

## Paper 15

# Field Portable X-Ray Fluorescence Geochemical Analysis – Its Contribution to Onsite Real-time Project Evaluation

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## ABSTRACT

*The field portable x-ray fluorescence spectrometer (FPXRF) has evolved to become a unique highly productive geochemical tool over the past 30 years. As with most highly sophisticated technological tools, it is deceptively simple to use, can easily be carried and operated using only one hand and can provide an onsite, nondestructive chemical analysis of about 30 elements ranging in concentration from about 10 ppm to 100 percent in less than minute. Its use is commonly judged by comparing its purchase price against laboratory analyses. However, the real value of the FPXRF goes beyond cost savings resulting from reducing the number of samples sent to a laboratory for chemical analysis. Onsite use of the FPXRF allows an accurate appraisal of a property, rocks, soils, ore grade, drill cuttings, cores, concentrates etc. in real time when and where correct decisions are needed. The use of this onsite FPXRF method has been objectively demonstrated to be three times more cost-effective than conventional methods of collecting judgmental samples for subsequent laboratory analysis. Laboratory analysis is not eliminated but fewer samples are necessary to appropriately document mineralization identified by FPXRF. The FPXRF capability has not yet evolved to a low enough detection limit for effectively determining gold and PGM in the field so indicator elements are used. Near laboratory quality results can be obtained when people using the instrument understand the basic principles of x-ray fluorescence spectrometry, the physical characteristics that control quality and protocols that can be used to enhance the data quality. This knowledge base is quantitatively described in this paper and the relative importance of each is documented by case histories of the onsite FPXRF use.*

## INTRODUCTION

X-ray fluorescence (XRF) is a technology that has been used to determine the chemistry of geological samples by commercial laboratories for 60 years. Applications within the mining industry have increased over this time period and field portable x-ray fluorescence instruments (FPXRF) represented 22 percent of the total x-ray spectroscopy demand in 2004 (Press, 2005). The mining industry has been actively engaged in the development of the FPXRF for the last 30 years. FPXRF instruments represented 36 percent of the total XRF spectroscopy market in 2005. The FPXRF geochemical tool currently weighs less than about 3 pounds and can be used onsite to chemically analyze any solid, and even liquids, for a broad suite of inorganic elements. Within tens of seconds to minutes FPXRF measurement readings are reported directly in parts per million (ppm) with an accuracy and precision that approaches that of commercial laboratory determinations.

Although commonly compared to laboratory analysis costs, the FPXRF should be considered a field tool. It allows geoscience professionals the opportunity to determine individual element concentrations at the site while evaluating potential

geological causes for the responses. Appropriate additional and more representative samples can then be collected for confirmatory laboratory analysis. The professional then knows the geochemical relationships of a broad suite of chemical elements while at a field site. The use of this onsite FPXRF method has been objectively demonstrated to be three times more cost-effective than conventional methods of collecting judgmental samples for subsequent laboratory analysis (Taylor et al., 2004). The real value goes beyond this cost savings. Onsite use of the FPXRF allows an accurate appraisal of a property, ore grade, drill cuttings, cores and concentrates in real time when and where correct decisions are needed.

The following sections briefly describe the principles of XRF analysis, evolution of the FPXRF, current status of instruments applied to mining industry applications, case histories and new technological developments in FPXRF that demonstrate its tactical and strategic use in the mining industry.

## BASIC PRINCIPLES OF XRF ANALYSIS

Operationally, the FPXRF instrument is a simple and dependable tool representing a product of complex and highly innovative technology resulting from the work of a great number

of scientists over the last 40 years. In fact, it continues to evolve and improve as new uses and needs for its capabilities increase. The basic nature of the instrument involves the controlled release of x-ray radiation energy, generated either by radioactive isotopes or by an x-ray tube beamed directed at a sample. This x-ray energy flux strikes the inner shell electrons of the atoms of elements within the sample with sufficient energy to cause an electron in the K- and L-shells to be displaced. The atom reestablishes equilibrium by another electron dropping into the vacated electron position. This return to atomic stability emits a photon of energy that is characteristic of each element present in the sample while the intensity of photon energy given off each element in the sample defines the amount of that element in the sample exposed to the x-ray flux.

FPXRF instruments perform an amazingly complex suite of operations. They rely on energy dispersive x-ray spectrometry for x-ray analysis as opposed to the wavelength dispersive x-ray instruments that are found in commercial and research laboratories. The energy levels are measured in thousands of electron volts (keV), ranging from about one to 100 keV. The FPXRF accumulates the photon energy suite, identifying and separating the amount of photon energy received from each element in the sample. Through internal software, the FPXRF corrects for a complex suite of intra- and inter-element overlaps as well as selected sample matrix characteristics to calculate the part per million concentrations of elements within the scanned sample. Unlike the laboratory wet chemical analysis that depends on a designated partial to total digestion, each FPXRF chemical analysis is a total analysis. The instruments increasingly perform most of the analytical work but the operator, and certainly those interpreting the analytical results, need to have a general knowledge of XRF spectrometry. FPXRF manufacturers provide users with manuals that give some basics but a small book by Jenkins (1999), is recommended for background on the practical aspects of XRF spectrometry.

The analytical results of more than 5,000 samples are stored within the FPXRF and are typically downloaded to a spreadsheet that includes not only the concentration but also a two or three standard deviation value for each element analyzed. This allows the assessment of the precision of each reported elemental concentration. In addition, and of considerably more importance, an x-ray spectra for each sample analysis is also stored with the analytical data. The spectra can be accessed to identify the potential for inter-element interferences. This assessment is also possible using published lists of elemental K- and L-shell energy levels but the process is more efficiently performed using the spectra provided by the FPXRF. The spectra can also be used to identify and quantify the concentrations of additional elements not reported on the spreadsheet. Each FPXRF generally reports the concentrations of a suite of 25 to 30 elements selected either when the FPXRF was purchased or, by the manufacturer providing a suite of elements commonly used by the mining or environmental industry.

