click System > Date and Time to make sure it is accurate > Save. Next, click Specs to verify date and time are the same > Return. Note: The current year may not be available for selection.
8. To enable the Easy Trigger: Select Advanced > Start/Stop setup > select Easy Trigger > Save > Return.
9. To Measure Samples: Select Sample Type > Soils and Minerals > Test All Geo. Confirm that 'Test All Geo' and 'Easy Trigger' are displayed in the upper-left portion of the camera window.
10. Name the sample and project by Data Entry > type in sample name > Return > ↑ > Info. Enter operator initials in the inspector field.

B. Laboratory Sample Analysis

1. Organize project sample bags before analysis to minimize sample identification errors and ensure accurate data entry.
2. Ensure that sample thickness is sufficient for analysis. Sample thickness should be approximately 1 cm or greater. If sample thickness is less than 1 cm, document the approximate thickness in laboratory notes or incorporate the information into the sample identifier.
3. Initiate analysis by pulling and releasing the trigger.
 - a. Indicator lights will illuminate while X-rays are being generated.
 - b. Three sets of beeps will indicate completion of the measurement sequence.
4. Once the four indicator lights located on the front and sides of the analyzer turn off, the analysis is complete and it is safe to proceed to the next sample.
 - a. Suggested sample analysis time: 120 seconds per sample.
5. Perform Quality Control analyses through analyzing the NIST 2709a Standard, SiO₂ blank, and duplicate measurements every 10 samples as outlined in the **Quality Control** section of this SOP.
6. Continue analyzing samples by entering the appropriate sample names. Once finished, return to the Main Menu. You may power off the instrument. The data will not be erased.

Data Acquisition, Calculations, and Reporting

To download data from the instrument to a computer:

1. Connect the analyzer to the computer using the USB cable provided in the XRF case.
2. Navigate to the NDT software. The program will start.
3. Click download > settings > Com4 <usb serial device> > ok > Connect to connect the analyzer to the program.
4. Test the connection is working by selecting > Test. The prompt "Hardware successfully communicating" should pop up. Click ok.
5. Click query readings to see all readings completed.
6. Select results that you need located in the white box.
7. Select destination folder and name the file appropriately.
8. Click download (and simultaneous download to excel if needed). After download is complete (bar at the bottom will read x of x complete), click done.

Calculations:

1. The X-ray intensity which is measured from the size of the spectrum peaks is directly proportional to the concentration of the elements in the sample:

$$I = N/t = \frac{(k)(I_0)(T)(C)}{H}$$

Where:

I = X-ray Intensity (counts per second)

N = Net count (minus background and overlap)

t = Measurement time (seconds)

k = Geometrical constant (sensor-sample geometry)

I_0 = Source strength (photons per second/steradian)

T = Excitation cross section for the element in question

C = Weight fraction of the element

H = Matrix absorption coefficient.

2. Reporting results: Results should be reported to 0.1 mg TN/L precision.

3. Relative percent difference (RPD):

$$\left(\frac{A - B}{\text{AVERAGE}(A, B)} \right) * 100$$

Where:

A = original sample concentration

B = duplicate sample concentration

4. Standard Deviation(s): The evaluation of MDL and precision requires calculation of standard deviation. Standard deviations should be calculated as in equation 2.

$$s = \left\{ \frac{\sum x^2 - [(\sum x)^2/n]}{n - 1} \right\}^{1/2}$$

Where:

n = number of samples

x = concentration in each sample

Note: This is the sample standard deviation calculated by the STDEV function in Microsoft Excel.

5. Coefficient of Variation (Cv%): The evaluation of accuracy requires the calculation of coefficient of variation which is the standard deviation of the multiple sample measurements divided by the mean of those measurements.

$$Cv\% = (s/\bar{x}) * 100$$

Where:

s = standard deviation

$\bar{x}$ = Mean

Computer Hardware and Software

1. Niton software installed on the analyzer.
2. Niton Data Transfer (NDT) software for downloading the results can be installed on any computer using the disc provided in the top folder of the XRF case, or through download using Niton online tools.
3. Microsoft Excel can be used for reviewing the final data from the instrument by checking the simultaneous download to excel button in the NDT program during initial download.

Method Performance

- Precision: $\pm 20\%$, precision data will be reported as relative percent difference and project managers will determine what data is used.
- Accuracy: $\pm 20\%$, accuracy data will be reported as relative percent difference and project managers will determine what data is used.
- All analytical results are reported with error quoted at two standard deviations (colloquially known as “two sigma”), which approximately corresponds to a 95% confidence level.
- The limit of detection for an individual analyte is numerically expressed as three standard deviations (or 1.5 times reported measurement error) measured on a sample with none or only a trace amount of the analyte present.
 - The Instrument Detection Limit (IDL) is the best possible limit of detection, calculated from a “clean” sample, i.e. one with no interferences. A method detection limit is the limit of detection for a specific sample type (matrix) using particular instrument conditions. Method detection limits (MDLs) are typically worse than IDLs by a factor of 2 to 5 times.
 - Detection limits used in Niton XL3 Series analyzers are specified following the US Environmental Protection Agency (EPA) protocol of 99.7% confidence level.
 - The instrument detection limit for select elements using this XRF are:
 - Cadmium (Cd) – 168.6 ppm
 - Iron (Fe) – 63.3 ppm
 - Manganese (Mn) – 45.1 ppm
 - Lead (Pb) – 5.4 ppm
 - Strontium (Sr) – 2.2 ppm
 - Zinc (Zn) – 11.2 ppm

Pollution Prevention

All waste from these procedures shall be collected and disposed of according to existing waste policies within the MSU College of Natural and Applied Sciences.

