



ALS Methods pXRF-34 pXRF-30

Portable XRF for Exploration & Mining

Analytical challenges and opportunities

Portable XRF (pXRF) is an exciting tool with many applications in mineral exploration and mining. Using pXRF, information on elemental composition can be generated faster than traditional laboratory assays in locations close to the field site for quick decision-making.

Applications include preliminary exploration data for on-demand drill hole planning, low-cost lithochemical characterization of drill core, ore routing in mineral processing, waste rock pile characterization, environmental soil analysis, Positive Material Identification of processed metal products for appropriate assay methods, and many others. Furthermore, with careful quality control and calibration, some elements that are traditionally quite expensive to analyze with wet chemistry can be determined in the geochemical lab at suitable precision for a low cost, such as silicon as a waste product in iron and base metal ore.

Like all geochemical analysis, however, pXRF can be used improperly to generate poor quality data that is not fit for purpose. All of the same considerations with respect

to method suitability for sample type and data precision expectations that are applied to traditional lab-based chemical analysis must also be considered when using pXRF instruments to avoid unacceptably poor precision, or worse, inaccurate results. Understanding these considerations can help you make excellent time-saving and cost-saving use of the technology while avoiding potential pitfalls with financial and legal consequences.

How it works

X-ray fluorescence, or XRF, works by bombarding a sample with x-rays which causes elements in that sample to emit more x-rays (this process is called fluorescence).

The wavelengths and energies of the emitted x-rays are characteristic of the elements they came from, and the intensity of the characteristic x-ray is related to the amount of the element emitting it. These features can be measured and used to identify which elements and how much of them are present in a sample. Large laboratory XRF instruments measure the wavelengths of the characteristic x-rays and is referred to wavelength dispersive XRF or WD-XRF. Portable XRF instruments usually measure the energies of the characteristic x-rays, a technology called energy-dispersive XRF or ED-XRF.



Challenges in pXRF analysis

Sensitivity by XRF for trace-level elemental analysis relevant to mineral exploration is lower than modern ICP-AES and ICP-MS techniques, which drive exploration for buried deposits. Both lab-based XRF and portable XRF have this issue; the best-case lowest detection limits for common exploration pathfinder elements are 1-10ppm, while a typical soil exploration package using acid digestion and ICP-MS measurement has lower detection limits of 0.01-1ppm.

The detectors in ED-XRF instruments have lower resolution than lab XRF, so elements with characteristic x-rays that have very similar energies may be difficult to tell apart. These are called interferences. For example, arsenic, tungsten and zinc may give false readings for gold, and lead may give false readings for arsenic. These inaccurate readings may be particularly dangerous since gold is a highly valued commodity, and arsenic can be a serious environmental hazard. Overstating the presence of either element is very undesirable.

X-ray tubes that generate the bombarding x-rays may be made of different materials, including rhodium, tungsten, gold, silver, and tantalum; each material has advantages and drawbacks depending on the elements being analyzed. For example, rhodium tubes are well-suited to geological applications, but can sometimes give false readings for silver content in the sample.

Bombarding x-rays must have more energy than the characteristic x-rays (energy in > energy out); readings at 40keV are common because it is better suited for analyzing light elements like silicon and sulfur, but 50keV may be required for analysing elements like the tin, and rare earths. If two bombarding x-rays hit the detector at the same time, they will read as one x-ray at double the energy, and may be identified as the wrong element by the pXRF software. This is referred to as "peak pile-up" and gets worse as the concentration of the problem element increases. Some examples include iron peak pile-up falsely reading as lead, and zinc peak pile-up falsely reading as molybdenum.

The sample itself can absorb characteristic x-rays before they make it to the detector, and even emit third-order x-rays because of this absorption. The various ways samples may alter the characteristic x-ray response are collectively called matrix effects. Matrix effects are the





reason that manufacturer's detection limits are rarely possible to attain in geological samples, with their complex crystal structures and chemical make-up. For example, samples with a matrix rich in heavy elements, which describes most precious and base metal ore samples/concentrates, may prevent detection of light elements like magnesium and aluminium even if they are present in concentrations.