## HISTORICAL EVOLUTION

A new form of electromagnetic radiation was discovered by Wilhelm Röntgen in 1895 while working with a cathode ray tube when fluorescent material some distance away from the tube lit up. He named this radiation "x-rays" reflecting its unknown nature. He demonstrated one example of the usefulness of these x-rays by making an x-ray photo of his wife's hand. Medical science had a new technology. In 1913 Max von Laue discovered that x-rays were uniquely diffracted in a reproducible manner by individual salt crystals, leading to the development of x-ray diffraction (XRD) identification of minerals. Improvements in x-ray diffraction lead to the use of crystals as filters of x-rays for chemical analysis by XRF. By the early 1920s the common characteristic elemental signatures were known leading to a paper by A. Hadding (1922) in which he described the use of XRF for the chemical analysis of minerals. It took another 8 years until Eddy and Laby (1930) were measuring parts per million trace elements on a practical basis using a Geiger counter detector to measure the spectra. However, it was not until 1947 that the laboratory XRF instrument configuration we use today was created, still using the Geiger counter detector. The first commercial floor standing x-ray spectrometer became available in the early 1950s as gas-proportional and scintillation detectors replaced the Geiger counter. These new detectors reduced background levels, detection limits and allowed much higher counting rates. The theoretical relationships between elemental concentrations and x-ray energies, "fundamental parameters" were similarly developed in the 1950s. Webber (1959) described the early application of XRF to geochemical prospecting using laboratory instruments. Laboratory x-ray instruments further evolved into the early 1960s with the development of lithium fluoride diffracting crystals, use of chromium and tungsten target x-ray tubes and multichannel analyzers. Fundamental parameter computer programs were developed for converting x-ray intensities into concentrations. These laboratory instruments continued to evolve through the 1970s with the development of the lithium drifted silicon detector and improvements in computers. Innovations continue through the present.

## FPXRF ORIGIN AND EVOLUTION

The concept of taking the XRF instrument to the onsite sample was initially developed by Bowie, Darnley and Rhodes who first described a FPXRF instrument they developed in 1965. They used a variety of radioisotopes and balancing crystals for XRF analysis in a battery powered instrument. This instrument was the basis of two subsequently developed FPXRF instruments, one produced as the Hilger PIF and a second produced by the Ekco Electronics Ltd in 1968. Both instruments determined one element at a time, required a trained operator and attracted the attention of Outokumpu Oy.

### Commercially Available FPXRF Instruments

Outokumpu Oy together with John Rhodes at Columbia Scientific Industries in Austin Texas produced the first practical FPXRF instrument for mining applications with the CSI-740 instrument. Commercially available in 1979, the CSI-740 included a much improved, high resolution gas proportional tube detector and eliminated the need to exchange filters making it easier to use but still requiring considerable training to operate effectively. The CSI-740 used separate probes for each radioisotope and standardized the four radioisotopes still used today for FPXRF instruments. The instrument weighed about 20 pounds, including the battery, and cost between \$25,000 and \$30,000 (1970s US dollars) depending on the number of acquired accessory probes. It could be used on either battery or line voltage and measured data were reported on computer in counts per second for each element. Interestingly, the initial major use of this FPXRF in the US was for scrap metal identification.

Another prototype instrument, the ATX-100, was designed in Salt Lake City during the same time period. It included the radioisotopes within the basic instrument package instead of as external probes. It weighed about the same as the CSI-740, read out in raw counts per second but did not evolve into a commercially available FPXRF.

Outokumpu and Columbia Scientific Instruments continued to develop the FPXRF. Improvements were made in ease of use, improved gas proportional counter, operating system with better data processing, increased memory, improved surface probe and other innovations, resulting in the introduction and evolution of the X-MET 880 in the late 1980s and into the 1990s. Still reading out in counts per second the 880 could include 32 calibration models using empirical matrix models based on laboratory analyzed samples. It weighed about 19 pounds and ranged in cost from about \$40,000 to \$60,000 (1980s US dollars). Leasing of the FPXRF was introduced with the increased use of the 880. A lithium-drifted silicon diode detector cooled by liquid nitrogen was available in 1991 that considerably lowered the detection limit. Instead of the 100 to 200 milligram per kilogram (mg/kg, equal to parts per million (ppm)) detection limits for copper, zinc, lead and arsenic using the gas proportional tube, the Si (Li) detection limits were on the order of 30 to 80 mg/kg.

In the late 1980s and early 1990s, TN Technologies in Texas produced the Spectrace 9000 FPXRF instrument using a mercuric iodide semiconductor detector that allowed detection limits approaching that of the Si(Li) detector under ambient temperature conditions. This FPXRF also used a fundamental parameter computer program in the instrument that allowed internal "standardless" calibration. Using the fundamental parameter algorithm, this FPXRF recorded concentrations in ppm. The instrument included the radioisotopes in a single probe and the instrument package weighed about 17 pounds, with the radioisotopes contained within a single probe. It could simultaneously analyze 25 elements, store 300 analyses and be purchased for about \$55,000 but it could also be leased.

Significant improvements in the late 1990s and early 2000s led to the FPXRF instruments in use today. Development of Peltier-cooling allows incorporation of the new Silicon Positive-

Intrinsic-Negative(PIN) diode detector, a miniaturized x-ray tube and improvements in data processing, thereby introducing a truly hand portable FPXRF. The miniature x-ray tube provides a higher x-ray flux than the isotope sources and, coupled with the Peltier cooled Si PIN diode detector, significantly reduced the resolution to about 0.2 KeV. It also had the affect of lowering the detection limit to a level that approaches laboratory bench-top and floor-standing XRF instruments for many elements. The improvements in computerized data processing allows increasingly accurate and precise measurements that covers an analytical range from detection limits of less than or equal to 10 ppm to 100 percent. The entire FPXRF only weighs 3 pounds, can easily be held and controlled by one hand. It includes a rechargeable battery that commonly lasts about 8 to 10 hours but can be easily exchanged in the field.

### CURRENT STATUS OF FPXRF INSTRUMENT OPTIONS

Niton (Thermo Fisher Scientific), Innov-X Systems, Inc. and Oxford Instruments are the three dominant FPXRF providers and innovators continuing the evolution of the FPXRF. All provide the most advanced tube type FPXRF in company-specific configurations and operating systems in a pistol form. Only Niton offers a radioisotope instrument in a smaller "phaser" form. All current (2007) tube type FPXRF weigh about three pounds and determine a standard default suite of about 25 elements unless the purchaser or renter requests a specific suite of elements of particular interest. Niton provides a radioisotope FPXRF instrument that is significantly smaller than the tube FPXRF and weighs only 1.7 pounds; it incorporates one or all three of the radioisotopes to analyze a full suite of elements.