Data Assessment and Acceptable Criteria for Quality Control Measures

1. The analyst should review all data for correctness.
2. Relative percent difference (RPD) should be calculated for pairs of duplicate analyses to determine precision.
 - a. The desired precision is $\pm 20\%$. Laboratory duplicate (LD) measurements will be randomly selected from each set of 10 samples in the batch and analyzed.

- b. There must be at least two LD analyses during each batch analysis. Precision data will be reported as relative percent difference and project managers will determine what data is used.
3. The soil check standard will be used to determine accuracy associated with each batch. The soil check standard is measured after each set of 10 samples or at least twice during each batch analysis.
 - a. The RPD between the average of the measurements of the check standard for each batch and the initial soil check standard report will be determined for each element and recorded with each laboratory report. The soil check standard concentrations are included in Table 3.
 - b. The desired accuracy is $\pm 20\%$. Accuracy data will be reported as relative percent difference and project managers will determine what data is used.
4. The completed Excel spreadsheet is reviewed by the analyst's supervisor or the OEWRI QA officer.

Corrective Actions for Out-Of-Control or Unacceptable Data

1. The results for precision and accuracy are compared to the acceptable value of $\pm 20\%$ for this analysis for all analytes. The initial soil check standard (2A1) report contains the concentrations of each element within the soil check standard and is included in Section 26.
2. Zinc, iron, chromium, and calcium concentrations are routinely found in blanks during batch analysis due to materials used to manufacture the sample holder.
3. If data is unacceptable for any reason, the analyst should review their analytical technique prior to conducting this analysis again.
4. When measurement time is increased the signal, N, increases. The time of analysis can be increased to increase precision and accuracy. The count rate should be increased by a factor of four to reduce the standard deviation by one-half.
5. If the sensor is not against the sample at a direct and consistent angle, the geometrical constant (k) will vary. Maintain direct and consistent angle of measurement.
6. The excitation cross section, T, varies with atomic number of the element and with source energy. The closer the element's absorption energy is to the source energy, the higher the excitation cross section. Certain elemental energies may further away from the source energy and will result in lower excitation efficiency.
7. The instrument may require troubleshooting techniques if the data are unacceptable. All instrument maintenance will be conducted by the QA/QC manager or sent to the manufacturer.

Waste Management

There is no waste generated using this method. All samples remain in sample bags and no other consumables are used.

Troubleshooting

- If the easy trigger is turned off:
 - Make sure you are logged in as OEWRI (name will be at the bottom of the logon screen). Navigate to Start/stop setup > check easy trigger

- *If the instrument will not perform an analysis of a sample:*
 - First, make sure that the instrument is powered on, and the software program has started. If that does not initiate analyses, follow the steps below:
 1. Make sure that the infrared sensor is covered completely with sample. The safety sensor must be activated before analyses can begin.
 2. Make sure the analyzer is correctly inserted into the holder and the window is clear of debris and human contact.
 3. If the sample surface is too darkly colored to reflect light, the infrared sensor may not activate. If the sample is clearly dark and the instrument will not perform an analysis, insert a piece of white paper between the sample and the infrared sensor.

References

- 19 CSR 20-10. "Protecting Against Ionizing Radiation". (2003). Missouri Department of Health and Senior Services.
- 29 CFR § 1910.1096 - Ionizing radiation. Occupational Safety and Health Administration. (n.d.). Occupational Safety and Health Standards (Subpart Z - Toxic and Hazardous Substances). Washington, DC: U.S. Government Publishing Office.
- N 43.2-2001, "Radiation Safety for X-ray Diffraction and Fluorescence Analysis Equipment", American National Standard Institute (ANSI)/Health Physics Society (HPS).
- NIST. 2018. National Institute of Standards and Technology, Certificate of Analysis: Standard Reference Material 2709a. Baseline Trace Element Concentrations.
- Thermo Scientific. n.d. Niton XL3t-500 Analyzer User's Guide. Version 6.5. Thermo Scientific

Tables, Diagrams, Flowcharts, and Validation Data

Table 1. Back scatter radiation levels in mRem/hr in various modes, with various substrates and distances from the side of the analyzer.

kVp	uA	Max in Following Modes* (Filter)	Substrate	Max @ 5cm (mRem/hr) Point A	Max @ 30 cm (mRem/hr) Point A'	Max @ Trigger (mRem/hr) Point B
40	50	G, D, E, H, A, P, F, M, J (Main Filter)	Aluminum	2.5	0.2	0.05
40	50	G, D, E, H, A, P, F, M, J (Main Filter)	Stainless	1.6	0.12	0.01
40	50	B (Main Filter)	Aluminum	0.4	0.04	0.01
40	50	B (Main Filter)	Stainless	0.14	0.01	0.01
50	40	H (Main Filter), D, E, M, S, J (High Filter)	Plastic	40	3.5	2
50	40	H (Main Filter), D, E, M, S, J (High Filter)	Soil	8	0.4	0.7
20	100	D, H, E, M, S, J (Low Filter)	Aluminum	0.015	0.01	0.01
20	100	D, H, E, M, S, J (Low Filter)	Stainless	0.015	0.01	0.01
20	100	D, H, E, M, S, J (Low Filter)	Plastic	0.13	0.015	0.015
20	100	D, H, E, M, S, J (Low Filter)	Soil	0.015	0.015	0.015
15	100	A, B (Low Filter)	Aluminum	0.015	0.015	0.015
15	100	A, B (Low Filter)	Stainless	0.015	0.015	0.015

