

# Handheld ED-XRF Instruments as a Quantitative Tool for Field or Lab Assessments of Metals in Rocks or Soil Contamination Studies

## Overview

In a time when data collection and analytics are required to be easy and almost instant, portable handheld energy dispersive x-ray fluorescence (ED-XRF) instruments have become an efficient tool for remote field and laboratory analysis of metals, metalloids and some non-metal elements in rock and soil samples. Incorporating XRF into a field program provides the flexibility of rapid, in-situ, elemental measurements and the ability to immediately delineate contamination hot spots. By refining the areal extent of contamination in the field, a detailed and precise sampling approach can be developed right away in order to obtain material for high precision laboratory analysis using other geochemical approaches such as mass spectrometry techniques in the laboratory. It is important to note that portable XRF geochemistry is not intended to replace traditional high-resolution geochemical methods but it provides a means for more direct and focused sampling, saving time and money when evaluating small and large field sites.

The use of portable ED-XRF instruments is well established and is used across many industries including pharmaceuticals, materials, agriculture, mining, petroleum

and environmental testing. For results to be meaningful and quantitative, XRF data from handheld devices must be calibrated to full scale wavelength dispersive XRF (WD-XRF) or inductively coupled plasma optical emission spectroscopy (ICP-OES) outputs. For the purposes of this study, ED-XRF data was compared and calibrated against ICP-OES and WD-XRF analyses.

A series of 20 unprocessed soil samples were analyzed using ICP-OES, WD-XRF and ED-XRF, on an as received basis with a total of 28 elements being measured and compared. For elements not analyzed with the ICP-OES, WD-XRF was used to calibrate the ED-XRF output. Results are provided for 13 elements between ICP-OES and calibrated ED-XRF data and 15 elements between WD-XRF and ED-XRF. Between ICP-OES and ED-XRF, eight of the 13 comparisons show a goodness of fit greater than 0.9. Between WD-XRF and ED-XRF, 11 of the 15 comparisons show a goodness of fit greater than 0.9. While there is a high degree of repeatability, some elements such as Sn and Co show lower correlation factors which highlights the need for laboratory validation testing to further refine and delineate calibrations of these elements for ED-XRF applications.

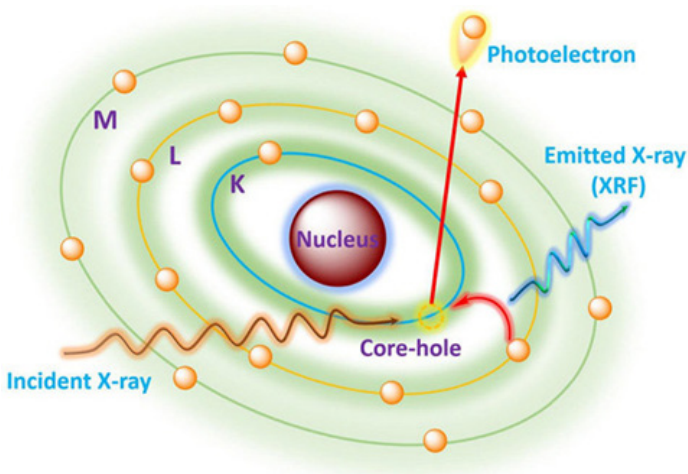
# Background

Traditional environmental testing of rock or soil metal contaminations involves acid soluble extractions and the use of ICP-OES techniques for measurement. An alternative, faster and less laborious method using energy dispersive x-ray fluorescence (ED-XRF) or handheld XRF has become more frequently used in recent years due to advancements in new designs and improved detector technology. Recent guidelines from the British Columbia Ministry of Environment and Climate Change Strategy in “Soil Sampling and Investigations”, now allow the use of ED-XRF as a testing methodology.