The FPXRF equipped with the x-ray tube has only had relatively limited use in field environments; it is therefore, too early to judge the tube life, durability and reliability. It produces a higher x-ray flux than radioisotopes are allowed by regulation to produce in a FPXRF but it generates a broader energy band than that of individual radioisotope sources. The three companies estimate the tube life ranging from two to five years. This is about the same time frame for replacing the cadmium-109 isotope source to maintain a reasonably low detection limit and low counting times (about four years). However, unlike isotope sources that decay at a predictable rate with time, the x-ray tube terminates abruptly when the tube burns out and requires replacement by the manufacturing company. This may be an issue when working in isolated terrain with limited access. Radioisotopes have a perceived risk sparked by the required radiation symbol on the FPXRF that may complicate transport and use in some areas, but there are also specific individual state requirements for the use of the x-ray tube FPXRF in some areas that are not required of the radioisotope sourced FPXRF. Each FPXRF company maintains state regulatory standards and has a ready reference for work in any state. The x-ray tube has the advantage that it is capable of determining the same suite of elements in one measurement that requires three isotope source measurements. However, if the intended use requires a selected suite of elements provided by a single isotope source then the radioisotope source may be preferable.

### Radioisotope Element Suite

Iron-55, with a half-life of 2.6 years, currently provides for the analysis of the light elements from about phosphorus through vanadium using their respective K-lines. Cadmium-109, with a half-life of 1.3 years, provides analyses of titanium through molybdenum using K-lines and tantalum through uranium using L-lines. Even with its short half life this radioisotope is the most commonly used because it covers most of the elements of interest in the mining industry. Americium-241, with a very long half-life of 433 years, provides analyses of zinc through barium using K-lines and tantalum through uranium using L-lines. These three are the most commonly used radioisotopes but curium-244 with a 17.6 year half-life, is also used in some cases to optimize a specific suite of elements. Curium-244 provides analyses of titanium through selenium using the K-lines and lanthanum through lead using L-lines.

### Detection Limits

The detection limits are variably listed as specifications for each of the FPXRF instruments ranging from an estimated 5 to 30 ppm for most trace elements. The detection limit is usually counting-time and sample-matrix dependent. The detection limit and the standard deviation around the element concentration decrease at about the square root of the time the sample is exposed to the sample (counting time). In other words, the detection limit decreases by half (a factor of 2) as the counting time is increased by a factor of four. A common practice is to use a count time of about 30 or 40 seconds for most semi-quantitative onsite sample analysis and up to two minutes for a quantitative determination of the sample chemistry using a sample cup and instrument stand. The sample cup and longer measurement time is recommended for disaggregated samples like soils and sediments that will be sent to the laboratory for confirmation analysis so that the laboratory is analyzing the same sample as analyzed by the FPXRF. The counting time can usually be set so that once the measurement is started, the shutter closes after the set time, the analysis is recorded along with its photon-energy spectrum and the instrument is ready for the next sample. Little further improvement in the detection limit is usually achieved for counting time longer than two to three minutes.

### X-Ray Spectra

Each of the instruments is set up so that the K and L photon energies from the sample for each of the elements are separated along the x-axis and the accumulated counts indicating the peak intensity are on the y-axis. Each also uses an internal standard to maintain calibration. These K and L energies and their respective peak heights are shown graphically when a spectrum for a specific sample is opened. A spectrum of each sample is stored with the suite of elements reporting to the spreadsheet usually representing the analytical values and their respective error. Each instrument usually has a low range calibrated model

for element concentrations less than about three to five percent and a high range calibrated model for element concentrations overlapping this range to 100 percent. The lower range is usually a Compton scatter model and the upper is a fundamental parameters model. Both models provide "standardless" calibration of each of the elements in the suite reported in the spreadsheet.

Elements not included in the spreadsheet suite are also included in the FPXRF analysis and their peak heights can be seen in each of the recorded spectra. The peak heights are usually in counts per second. Peak heights can be then used with a few laboratory-analyzed samples to establish a calibration for other elements of interest. The spectra should also be investigated to visually see the potential element(s) that can be interfering in a desired element concentration. Everyone interpreting FPXRF derived data should inspect the spectra for these potential interfering elements.

### SAMPLE MATRIX

Sample matrix refers to physical characteristics of the sample. These include particle size distribution, mineralogy, heterogeneity, moisture content and extraneous material. The area of the sample exposed to the x-ray flux is essentially the size of the opening in the front of the instrument (SAFETY WARNING: look only when the shutter is closed). The FPXRF analyzes all the rock mineralogy or other media within this area. The depth of penetration is essentially proportional to the bulk density of the material being analyzed, ranging from as low as a few millimeters on sulfides to as much as a centimeter or more on light soils. The depth of material being analyzed decreases geometrically with depth so the first few millimeters of geological materials may well represent 60 to 80 percent of the depth analyzed. All of the above parameters can be as important for rock surfaces as for disaggregated soils and sediments.

### Particle Size and Heterogeneity

The ideal sample for XRF analysis is one that has been pulverized, homogenized and fused into a glass in the laboratory eliminating particle size and homogeneously distributing the element concentration throughout the glass sample. Variability of FPXRF elemental concentrations for any sample compared to the laboratory analysis will increase with increasing particle size. Fine-grained homogeneous materials, like soil horizons have a minimum degree of analytical variability but can still have considerable natural physical variability. Even homogenous samples as coarse as a couple of millimeters commonly have reasonably low analytical variability. However, as the grain size increases, the potential variability increases geometrically because of both grain size and lack of true homogeneity of the sample exposed to the x-ray beam. The analytical variability decreases again as the sample approaches a flat mono-mineralogical particle (single mineral rock) that covers the area analyzed by the FPXRF window.

Rock samples, particularly fine-grained breccias, typically result in similar highly variable chemical data when compared to laboratory analysis. Variability increases with increasing particle

size heterogeneity of the minerals in the sample. However, as described in a case history, this condition is one of the primary benefits of the FPXRF over the laboratory as the FPXRF can identify specific mineralogical or particle characteristics within the rock that contain the majority of the desirable mineralization. On the other hand, the laboratory chemical analysis is a partial to complete digestion of a portion or perhaps the entire rock that it receives depending on its size. This difference in what part of the sample is being analyzed by the laboratory compared to the onsite FPXRF is generally the major source of variability when comparing laboratory elemental concentrations with those from the FPXRF.

