Portable XRF in the Mining Industry

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 settings close to the field site for quick decision-making.

Applications include preliminary exploration data for on-demand drill hole planning, low-cost lithogeochemical characterisation of drill core, ore routing in mineral processing, waste rock pile characterisation, 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 QAQC considerations 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. Portable and benchtop XRF instruments usually measure the energies of the characteristic x-rays, a technology called energy-dispersive XRF or ED-XRF. ED-XRF has no moving parts, so it can be easily miniaturised and turned into rugged, portable instruments.

Challenges in pXRF analysis

Sensitivity by ED-XRF for trace-level elemental analysis relevant to mineral exploration is lower than modern analytical geochemical 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.

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The detectors in ED-XRF instruments have lower resolution than lab XRF, so elements with characteristics 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 in the samples you want to analyze. 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); 40keV instruments are common because they are better at analyzing the light elements like silicon and sulfur, but 50keV instruments may be required for analyzing elements like the precious metals, 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 aluminum 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 pulverising to a standard grain sise to homogenise 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, pXRF technology is still developing and sometimes prone to failure. X-ray tubes can crack and batteries can degrade, 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 normalisation, often called 'soils' mode, works best in light sample matrices (soils and unmineralised 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 identify where the software may be limited in its' ability to correct for problems. QAQC for pXRF should follow all the same procedures as the industry standard in your region for traditional geochemical laboratory analysis. At a minimum, the manufacturer's directions for calibration checks should be followed exactly and regular control samples, preferably certified reference materials (CRMs), should be inserted into the

sample flow at 10% frequency. One caution is that matrix-matched CRMs are extremely important in the case of pXRF due to matrix effects. Not all CRM manufacturers describe what kind of ore deposit their product was made from, so you should inquire with your supplier if necessary. 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.

Custom instrument calibrations can also be undertaken to improve the accuracy and precision of pXRF for specific sample types. A custom calibration involves matrix-matched CRMs and representative samples prepared in the same way that field measurements will be taken, which have been previously analyzed with the relevant wet chemistry techniques. The pXRF results on these samples are corrected to the known values over a range of concentrations relevant to the sample type, and the calibration saved so that the instrument can accurately measure unknown samples of the same matrix. Custom calibrations greatly expand the possibilities of pXRF analysis, but it is very important to understand that changing the sample type or preparation method without also changing the calibration can result in inaccurate results.

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% when the instrument is used correctly and a robust QAQC program is in place. This is on par with exploration geochemistry and indicative methods, but it is much poorer than that of the assay techniques used for financially sensitive data (1.5 to 5%, or even less). 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% ± 5% 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 a indicative geochemistry tool best used in support of field-based decision making, and it requires all the normal 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 by a knowledgeable operator in a fit-for-purpose application.

References and Further Reading

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