* G = Alloy, B = Alloy Electronics, F = Dental Alloy, P = Precious Metals, M = Mining, D = Soil, J = Exploration, A = Lead Paint, E = Thin Sample, H = Plastic.

Table 2. Quality control samples and acceptance criteria.

Check	Acceptance Criteria
Blank	≤ MDL
MD	± 20% of each element
Soil Standard	± 20% of each element

Table 3. Certified values for elements in the NIST Standard Reference Material 2709a Soil Standard (NIST, 2018).

Element	ppm
Barium (Ba)	979
Cadmium (Cd)	0.371
Cobalt (Co)	12.8
Lead (Pb)	17.3
Manganese (Mn)	529
Strontium (Sr)	239
Iron (Fe)	33,600
Magnesium (Mg)	14,600
Calcium (Ca)	19,100
Aluminum (Al)	73,700

Table 4. Instrument limits of detection (LODs) determined from 20 analyses of an SiO₂ blank sample using the average LOD reported by the XRF analyzer for each element.

Element	ppm
Cadmium (Cd)	168.6
Lead (Pb)	5.4
Manganese (Mn)	45.1
Strontium (Sr)	2.2
Iron (Fe)	63.3
Cobalt (Co)	22.8

Table 5. Summary of available modes for the XRF analyzer.

Mode	Material / Matrix
TestAll Geo	Samples containing a mixture of metallic and nonmetallic materials
Soils	Samples with low concentration elements at 0.5% (5,000 ppm) or less.
Mining	<p>Samples with concentrations of all elements that are 0.5% (5,000 ppm) or greater, or high concentration samples. Mining mode is a fundamental parameters calibration and will do the best job for all elements, even those at lower concentrations, as long as there are high concentrations of any elements present in the sample.</p> <p>Handheld XRF technology cannot distinguish between direct overlaps between the spectral peaks for copper (Cu) and tantalum (Ta) and zinc (Zn) and hafnium (Hf). Cu and Zn are associated with each other as are Ta and Hf. Therefore, if the samples contain Cu or Zn, choose Mining Cu/Zn; if the samples contain Ta or Hf, choose Mining Ta/Hf mode.</p>

**for samples containing high concentrations of elements (>5,000 ppm) other than those of primary interest, it is best to use Mining Mode for analysis.*

a		<p>Incorrect Procedure:</p> <p>All persons not directly involved in operating the instrument will remain three feet away from the instrument during analyses.</p>
b		<p>Incorrect Procedure:</p> <p>Do not hold a sample in front of the measurement window with the fingers in the direct beam or point the beam at any part of the body.</p>
c		<p>Incorrect Procedure:</p> <p>Never hold the instrument away from the sample.</p>
d		<p>Correct Procedure:</p> <p>Use of the appropriate 90° angle of measurement.</p>