### Moisture

The FPXRF can handle fairly moist samples but if the sample pores are saturated with water, the sample should be set aside until water is no longer draining from the sample and the surface appears dry. This condition typically represents less than about 20 percent moisture. High levels of moisture can be handled and even the moisture content can be measured by the FPXRF using the backscatter part of the spectra. However, this process can take additional time to correct for the moisture content. This correction requires laboratory analysis of dried samples to determine correction factors needed to calculate sufficiently accurate and precise element concentrations. This process establishes an empirical calibration that can be applied for specific purposes. Sample gels with less than 20 percent solids have been analyzed in this manner by a FPXRF allowing not only a chemical analysis but also the moisture content to be determined on an onsite sample.

### Extraneous Material

Unlike the laboratory, the FPXRF analyzes everything within the open shutter area and that will include organic debris, brick, tile and other extraneous material in the soil and stream sediments. The laboratory may either remove most or all of this extraneous material or simply crush and pulverize it with the sample. Most of the material will generally dilute the geochemical signature that is of interest, but not always. Organics can be dilutants but can also sorb sufficient metals that they can create a false anomaly. Therefore, it is best to screen out roots, leaves, needles and other extraneous material using a relatively coarse screen size (40 mesh or less) for soils and stream sediments. FPXRF of both the sieved and unsieved sample is recommended as part of the early site work. It is always a good idea to also check the elemental composition of the extraneous material, particularly the organic-rich material. This ability to determine the composition of all types of media is another of the advantages of using the FPXRF.

The maximum volume necessary for either the laboratory or the FPXRF is the volume that fills the plastic cups that usually comes with instrument. The cups should be used and labeled for those samples that will be sent to the laboratory for confirmation purposes. Each cup might hold much more than what the

laboratory needs but more importantly, it represents the same sample analyzed by the FPXRF.

### CONFIRMATION/CALIBRATION SAMPLES

Everyone operating a FPXRF, particularly those interpreting FPXRF analytical results, should have a basic understanding of sample matrix issues. The US EPA provides a protocol for the use of a FPXRF that broadly covers many of the aspects that need to be considered to acquire appropriately accurate and precise analytical data using the instrument in the field. This U.S. EPA Office of Solid Waste SW-846 Method 6200 can be accessed at <http://www.epa.gov/sw-846/main.htm>. This site also contains a suite of other analytical methods that can be applied in the field. It also contains links to the U.S. EPA Environmental Technology Verification Program evaluation of seven FPXRF instruments in 1995.

The operating procedure described by Method 6200 has been demonstrated to yield reliable analytical results. In addition, if this procedure is used to acquire the data, the data are of "known quality" and can later be used for environmental purposes as well as exploration and feasibility purposes. This protocol is also commonly available at instrument manufacturer's websites.

The FPXRF is analyzing as much as an order of magnitude more of the sample than the laboratory analysis. Therefore, based on volume of sample analyzed, the FPXRF analysis is generally more representative of the soil or stream sediment than the laboratory analysis.

After accounting for element interference, the most significant problem with the confirmation and calibration samples sent to the laboratory involve sample heterogeneity. Unless the sample is sent to the laboratory in a cup analyzed by the FPXRF, the laboratory is not usually analyzing the same sample analyzed by the FPXRF. Soil and stream sediment samples sent to the laboratory commonly have 15 to 30 percent variability even after homogenization and the laboratory does not homogenize a sample unless homogenization is requested as part of the analytical schedule when the sample is submitted. Homogenization of the sample both prior to and following laboratory sample preparation should be a standard practice for analytical schedules sent along with samples to the laboratory.

### Heterogeneity of a Single Sample

As one example of heterogeneity on a single sample, repeated random analysis of a single homogenized sample by a tube-type FPXRF resulted in a standard deviation of 2.5 ppm (9 percent) on a stream sediment sample containing 26 ppm copper. The homogenized sample in a cup was analyzed 10 times using a 120 second count time on the same cup. However, using the FPXRF on 10 different locations on the well homogenized sample bag of the same stream sediment using a 120 second count indicated that sample heterogeneity produced a standard deviation of 8 ppm (28 percent). Using two standard deviations for the 95 percent confidence limit, these relationships indicate that the laboratory analysis of even this well-homogenized sample

containing 26 ppm may range from as low as 10 to as high as 42 ppm. This means that there may be considerable scatter away from a 1:1 relationship between the FPXRF and the laboratory analysis of calibration/confirmation samples simply from sample heterogeneity. It is a good practice to homogenize the sample in the field prior to using the FPXRF on the sample but also to check a few samples containing variable elemental concentrations to determine the level of heterogeneity of the soil and stream sediment samples.

### **Heterogeneity – Suite of Soil Samples**

As an example of both heterogeneity and element interference on a suite of samples, a tube-type FPXRF was used to analyze a suite of 1,500 soil samples for metals and arsenic. Homogenization was not requested on the initial laboratory sample analysis. A subset of 150 samples were selected that included samples that were both well correlated with laboratory analysis and those that departed broadly both above and below the 1:1 laboratory concentrations for arsenic. The laboratory arsenic concentration ranged from less than the detection limit to 1,100 ppm with a mean of 34 ppm. The correlation coefficient ( $r$ ) between the laboratory and field-determined FPXRF arsenic concentrations was initially 0.70 indicating that the comparison between the two accounted for only 49 percent of their total variance.

The samples were sent back to the laboratory requesting homogenization. These reanalyzed laboratory arsenic concentrations compared to the original onsite FPXRF analyses resulted in an increase in the correlation coefficient to 0.82, accounting for 68 percent of the total variance. Homogenization, therefore, accounted for about 20 percent of the difference between the laboratory and the field-determined FPXRF arsenic concentration. This means that if the laboratory does not homogenize the sample, a correlation coefficient of less than about 0.90 is about the best that can be expected. However, there is clearly something else contributing to the difference between the laboratory and the FPXRF arsenic concentrations on this suite of soil samples.