X-rays only penetrate the very surface of the sample and the window of the detector is small. This means sample homogeneity is a major concern for data quality in pXRF. If the sample is already fairly homogenous, like concentrates or processed metal products such as blister copper, it may be sufficient to take multiple (5-10) readings across the sample and average the result. For rocks, drill core or raw ore, the sample should be prepared by crushing (if necessary) and pulverizing to a standard grain size to homogenize it before pXRF analysis.

The distance between the sample and the detector, the sample surface geometry, and the container the sample is in (surface effects) can all affect the data quality. Moisture causes many issues in pXRF analysis, so it is best if the sample is dry before analysis.

Finally, X-ray tubes can fail and degrade over time as can batteries, causing random fluctuations in measurement results that can be difficult to isolate from "real" effects caused by the physical sample or fundamental chemistry. Voltage fluctuations in electrical power supply, extreme ambient temperatures and vibration may also artificially affect results from a pXRF instrument.

pXRF software, QAQC and custom calibration

The software that pXRF manufacturers include with their instruments solves many of these problems through mathematics and signal processing, but not all of them, and not always in a consistent way. By necessity, default instrument analysis modes must balance performance across a wide range of elements and sample types against possible pitfalls due to the challenges outlined above.

Many instruments have more than one operating mode that focus on a particular application. A mathematical method called fundamental parameters, often called 'geo' or 'mining' mode on the instruments, can handle heavy sample matrices (ores and concentrates) and it can sometimes measure the light elements, but detection limits are high. Compton normalization, often called 'soils' mode, works best in light sample matrices (soils and unmineralized samples) and can achieve single digit ppm detection limits, but it cannot measure iron or lighter elements. For analysis of processed metal products like copper anode or steel, a special 'alloy' mode or a different instrument entirely may be required.

Fortunately, a robust QAQC protocol can help identify where the software may be limited in its' ability to correct for problems. However, off-the-shelf certified reference materials often utilized for QAQC do not always reflect the matrix of a sampling program. One caution is that matrix matched CRM's are extremely important in the

case of pXRF due to matrix effects. For example, samples from a sediment-hosted copper deposit will behave quite differently from copper-bearing VHMS in pXRF analysis, even if they have the same copper grade.

Not all CRM manufacturers describe what kind of ore deposit their product was made from, so you should inquire with your supplier if necessary.

Another option is to choose a selection of samples for analysis by traditional analytical techniques to compare against pXRF results to ascertain what matrix effects may be present.

QAQC for pXRF should follow all the sample procedures as traditional geochemical laboratory analysis. At a minimum the manufacturer's direction for calibration checks should be followed and regular control samples inserted.



Accuracy and precision of pXRF results

The challenges described here outline the potential for inaccurate results, but they also contribute to relatively poor analytical method precision. Method precision is the amount the value of a data point from a single measurement may deviate within a range due to uncertainties in the analytical method in use. In pXRF analysis, method precision may range from 5 to 20% or even more, depending on the element, when the instrument is used correctly and a robust QAQC program is in place. This is similar to the 10% precision expected with exploration geochemistry and indicative methods, but it is much poorer than that of the assay techniques used for financially sensitive data (1 to 5%). This difference in precision should always be taken into account when comparing pXRF results to traditional assay results done

on the same material. For example, a letter of credit for a banking institution requires a definitive result, such as 22.34% copper content, while pXRF results may be stated as 20% ± 10% copper content.

Summary

Due to potential matrix effects, sample heterogeneity issues, and the other challenges mentioned in this technical note, use of pXRF for mineral resource and reserve estimation, valuation in commercial exchange, commercial settlement, and government purposes carries significant risk. Portable XRF is ultimately an indicative geochemistry tool best used in support of field-based decision making or to provide enhancement to multi-element geochemical analyses, and it requires care and consideration of appropriate sample handling and QAQC protocols in order to generate data that can be used with confidence. pXRF can save time, lower costs and add value to mineral exploration and mining settings when it is used in a fit-for-purpose application.

