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Bruno Lemiere, Y Uvarova

### **► To cite this version:**

Bruno Lemiere, Y Uvarova. Conclusion: Field portable geochemical techniques and site technologies, and their relevance for decision making in mineral exploration. . Exploration 17, Field Analysis Workshop , Oct 2017, Toronto, Canada. hal-01740974

**HAL Id: hal-01740974**

**<https://hal-brgm.archives-ouvertes.fr/hal-01740974>**

Submitted on 22 Mar 2018

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# Conclusion: Field portable geochemical techniques and site technologies, and their relevance for decision making in mineral exploration.

Lemière, B. <sup>[1]</sup>, Uvarova, Y. <sup>[2]</sup>

1. BRGM D3E, 45060 Orléans, France

2. CSIRO Mineral Resources, Kensington WA 6151, Australia

## ABSTRACT

*Field portable geochemical techniques and site technologies offer now instant response and flexibility for most exploration tasks. By providing relevant data within minutes, they allow safer field decisions and focus on the most promising finds, while saving valuable resources in sampling grids or drilling. More efficient laboratory analysis programs are supported by sample screening and homogeneity checking on site. Field analyses are not always as accurate as laboratory ones, but most of the time, can be correlated with them, allowing reliable decisions. The level of confidence in field-made decisions needs to be compared between later and less numerous laboratory analyses, and less precise but more abundant and immediate field analyses. It may be demonstrated that in many cases, the fit-for-purpose of the latter allows a better confidence level. Quality compromises associated with field analyses can, be reduced by the application of better sample preparation and QA/QC procedures. Most of the further development of on-site chemical analysis is expected to be based on its integration with lab methods and on sound QA/QC practice, allowing a precise evaluation of its confidence level and uncertainties. Mineralogical analyses are less demanding but offer promising approaches in both surface and drilling exploration campaigns.*

## REAL TIME DECISION BASED ON FIELD ANALYSES - BENEFITS FOR EFFICIENCY AND COST-EFFECTIVENESS

Most mineral exploration decisions are based on flexible thinking rather than on a pre-set framework of investigation.

One of the key benefits of real-time analyses, or short delay analyses (less than a day) is a possibility to adjust sampling plans, test hypotheses based on ongoing results, and make fast decisions for exploration work. Examples of such include:

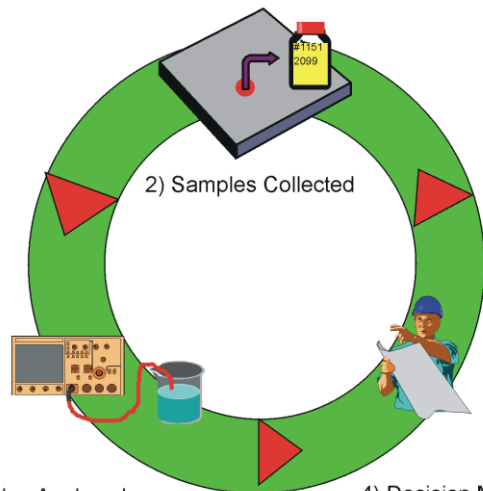
- decisions on further drilling and/or sampling, based on commodity element concentrations or on key geological markers, more easily recognised than by the geological logging work on its own;
- increasing sample density in the most promising parts of a looser grid, allowing deployment of sampling staff or analytical resources where it matters;
- exploring promising areas beyond the original grid without extending the whole grid too far,
- applying further field techniques or more focused calibration schemes on identified targets to gain quickly a better knowledge of them.

This is particularly important for remote locations, where sample delivery logistics to a laboratory may become time-consuming and laborious. This may also apply in highly competitive situations, where the exploration team wishes to keep as much as possible of the information internal before a decision is made or publicised.

This is similar to strategies such as ASAP (Adaptive Sampling and Analysis Programs, US-DOE, 2001, and Figure ), dynamic workplans (Robbat, 1997) or TRIAD (US-EPA, 2008) in environmental investigations. The cost-effectiveness of these strategies was demonstrated in comparison to predetermined sampling strategies.



1) Planning Phase



3) Samples Analyzed

4) Decision Made

Figure 1: Adaptive Sampling and Analysis Program design and execution (from US-DOE, 2001)

Besides their use for immediate decisions, field analytical techniques also offer cost-effective screening capabilities while selecting the samples to be submitted to a laboratory for conventional analysis. They significantly improve the efficiency of smaller sample sets on a more limited budget.