### **Element Interference and Heterogeneity – Suite of Soil Samples**

Since the strongest XRF peak (primary) L-alpha peak for lead almost exactly coincides with the primary K-alpha of arsenic (10.55 and 10.54 KeV respectively) there is good reason to check if the lead concentration has been adequately corrected for by the software in the FPXRF. The manufacturer's software uses the secondary L-beta peak (12.61 KeV) for lead to internally correct both the lead and arsenic concentrations reporting to the spreadsheet. However, as the lead to arsenic concentration ratio increases to about 10 or decreases to less than 0.10, this internal correction factor becomes increasingly erroneous. The tube-type FPXRF lead concentration for the above suite of 150 soil samples ranged from non-detect to 950 ppm with a mean of 260 ppm. The lead concentration range is about the same as that of the arsenic but the lead mean

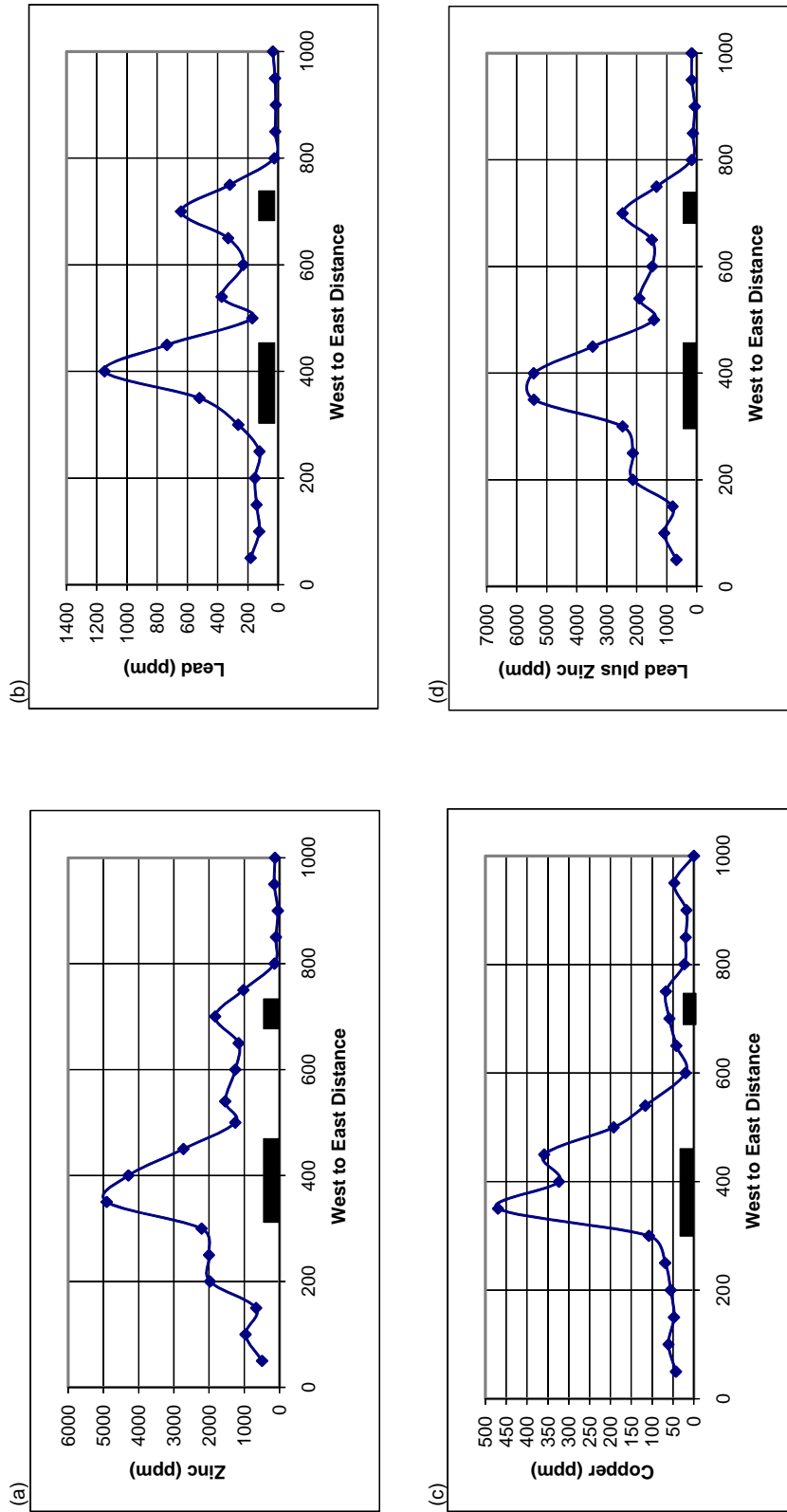
concentration is almost 8 times higher than that of the arsenic on this suite of samples. A multilinear least square fit that included both the field-determined FPXRF arsenic and lead concentrations versus the laboratory arsenic concentrations resulted in a correlation coefficient of 0.97 accounting for 94 percent of the total variance. Therefore, interference of the lead concentration on the arsenic concentration accounted for 26 percent, and heterogeneity accounted for 20 percent of the difference between the laboratory and the FPXRF arsenic concentrations. This equation was applied to all 1,500 soil samples in the original suite of soil samples to correct the arsenic concentrations for both lead interference and heterogeneity.

A second interference involves the iron interference with cobalt causing highly elevated cobalt concentrations reporting to the FPXRF spreadsheet. Iron concentrations at many if not most of mineralized areas are very high, commonly from a few percent to as much as 60 percent plus. The K-beta peak of iron (7.06 keV) is sufficiently close to the K-alpha peak of cobalt (6.93 keV) that at three to five percent iron percentages the cobalt concentration is affected, resulting in increasingly false elevated cobalt concentrations reported on the FPXRF spreadsheet. The presence of elevated cobalt concentrations can be checked by inspecting the peak height of the secondary cobalt K-beta peak at 7.65 keV on the spectra. This interference problem restricts the detection of low cobalt concentrations at most exploration sites.

With the increasing power of the tube type FPXRF coupled with more sensitive detectors being developed, interferences between more L and even M electron shell emissions of elements on K and L peaks of selected elements can be expected. In fact, they are already occurring where high grade ores are being analyzed. This means that the recorded sample spectra becomes an increasingly valuable asset to be investigated when interpreting the FPXRF analytical data.