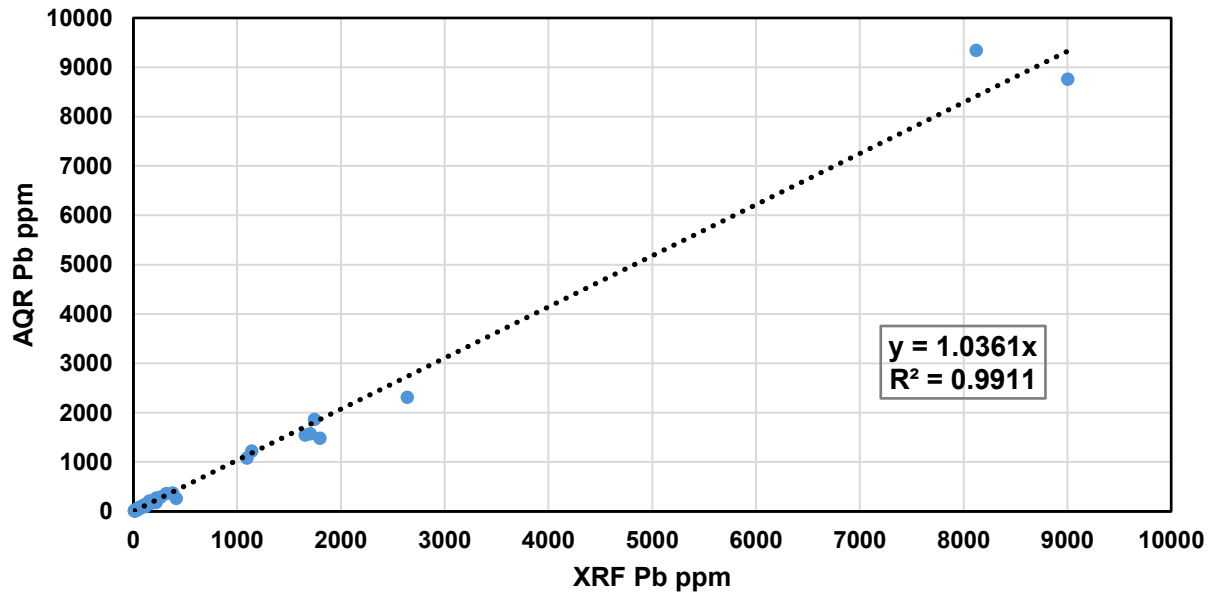
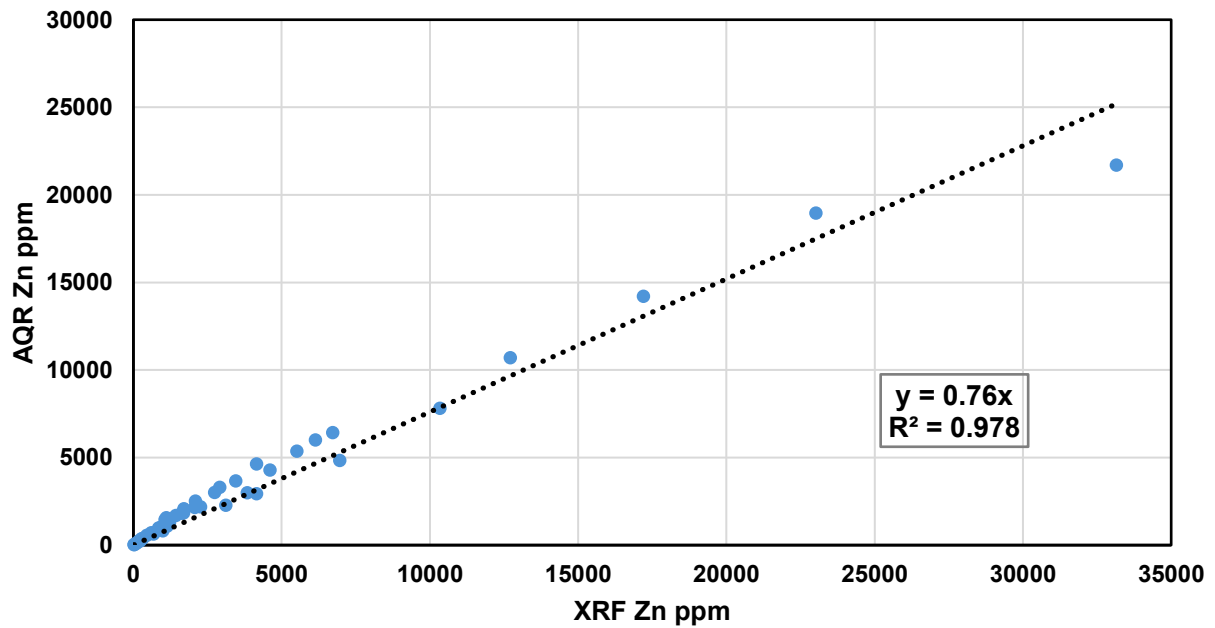
Figure 1. Incorrect and correct procedures for safe operation of the Niton XL3t 500 series handheld XRF analyzer.