It is also more than balanced by the better relevance of the field data set, resulting from dynamic sampling and faster decision making. Being able to resample or refine the sampling pattern on site gives the opportunity of pre-processing on-site data and provides more focused exploration information before the team actually leaves the site.

### DATA QUALITY VS DATA DENSITY: WHICH IS BEST FOR EXPLORATION EFFICIENCY?

The reliability of a professionally sampled, professionally analysed (laboratory) data set should be better than the reliability of a data set collected with field portable techniques due to limitations in sample preparation and field analysis. This was discussed mainly for pXRF, which is currently the main technology for on-site analysis. The lessons in its deployment can be applied to the other techniques here.

However, budget and delay constraints imply that the data set generated by the former may be much smaller than the latter, with a much lower data density. The number of data points for a given budget may be up to ten times smaller when using a conventional lab analysis instead of a field or on-site analysis. The cost ratio depends actually on the sampling strategy. On a pre-set sampling plan such as a regular grid, with strict sampling procedures, the cost of sampling may exceed by far the analytical budget, even with shipping costs, and the benefit of field analyses will not be obvious. Benefits from on-site analyses can be expected for flexible sampling plans, or where sampling procedures can be simplified for on-site analysis.

Data quality, or fit-for-purpose ability (Ramsey & Boon, 2012) is a measurement of how far the geochemical data set will be representative of the explored object, and how far exploration decisions based on it will be reliable, in terms of effectiveness and financial consequences. The usually lower quality of field analyses is more than balanced by the much larger number of analyses made possible by on-site methods. For instance, a target may be missed by a less dense lab sampling grid because it was either too small or its definition was not sharp enough. This can happen with deep targets or targets under cover.

The benefits of larger or denser data sets are observed also during later data processing and modelling. The application of geostatistics to on-site data, especially from pXRF (for instance Eze et al., 2016), is facilitated by their higher spatial density, by their multi-element coverage, and by their more detailed uncertainty data matrixes. The same applies to geometallurgy (Gazley & Fisher, 2014), taking advantage of multi-element data for several different applications of the information system (geologic model, ore reserves, mechanical stability, waste management, all used for profitability optimisation), and for spatial modelling.

## FIELD AND ON-SITE DATA LEVEL OF CONFIDENCE IN EXPLORATION DECISIONS

### Precision, accuracy and relationship with laboratory results

The consistency between field measurements and laboratory analyses is frequently discussed for pXRF, which is the most documented technique to date. Most laboratory analyses for exploration are however performed by ICP or AAS spectrometry after acid sample digestion. In favourable cases, field measurements and these laboratory analyses show a good correlation (Figure ). In other cases, reproducible field measurements and laboratory analyses show a biased correlation (Figure ). Such a bias happens more frequently for elements which are more difficult to analyse for spectral reasons, even by laboratory XRF, or by pXRF for instrumental compromises. However, a bias may be the result of spectral interference by a locally abundant element, hampering the analysis of an otherwise easy element. This is particularly true with iron, a ubiquitous element in exploration, which tends to interfere with other transition elements. Bias is not only element-specific but also matrix-specific. For instance, Zn can be well correlated between pXRF and laboratory analyses in a sandstone and slightly biased in a limestone. From the authors' experience, some elements are more prone to bias (Al, Si, P, S, Ti, V, Cr, Co, Ni, Se, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ba, W, Hg, Bi) and some are more often well correlated (K, Ca, Mn, Fe, Cu, Zn, As, Rb, Sr, Pb) but there is no systematic rule about this.

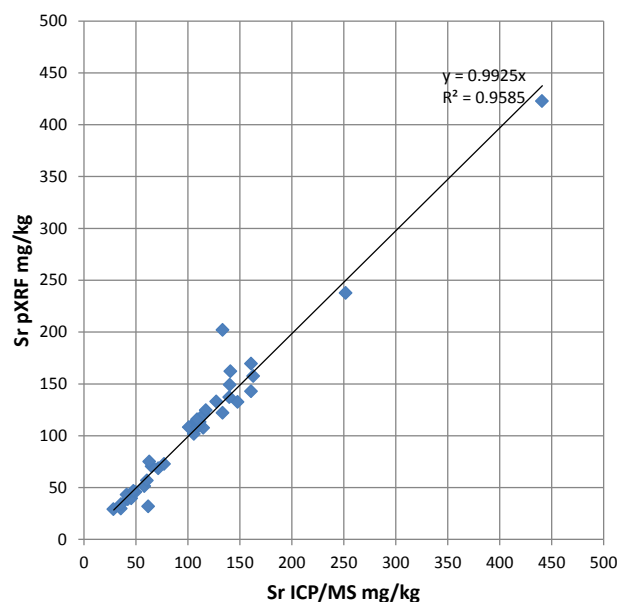


Figure 2: Correlation between laboratory and pXRF data, on a favourable case (strontium in sandstone)