### **CASE HISTORIES**

Technological improvements in the capabilities of the FPXRF in the last few years described above have made it truly a field portable "exploration" tool. The tactical use of these capabilities provides opportunities for timely, efficient and effective decision making in exploration and mineral development. The number of FPXRF case histories in the mining industry in the literature is limited at this time. Many companies are currently evaluating this instrument and it can be expected that the number of case histories in the literature will increase in the near future. Instrument manufacturers provide sources of case history materials and anecdotal experience. A few examples from the literature and presentations are presented to illustrate the experience and advantages of using the FPXRF in the mining industry. The first case history is from late 2006 exploration in northern Colorado followed by a few case histories from the literature.



**Figure 1:** FPXRF analyzed zinc (a), lead (b), copper (c) and zinc plus lead (d) concentrations versus the west to east distance on a soil survey line. The black boxes at the base of each graph represents the mineralization intersected at depth by drilling.

### Exploration in Northern Colorado

The tube type FPXRF was used in Northern Colorado on an undeveloped silver-rich lead-zinc-copper massive sulfide prospect. The mineralization occurs in soil covering a greenschist facies metavolcanic-metasedimentary assemblage mapped by Paul Klipfel (1992) in Northern Colorado and Southern Wyoming. Several drill holes in the area identified sulfides and gahnite occurring in thick lenses within garnetiferous quartz-feldspar-biotite gneissic host rocks. Massive sulfides have not been visible in the occasional outcrop of the nearly vertically dipping stratiform mineralization identified in drill cores. The sulfides are commonly granoblastically intergrown with the silicates or occur as massive granular aggregates while the gahnite occurs as discrete crystals. Several exploration lines have been analyzed across mineralized zones identified from drill cores initially using a FPXRF equipped with iron-55, cadmium-109 and americium-241 isotope sources and subsequently with a tube-type FPXRF. Figures 1a through 1c show the lead, zinc and copper concentrations in soils from one such line on 50 foot centers analyzed onsite using a x-ray tube-type FPXRF.

The lead, zinc and copper concentrations in the soils clearly define two mineralized zones that essentially coincide with two subsurface mineralized lenses identified in drill cores. Zinc dominates the three metals ranging from 46 to 4,903 ppm with a mean concentration of 1,500 ppm for the 23 soils. Lead ranges from 16 to 1204 ppm with a mean of 308 ppm while copper ranges from 18 to 470 ppm with a mean of 115 ppm. Figure 1d is a lead plus zinc concentration to compare with an original conventional soil survey.

An original laboratory soil analysis using an aqua regia digestion of samples collected on lines nominally spaced 200 feet apart with 100 foot centers identified erratic, single-point lead plus zinc anomalies within an area about 1,400 feet by 1,600 feet. Lead plus zinc concentrations of these 123 soil samples ranged from 44 to 19,170 ppm with a mean of 1,790 ppm. A probability plot estimated a threshold of 330 ppm between the background and the lead plus zinc anomaly but no trend was apparent when the data were plotted on a map. The background for lead is broadly higher than the typical geometric mean background for U.S. soils of 16 ppm (Helmke, 2000) because the bedrock feldspar in the area of mineralization includes amazonite. Similarly the zinc background is significantly higher than the typical geometric mean background for U.S. soils of 48 ppm because of the sparingly soluble gahnite associated with mineralization. Therefore, even though a combined mean would have suggested a lead plus zinc background of about 64 ppm, the native soils established on the bedrock containing mineralization had an appropriately higher background of 330 ppm.

Development of the threshold concentrations is important for both separating background from anomalous concentrations for exploration purposes but it also establishes a site-specific pre-mining background that will be of equal importance to that for exploration if the property evolves to a mining site. The site-specific background for this property is five times the default background that might have been used by regulatory agencies

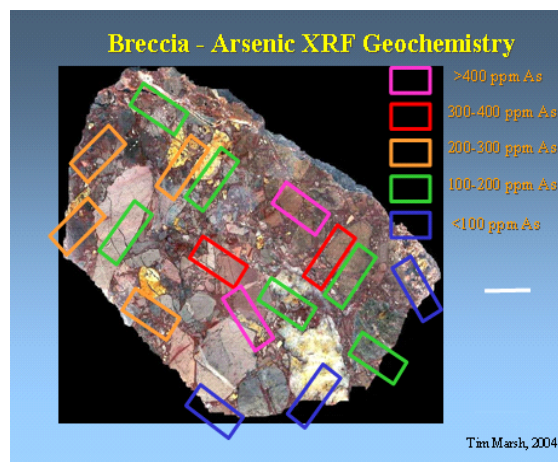
for post-mining environmental remediation purposes had the actual background not been determined during the exploration phase of the mine development. Given the testing of the FPXRF instruments, the elemental concentrations determined by the FPXRF are data of "known quality" and, therefore, generally accepted as usable data for environmental purposes as well as mineral industries purposes. FPXRF data and confirmatory laboratory chemical data should be archived as permanent records to document the pre-mining background in a future post-mining environmental evaluation.

The FPXRF lead plus zinc concentration for the line ranges from 62 to 5,770 ppm with a mean of 2,030 ppm (Figure 1d). This mean is higher than the overall mean for the total area using the original soil survey results but the median of 1,710 ppm is close to the overall mean of the original laboratory data. This at least provides partial confirmation of agreement between the FPXRF data and the original laboratory soil analyses of lead and zinc concentrations.

The real importance of the use of the FPXRF however, is that in only a single day, this soil line provided a clear definition of subsurface mineralization as a drilling target. The subsequent multiple lines provided not only the location of the main mineralization but also the strike and therefore the continuity of the mineralization across the generally anomalous area previously indicated by conventional soils sampling and laboratory analysis.

#### Hand Sample Identification of Anomalous Lithological Phase

Marsh (2004) provides an example of assessing the arsenic concentrations in various parts of a slab of heterolithic breccia (Figure 2). Previously analyzed samples using fire assay gold concentrations and laboratory arsenic concentrations indicated that the two elements were significantly correlated with one another. Therefore, arsenic was used as an indicator element in the field to identify potential gold mineralization. Each colored rectangle on Figure 2 shows the area of the slab analyzed by individual FPXRF measurements. The colors show the relative arsenic concentration between measurements that ranged from less than 100 to greater than 400 ppm. The distribution is quite variable but the FPXRF measurements clearly indicate the phases containing the higher arsenic concentrations.