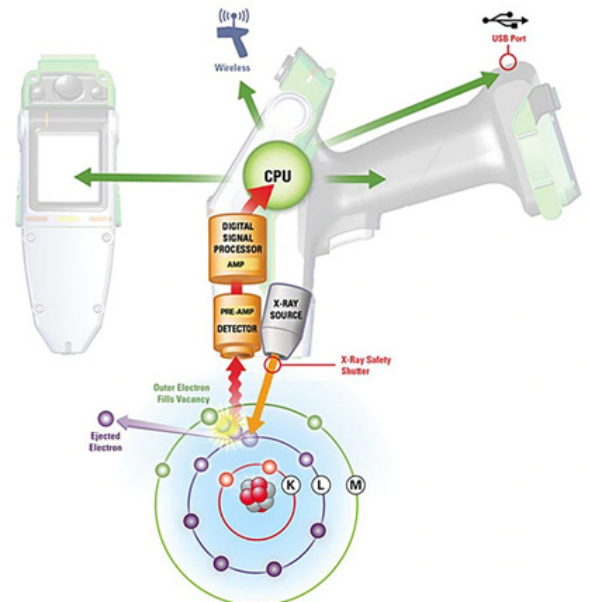
ED-XRF is a fast and efficient method that takes on the order of 2 to 3 minutes after preparation to analyze a sample. In order to effectively utilize ED-XRF technology as a quantitative tool, the instrument must be calibrated properly for materials targeted for analysis. Calibrations of ED-XRF instruments are based on other geochemical analytical instruments with high-precision and internal standards to provide data comparisons with the ED-XRF signal counts. The underlying principle behind all XRF applications is an x-ray source which excites electrons within the orbitals of an atom. Based on the elements, electrons from the K, L, or M orbitals are knocked off and an electron from an outer orbital moves in to fill the hole created. As the electrons change orbitals, a unique energy is emitted, which is specific to each element (Figure 1).

There are two main differences between WD-XRF and ED-XRF methodologies. First, the energy of the WD-XRF system is considerably higher which allows for better detection limits, particularly with light elements like sodium. Secondly, WD-XRF systems use internal crystals which diffract the x-rays directly to the detector. By changing the angle of the crystal, specific wavelengths are targeted resulting in a higher degree of resolution. ED-XRF instruments are much simpler (Figure 2) and collect a broad spectrum of emission x-rays.

In order to calibrate ED-XRF data, lab data from WD-XRF/ICP-OES is compared against the ED-XRF spectral intensities for a range of elements typically found in contaminated soils. Where possible, elemental concentrations should cover a wide range which allows for a better correlation fit and a more versatile calibration. For soils with anomalous elemental compounds or concentrations, a specific calibration should be built. In this study, the empirical coefficient model proposed by Lucas-Tooth and Price (1961) is used for calibration of ED-XRF concentrations.

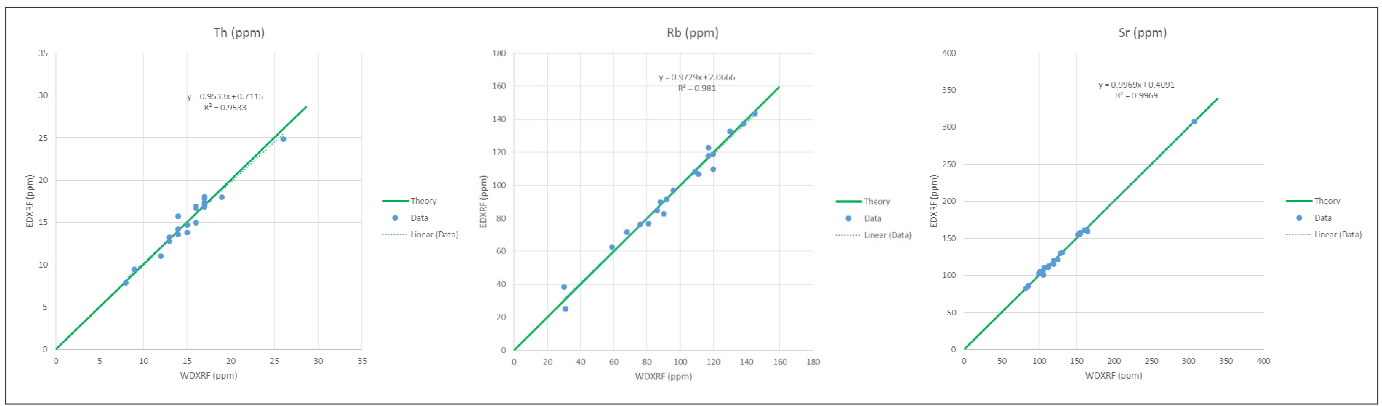


**Figure 1:** Excitation of orbital electrons results in characteristic emission spectra that then provide information about the element present (Zhang et al 2018).