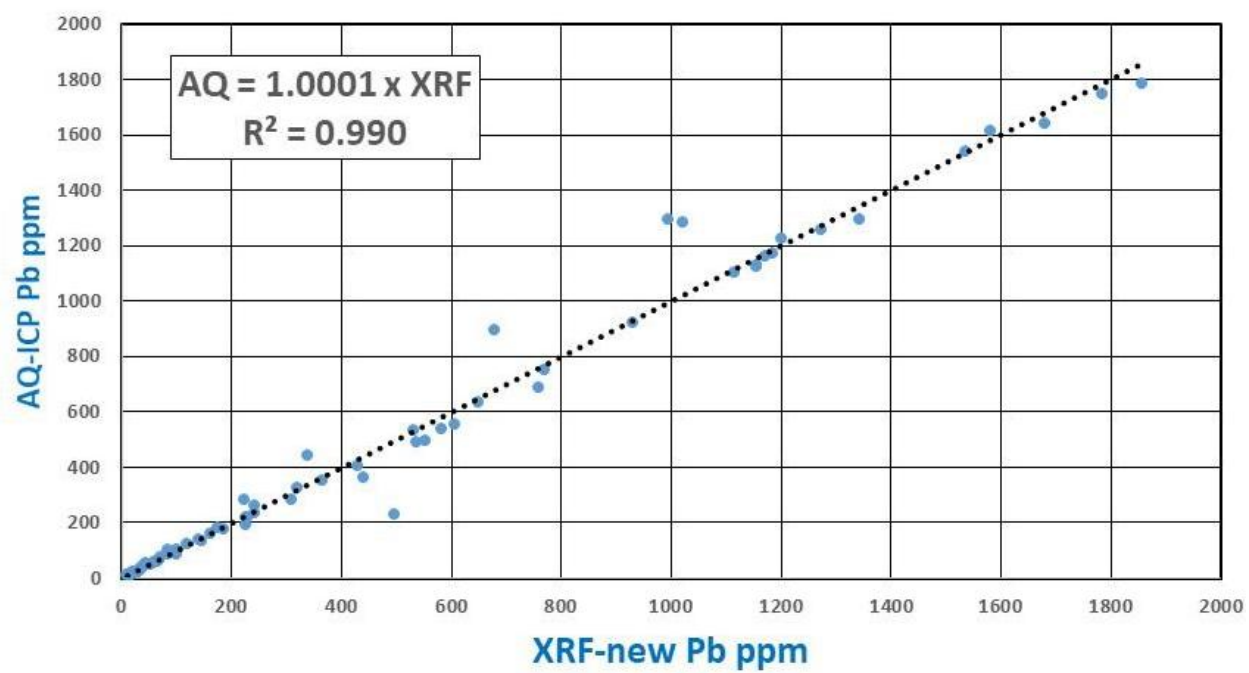
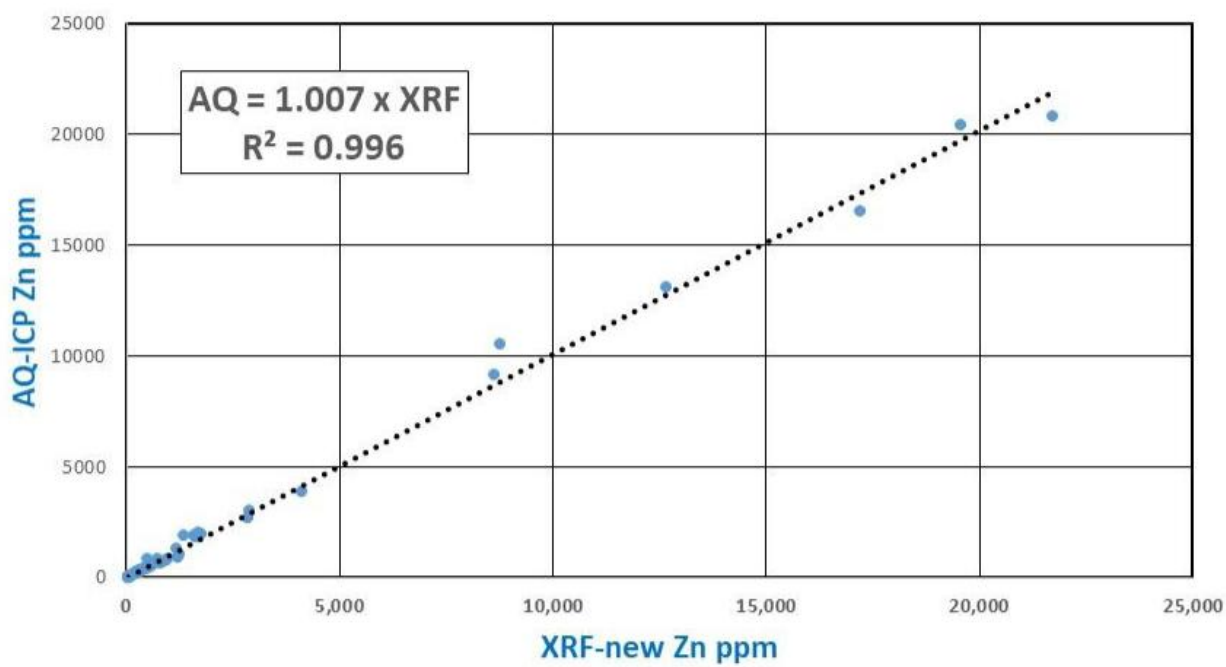