A tool for time sensitive decisions

ALS Geochemistry offers semi-quantitative pXRF analysis on pulps immediately after sample preparation, within five days of receipt at the lab. pXRF analysis on a pulverized sample produces a more representative view of the sample's geochemistry than an analysis taken on a rock or drill core surfaces, and the results are available while traditional geochemical analyses are pending in the laboratory. ALS's signature quality control and decades of XRF expertise are applied to a selection of elements relevant to exploration for many types of deposits. Detection limits, precision and accuracy of the method are suitable for identifying anomalous samples to aid in resource identification and exploration drilling.

Breaking boundaries with innovative solutions

ALS Geochemistry's innovative application of pXRF after sample preparation breaks through barriers to effective implementation. Like any instrument used in analytical

geochemistry, portable XRF requires regular calibration, quality checks with reference materials, personnel training and detailed attention to sample representivity to produce dependable results. All of these considerations take up a geologist's time and distract from the task at hand – deciding where to drill next. Your project now has access to the rapid turnaround benefits of reliable pXRF results while avoiding the capital and overhead costs inherent to on-site analysis.

pXRF-30 Semi-quantitative scan by pXRF

ALS Geochemistry has tested and validated the suite of elements offered by portable XRF to ensure reliable results suitable for snap drilling decisions. Not every element is suitable for analysis by portable XRF; it is well known that gold, unfortunately, cannot be reliably measured using this technology.

If there are key exploration elements that indicate proximity to mineralization for a project that are not included in the pXRF suite listed, please contact us and we can discuss the possibility of analysis. ALS is excited to help you implement a pXRF program that provides value to your operations. Please contact one of our client services teams for more information.

A pulverized sample is analyzed immediately following sample preparation using pXRF. The samples are scanned using a rhodium anode and custom calibration.

The method is a semi-quantitative scan aimed at quickly identifying anomalous samples. A set of key exploration elements are reported at detection limits relevant to identifying geochemical anomalies and aiding in drilling decisions. Precision and accuracy for the method is $\pm 20\%$.

Analyte	Symbol	Units	Lower Limit
Copper	Cu	ppm	50
Lead	Pb	ppm	50
Zinc	Zn	ppm	50
Nickel	Ni	ppm	50
Arsenic	As	ppm	50
Manganese	Mn	ppm	100
Chromium	Cr	ppm	100
Iron	Fe	%	0.5
Calcium	Ca	%	0.5
Sulfur	S	%	0.1

pXRF-34 for Litho geochemistry

pXRF-34 can be added to any ALS four-acid multi-element method to produce a more complete element suite. The crucial litho geochemical elements Si, Ti and Zr are under reported in four-acid digestion analyses due to incomplete





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dissolution of resistive minerals and volatile loss during heating. Titanium and Zr are generally present in resistive minerals such as rutile and zircon which are often not fully dissolved during four-acid digestion and therefore under reported in the analyses. Silicon is lost during four-acid digestion as the volatile species SiF_4 and therefore is not reported for 4-acid digestion methods. All three elements are representatively reported by pXRF to provide additional element information that can add value to your data set and make data more meaningful.

Element	Symbol	Range %
Silicon	Si	0.5-47
Titanium	Ti	0.1-60
Zirconium	Zr	0.0005-5

References and further reading

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Natural Resources Canada (December 2010). "Operator of Portable X-ray Fluorescence Analyzers Certification Information and Examination Preparation Booklet", Version 3.

Gwendy Hall, Graeme Bonham-Carter & Angelina Buchar (March 2014). "Evaluation of portable X-ray fluorescence (pXRF) in exploration and mining: Phase 1, control reference materials", Geochemistry: Exploration, Environment, Analysis, Vol. 14, pp.99-123.

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