**Figure 2:** Areas on a slab of brecciated rock analyzed for arsenic using the FPXRF. The white bar is a two centimeter scale.



These phases can be visually identified in the field, focusing the exploration on mapping mineralization, confirming the mineralization using FPXRF and collecting appropriate samples for fire assay that document site mineralization. These results significantly reduced the time to appraise the property and allowed onsite mapping of the mineralized zones.

This example further illustrates the reasons for variability between the FPXRF and confirmation laboratory analysis of a rock sample. Figure 2 indicates that if only a piece of the rock slab was pulverized for digestion and analysis the arsenic concentrations could range anywhere between less than 100 to greater than 400 ppm. Alternately, if the entire rock was pulverized, homogenized, totally digested and analyzed for arsenic, the concentration would probably have been in the 200 ppm range. The FPXRF provides more information for the exploration professional while still onsite when sampling decisions determine the potential value of a property.

### Stream Sediments

Marsh (2004) has described the application of a FPXRF in a reconnaissance stream sediment sampling program that covered a 140 square mile area in Nevada. The FPXRF provided onsite data that were used to identify anomalous drainages that were immediately followed-up. The multi-element signatures of the anomalies provided insight into the probable source and significance of the anomalies. The multi-week turnaround time required for conventional analytical results from the laboratory were avoided and significantly fewer trips back to the field were required to prioritize the prospective area. A small number of high priority samples were collected within the prospective area for detailed laboratory analysis. The saving in survey time and the associated initial analysis costs significantly contributed to both exploration efficiency and effectiveness.

### Core and Reverse Circulation Chips Samples

Marsh (2004) describes the application of a FPXRF to a reverse circulation drilling project for Carlin-type gold mineralization. Some 1200 chip samples were analyzed in their chip trays for arsenic using a 30 second count time. Even though the variance between the FPXRF and laboratory analytical data were subsequently high due to the coarse nature and heterogeneity of the RC chips, it was possible to select and prepare appropriate core sections to be sent to the laboratory for analysis and guide ongoing drilling. This latter aspect improves the selection of drill-hole locations, provides onsite, real time data correlating between drill holes and eliminates the common problem of stopping the drill in anomalous zones. This will generally require remobilization of a drilling rig in a subsequent drilling program followed by conventional laboratory analysis of selective sampling of cuttings, resulting in significantly higher exploration costs, reducing exploration funds that could have been applied to other exploration sites.

### Onsite Grade Control

Houlahan (2003) describes the use of a FPXRF at the Bowdens Silver Project, Australia. An initial test was undertaken to compare the accuracy and precision of FPXRF data versus traditional assay data for Ag, Pb, Zn, and As on drill cuttings. No significant differences were found. Subsequently the company used the FPXRF to reduce assay costs and for field-based grade control. With these FPXRF data in hand, the drilling program was assessed on site, allowing more rapid adjustment of day-to-day changes. In addition, selected samples were sent in for confirmation by traditional assay procedures. Trench and other sampling characterization could be undertaken in similar fashion.

Houlahan, Ramsay and Povey (2003) describe three case histories where recently developed FPXRFs have been tested and successfully applied for grade control in a variety of geological deposit types. Each site presented specific issues that needed to be addressed. Grain-size, homogenization and lack of operator training were the three primary issues that needed to be addressed. Once resolved and implemented, the FPXRF became an effective tool that contributed to enhanced productivity and cost savings.

At one of the three sites, only mixed success was achieved. The authors attributed this condition to "the absence of a technically competent person to be responsible for the operation and overall management of the FPXRF on a day-to-day basis." Similar to any tool, the successful use of a FPXRF depends on the operators understanding the appropriate use of the tool for the intended purpose. The current FPXRF instruments are relatively simple to use, the point and shoot capability is deceptively simple, but most errors result from the operator's lack of training and understanding how the FPXRF functions. Each site should include an initial orientation survey by a knowledgeable professional to determine and alleviate these potential problems. Periodic follow-up by a knowledgeable professional is also advised where the FPXRF is being used routinely in grade control.

Winterburn, et al. (2007) presented a systematic evaluation of the use of the FPXRF at exploration and mine sites in India, South Africa, Namibia, Canada, Venezuela and Ireland. They concluded that the FPXRF is easy to use, provides rapid chemical analysis and is safe and applicable for exploration, waste to ore evaluation and ore control. However, they identified problems with iron interference and found that its use requires well defined procedures and methodologies. These problems restate the need for training operators and performing site specific tests at any site before routine use by inexperienced operators.

### OTHER FIELD-PORTABLE INSTRUMENTS

Miniaturization of laboratory instrumentation has not only enabled the current state of FPXRF instruments but also a host of additional field portable analytical instruments that also add significant real time onsite data acquisition for exploration purposes. Most explorationists commonly use GPS systems to establish field locations and these systems are now being

integrated into the FPXRF instruments to record the location of each sampling point in the analytical spreadsheet. Similarly, the PIMA and Analytical Spectra Device, Inc. field portable infrared (IR) instruments for mapping alteration mineralogy are also becoming increasingly used for exploration purposes. Raman spectrometry is a relatively newer complementary analytical method of determining mineralogy in the field using a laser beam and recording the photon energy emitted by each of the minerals in the sample. Environmental and home security needs have led to several field portable Raman spectrometers. DeltaNu ([www.deltanu.com](http://www.deltanu.com)) has developed a field portable Raman spectrometer specifically for exploration and mineralogical purposes that includes an extensive Raman spectral data base that is equivalent to and in many cases provides more definitive mineralogical identification for darker minerals than that available for the IR spectrometer.

### FUTURE FPXRF DEVELOPMENTS

New generation FPXRF instruments include higher powered x-ray tubes and detectors that have a higher degree of discrimination as well as higher counting rate capabilities that decrease both the detection limits and element interferences. These developments will continue along with higher levels of computer modeling that will be incorporated into the FPXRF instrument. Light elements beginning with sulfur are now able to be determined by FPXRF instruments and further development to determine even the lighter elements is ongoing. Use of helium purging with a FPXRF enables the determination of light elements magnesium, aluminum, silica and phosphorus. Easily mobile systems that enable evacuation of air are another method being investigated to determine the light elements.