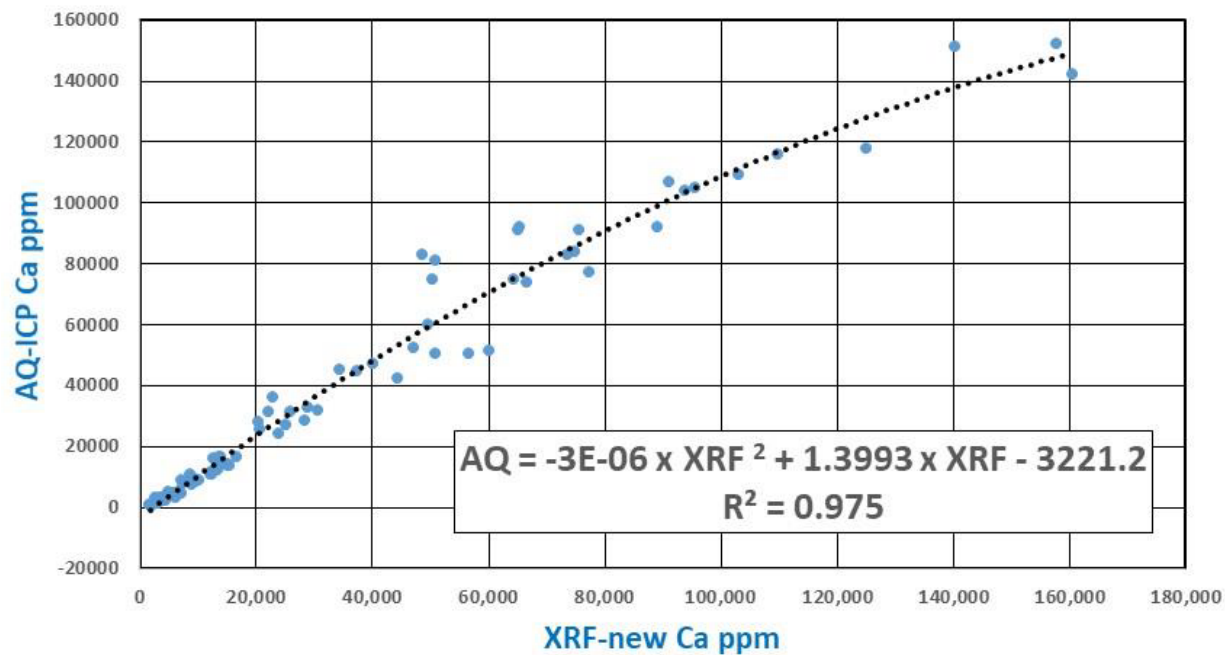
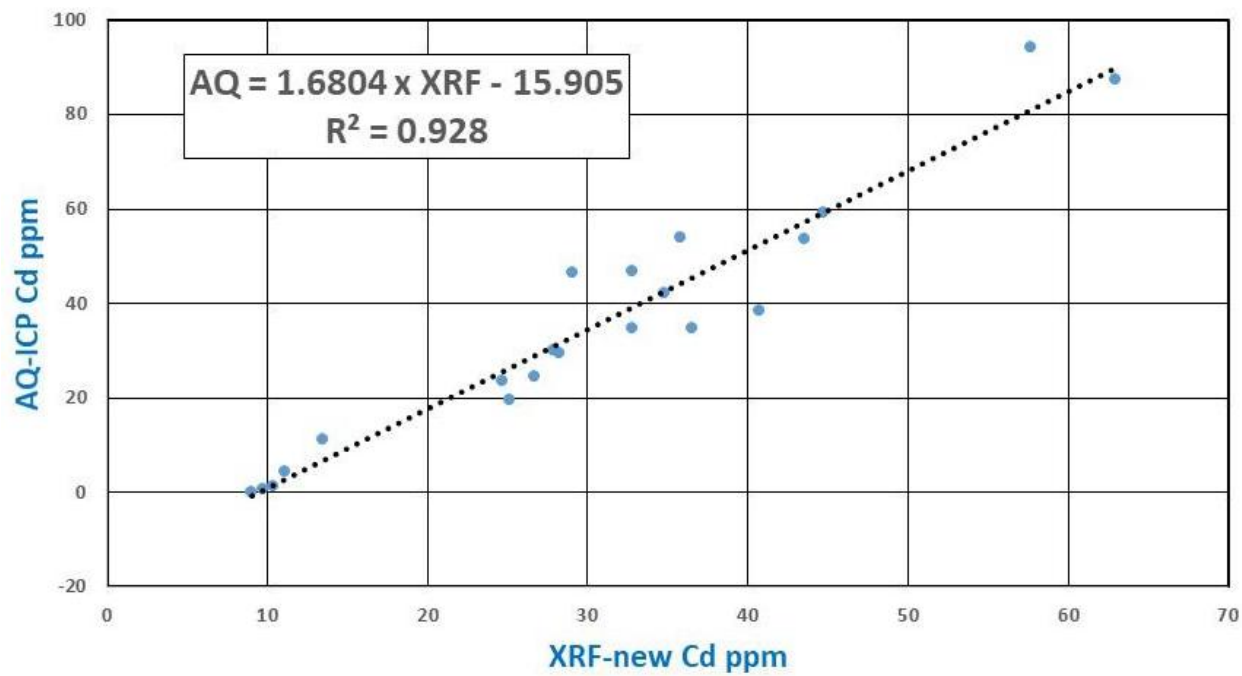
Figure 2. Instrument position in bench top stand.