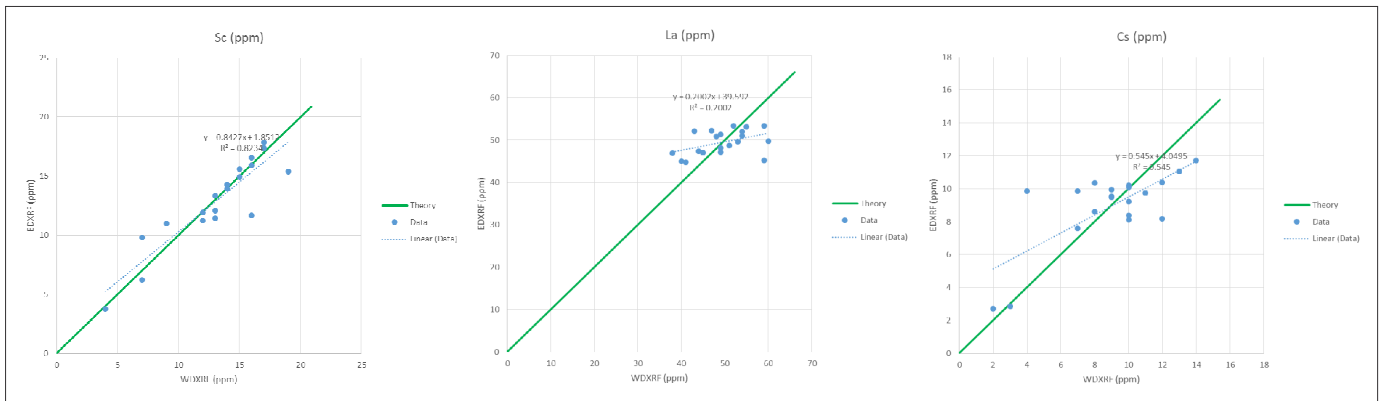


**Figure 2:** Schematic of handheld ED-XRF unit (ThermoFisher).

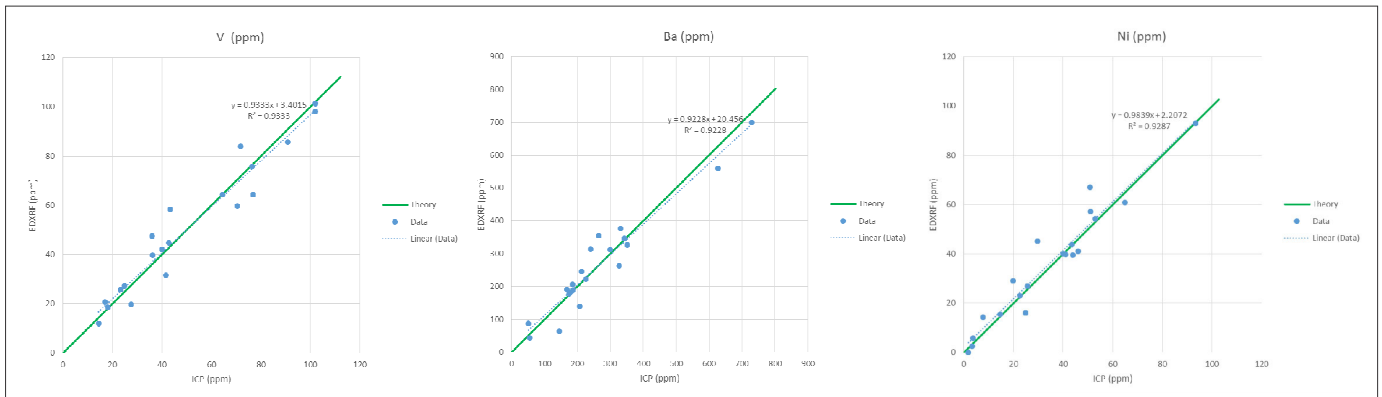




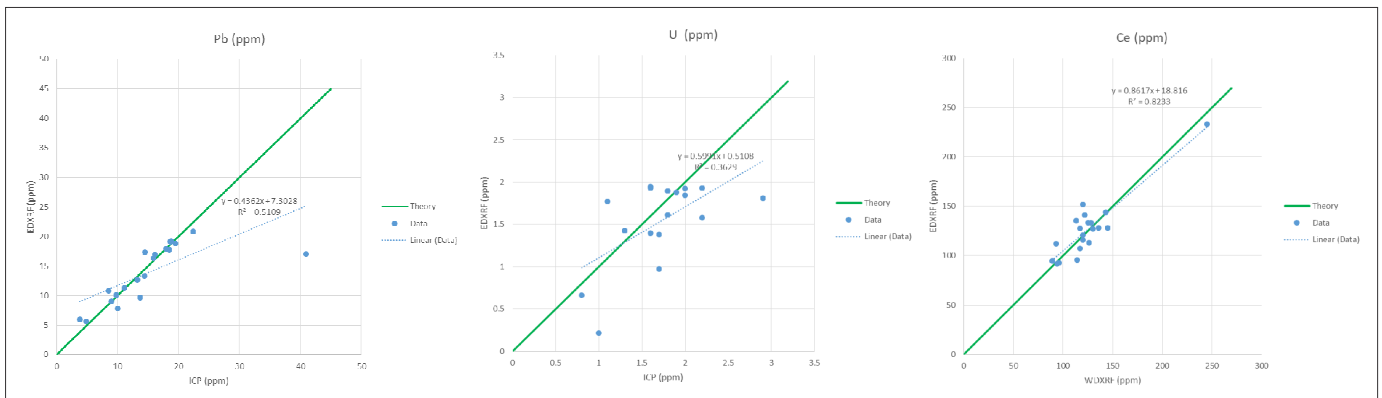
**Figure 3:** WD-XRF to ED-XRF data comparisons with strong correlation coefficients.



**Figure 4:** WD-XRF to ED-XRF data comparisons with weak correlation coefficients.



**Figure 5:** WD-XRF to ED-XRF data comparisons with weak correlation coefficients.



**Figure 6:** ICP-OES to ED-XRF data comparisons with weak correlation coefficients. Note that Pb has an outlier that significantly skews the correlation.

## Samples

The potential of using portable ED-XRF testing as a field and screening tool for measuring trace metal concentrations on contaminated soil sites was evaluated for this study. Portable XRF analysis provides a quick, easy and non-destructive approach that is cost effective. The intent of the ED-XRF field methodology is to facilitate efficient delineation of contaminated zones vertically and laterally, allowing for focused sampling in order to obtain the most critical samples for laboratory verification and high-precision metal contamination data using other methods (ICP-OES, etc). The test program evaluated the correlation and strength of fit for elemental analyses when comparing geochemical metal data of different methods such as XRF and ICP-OES. The use of ED-XRF testing as a rapid test tool is incumbent upon the development of a robust calibration. Without proper calibration, datasets lose the accuracy and reliability required for onsite assessments. Through the stringent development of a metals calibration, results show that there is a strong correlation between ED-XRF and ICP-OES methodologies for most elements and would provide an effective tool for field testing.

## References

Zhang R., Li L., Sultanbawa Y. and Xu Z.P. X-ray fluorescence imaging of metals and metalloids in biological systems. *American Journal of Nuclear Medicine and Molecular Imaging* 2018; 8(3): 169.188.

Thermo Fisher, <https://www.thermofisher.com/ca/en/home/industrial/spectroscopy-elemental-isotope-analysis/spectroscopy-elemental-isotope-analysis-learning-center/elemental-analysis-information/xrf-technology.html>

Lucas-Tooth, H. J. and Price, B. J. A Mathematical Method for the Investigation of Interelement Effects in X-Ray Fluorescence Analysis, *Metallurgia*, Vol. 64, No. 2, 1961, pp. 149-152.



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