A significantly reduced detection limit for gold will be available for the FPXRF in the near future with the new generation of FPXRF instruments. The evolving tube and detector development will also enable the use of high-energy spectral regions of the K x-ray lines of gold and platinum group elements. Recent development of an automated laboratory energy dispersive XRF spectrometer capable of determining gold to less than one ppm that is competitive with fire-assay (Robertson and Feather, 2004) indicates the future possibilities for the FPXRF.

FPXRF instruments are also being currently designed for specific applications. For example, a FPXRF with a small area focused x-ray beam has been developed to analyze individual crystals/minerals. This instrument is specifically for the gem market but is applicable for many other uses where a very small area needs to be analyzed. It would allow elemental data to be obtained on an approximately 4 mm diameter spot analyzed by Raman laser spectrometry for mineral identification, thus providing a complete mineral analysis.

Color displays for both the operating systems and the spectral data are currently available. Miniature cameras now allow the operator to view the area of the sample being analyzed.

Increased processing capability in the FPXRF will allow more complete reporting to the spreadsheet results and, of considerably more significance, the application of more

advanced chemometrics. Currently there are no messages on the spreadsheet reports indicating that there are potential interference problems with specific elements on the spreadsheet. This is a critical operator problem whereby the operator rarely if ever checks the spectral file before using and interpreting the spreadsheet data. The importance of the spectral file cannot be exaggerated.

In the near future computer modeling will allow the combination of fundamental parameter models with neural networks (Luo, 2006). This combination will allow the capability of dealing with non-linear relationships and a more robust treatment of outliers than the current fundamental parameter models. In other words, this combined model will improve the accuracy and precision over a wide dynamic range for individual element concentrations.

The increased computer capability will also be necessary to deal with the multiple effects of higher shell electron spectra generated by the higher powered x-ray tubes. The current FPXRF instruments currently use the K and L lines of the elements but even today the M lines can interfere with some element concentrations. These interferences become increasingly serious with samples containing very high concentrations of elements, specifically ore samples.

Finally, current and future improvements and breakthroughs in battery technology will open the possibility of including other analytical technologies into the FPXRF enabling much more information and data to be provided on each individual sample analysis with a single instrument. For example, with a more powerful and efficient battery, the Raman spectrometer could be incorporated into the FPXRF. This would result in collecting both the mineralogy and chemistry of the sample with one instrument at the same real time. The camera would record a picture of the sample area analyzed and the GPS unit will add the location. The future is nearer than we imagine.

### CONCLUSIONS

FPXRF instruments easily operated by a single hand are now available to the mining industry to provide an onsite, real-time, chemical analysis of a broad suite of elements within about a minute resulting in the total concentration of each element present in virtually any solid. These characteristics enable significant savings in both time and exploration budgets while allowing better and more timely exploration decisions in evaluating properties. FPXRF instruments compliment rather than replace traditional laboratory analyses. Detection limits for gold, PGE, and elements lighter than about sulfur are being lowered with the newer evolving FPXRF technology. Traditional laboratory chemical analyses continue to be used for confirmation and, in some cases, site-specific calibration.

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## REFERENCES

- Bowie, S.H.U., Darnley, A.G. and Rhodes, J.R., 1965, Portable Radioisotope X-Ray Fluorescence Analyzer: *Trans. Instn. Mining and Metall.*, 74, pp. 361-379 and pp. 557-563. Bowie, S.H.U., 1968, Portable X-Ray Fluorescence analyzers in the Mining Industry: *Mining Magazine*, 118, no. 4, pp. 230-239.
- Eddy, C.E. and Laby, T.H., 1930, Quantitative Analysis by X-ray Spectroscopy: *Proc. Royal Soc. (London)*, 127A, pp. 20-42.
- Helmke, P.A., 2000, The Chemical Composition of Soils: in *Handbook of Soil Science*, Ed. M.E. Sumner, CRC Press, pp. B3-B24.
- Houlahan, T., 2003, Case Studies Using Portable XRF Analyzers During Soil Contamination and Mineral Exploration Projects: 21st International Geochemical Exploration Symposium in Dublin, PDF in meeting CD.
- Houlahan, T., Ramsay, S. and Povey, D., 2003, Use of Field Portable X-Ray Fluorescence Spectrum Analyzers for Grade Control – A Presentation of Case Studies: in 5th International Mine Geology Conference Proceedings Volume, Australasian Institute of Metallurgy, 377-385.
- Jenkins, R., 1999, *X-Ray Fluorescence Spectrometry*, Second Edition: John Wiley & Sons.
- Klipfel, P.D., 1992, *Geology and Metallogeny of the Southern Portion of the Encampment District, Colorado and Wyoming*: Unpublished PhD dissertation T-4080, Colorado School of Mines.
- Luo, L., 2006, Chemometrics and its applications to x-ray spectrometry: *X-Ray Spectrometry*, 35, 215-225.
- Marsh, T.M., 2004, Real-Time Geochemistry via X-Ray Fluorescence: Abstract and oral presentation at Society of Mining Engineers Annual Meeting in Salt Lake City, Utah.
- Press, S., 2005, Market Profile: EDXRF: Spectroscopy, 20, p. 12
- Robertson, M.E.A. and Feather, C.E., 2004, Determination of gold, platinum and uranium in South African ores by high-energy XRF spectrometry: *X-Ray Spectrometry*, 33, 164-173.
- Rhodes, J.R. and Furuta, T., 1968, Applications of a Portable Radioisotope X-Ray Fluorescence Spectrometer to Analysis of Minerals and Alloys: in *Advances in X-Ray Analysis*, 11, 249-270.
- Taylor, P.D., Ramsey, M.H. and Potts, P.J., 2004, Balancing Measurement Uncertainty against Financial Benefits: Comparison of In Situ and Ex Situ Analysis of Contaminated Land: *Environ. Sci. & Tech.*, 38, 6824-6831.
- Webber, G.R., 1959, Application of X-ray Spectrometric Analysis to Geochemical Prospecting: *Econ. Geol.*, 54, 816-828.
- Winterburn, P.A., Polito, P., Barr, J., Potgeiter, P., Chavez, N. and Christo, M., 2007, The Application of portable XRF: Exploration, Evaluation and Mining: Abstract and oral presentation at 23<sup>rd</sup> International Applied Geochemistry Symposium in Oviedo, Spain.