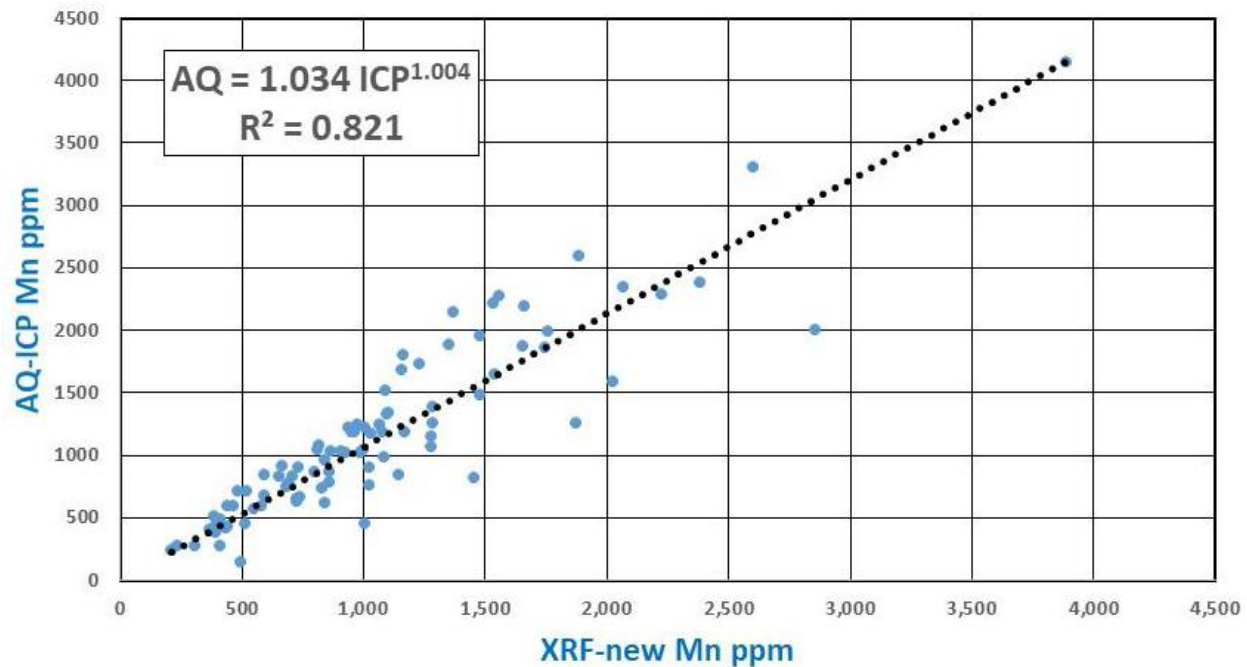
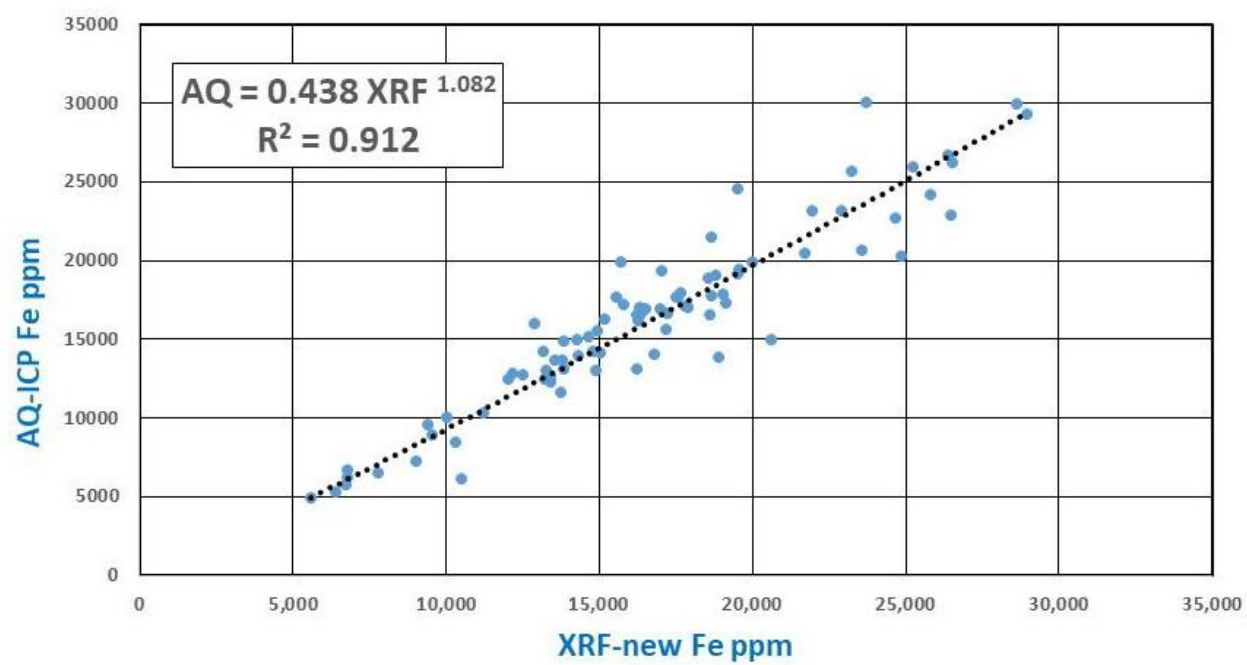
Appendix

Appendix A. Aqua regia values over XRF. Equations provided may be used to convert XRF to Aqua regia values when measuring the < 2 mm fraction.









Appendix B. Certified Values for Elements in the National Institute of Standards and Technology (NIST) Soil Reference Material (SRM) 2709a (NIST, 2018).

Table 1. Certified Values^(a) (Dry-Mass Basis) for Elements in SRM 2709a

Element	Mass Fraction (%)	Coverage Factor, <i>k</i>	Element	Mass Fraction (mg/kg)	Coverage Factor, <i>k</i>
Aluminum (Al)	7.37 ± 0.16	2.04	Antimony (Sb)	1.55 ± 0.06	2.36
Calcium (Ca)	1.91 ± 0.09	2.05	Barium (Ba)	979 ± 28	2.57
Iron (Fe)	3.36 ± 0.07	2.23	Cadmium (Cd)	0.371 ± 0.002	2
Magnesium (Mg)	1.46 ± 0.02	2.02	Chromium (Cr)	130 ± 9	2.05
Phosphorus (P)	0.0688 ± 0.0013	2.12	Cobalt (Co)	12.8 ± 0.2	2.45
Potassium (K)	2.11 ± 0.06	2.45	Lead (Pb)	17.3 ± 0.1	2
Silicon (Si)	30.3 ± 0.4	2.57	Manganese (Mn)	529 ± 18	2.16
Sodium (Na)	1.22 ± 0.03	2.02	Strontium (Sr)	239 ± 6	2.26
Titanium (Ti)	0.336 ± 0.007	2.26	Vanadium (V)	110 ± 11	2.10
			Zirconium (Zr)	195 ± 46	2.10

^(a) Certified values for all elements except cadmium and lead are the equally weighted means of results from two or three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of between-method and within-method components of uncertainty, following the ISO/JCGM Guide [3,4]. A component for material heterogeneity is incorporated into the uncertainties of aluminum, calcium, chromium, manganese, and sodium. The coverage factor (*k*) is determined from the Student's *t*-distribution corresponding to the appropriate associated degrees of freedom and approximately 95 % confidence for each analyte.

The certified values for cadmium and lead are each results from a single NIST method (isotope dilution (ID)-ICP-MS, see Table 4) for which a complete evaluation of all sources of uncertainty has been performed. The uncertainty provided is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and Type B uncertainty components related to the analysis, and *k* is the coverage factor corresponding to approximately 95 % confidence for each analyte.

Table 2. Reference Values^(a) (Dry-Mass Basis) for Elements in SRM 2709a

Element	Mass Fraction (mg/kg)
Arsenic (As)	10.5 ± 0.3
Cerium (Ce)	42 ± 1
Cesium (Cs)	5.0 ± 0.1
Copper (Cu)	33.9 ± 0.5
Europium (Eu)	0.83 ± 0.02
Gadolinium (Gd)	3.0 ± 0.1
Lanthanum (La)	21.7 ± 0.4
Mercury (Hg) ^(b)	0.9 ± 0.2
Nickel (Ni)	85 ± 2
Rubidium (Rb)	99 ± 3
Scandium (Sc)	11.1 ± 0.1
Thallium (Tl)	0.58 ± 0.01
Thorium (Th)	10.9 ± 0.2
Uranium (U)	3.15 ± 0.05
Zinc (Zn)	103 ± 4

^(a) Reference values for all elements are based on results from one analytical method at NIST. Uncertainty values represent the expanded uncertainties about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and type B uncertainty components related to the analysis, and *k* is the coverage factor (*k* = 2) corresponding to approximately 95 % confidence for each analyte.

^(b) The reference value for mercury represents the average value from analysis of portions from six bottles using ID-cold vapor (CV)-ICP-MS. Results indicate significant material heterogeneity; values ranged from 0.8 mg/kg to 1.1 mg/kg. The uncertainty for this reference value is in the form of a prediction interval.



XRF SOP ACKNOWLEDGMENT FORM

Name _____ SS # _____

Address _____
Street/Box City State Zip

Phone (local): _____ (permanent) _____

ACTIVITY INFORMATION

Type of Activity: Operation of the Niton XL3t 500 series handheld elemental analyzer for heavy metal screening and measurement of contaminated soil.

ACKNOWLEDGMENT

"I, the undersigned participant, being the age of 18 or above, desire to participate in the Activity described above, which includes transportation to and from Springfield. The Activity is potentially hazardous, and I have read and understand the standard operating procedures (SOP) associated with this instrument. I should not engage in the Activity unless I am alert and observant, which I represent myself to be. I assume any and all risks associated with the Activity including but not limited to, fall, personal injury, collision with other persons, the effects of weather, including high heat and humidity and motor vehicle transportation, all such risks being known and appreciated by me. I attest that I am sufficiently physically fit to participate in this Activity.

Knowing the risks, and in consideration of being permitted to participate in the Activity described above, I for myself and my personal representatives, heirs, and assigns, do hereby hold harmless and release, waive discharge and covenant not to sue the board of Governors of Missouri State University from any and all claims or liability on account of death or injury to person or property of the undersigned of any kind of nature whatsoever arising out of or in any way connected with, the undersigned's participation in the Activity and transportation activities, even though the claim or liability may arise out of the negligence or carelessness on the part of Missouri State University, or any third person, whether foreseen or unforeseen, known or unknown. The undersigned hereby expressly agrees that this release and waiver is intended to be as broad and inclusive as permitted by the laws of the State of Missouri and that if any portion hereof is held invalid, it is agreed that the balance, notwithstanding, continues in full legal force and effect.

The undersigned further states that he/she has carefully read the foregoing Release and Waiver of Liability, knows the contents thereof, and has agreed to sign this Release and Waiver of Liability as his/her own free act and deed.

I also declare that I will take all necessary and/or recommended precautions to insure my own person against physical and/or mental injury and property loss or damage. This includes, but is not limited to, following printed or verbal instruction given by the activity leader(s).

I further declare that I assume responsibility for my actions or behaviors that may conflict with accepted standards, university requirements for participants, common sense or the instructions I receive from Activity leader(s) either before or during the activity.

I do hereby affirm that I am covered under my guardian's medical policy or otherwise have adequate medical insurance.

I have read the above release and agree to the provisions contained herein. I have also informed my Guardian.

For the participant:

If under 18 years of age:

Participant's Signature Date

Guardian's Signature Date

This form should be returned to the QA/QC manager.