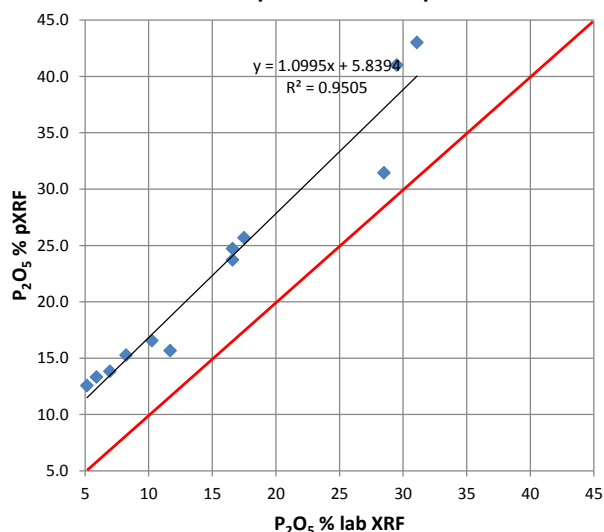


Figure 3: Correlation between laboratory and pXRF data, on a less favourable but viable case (phosphorus in carbonate rocks)

Bias depends also on the type of digestion to which pXRF results are compared. Results obtained by pXRF are often higher than laboratory results based on the standard aqua regia digestion (Figure ), especially for refractory minerals such as cassiterite (Sn), wolframite (W) or rutile (Ti). In this case, pXRF analyses carried out on laboratory standard pulps will often be more accurate than standard laboratory analyses, unless total digestion techniques are used (Figure ).

The comparison between field and laboratory analyses should strictly speaking be made with laboratory XRF, which is based on the same principles as pXRF but benefits from better instrumental and laboratory conditions. However, a large part of geochemical exploration is based on wet chemical methods, especially ICP/AES, ICP/MS and AAS. This led to improper bias controversy when laboratory results based on partial digestion were opposed to pXRF total analyses. Any reported bias should be first checked using total digestion techniques such as HF-based digestion or alkali sintering.

Field analyses and on-site analyses cannot compete with laboratory analyses in terms of sensitivity, precision or accuracy due to compromises in sample preparation, instrument performance and work environment. From this perspective, field and on-site results must be always controlled by a subset of laboratory samples. However, ultimate laboratory accuracy is not generally required for exploration decisions.

Field and on-site results must only achieve the level of confidence expected from the decision. Bias can be corrected for with the use of appropriate standards or with site samples already analysed by a laboratory. Precision is usually at least acceptable and the only real issue is sensitivity for ultra-trace or nugget commodities. This issue may be often overcome using companion or trace elements in combination. A careful confidence evaluation is always necessary, based on field and lab analyses, before field or on-site methods are used for decision-making.

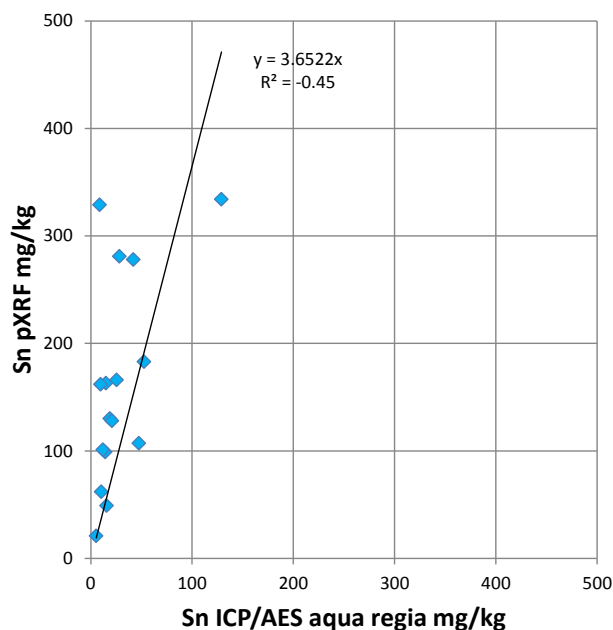


Figure 4: Correlation between aqua regia ICP and pXRF data

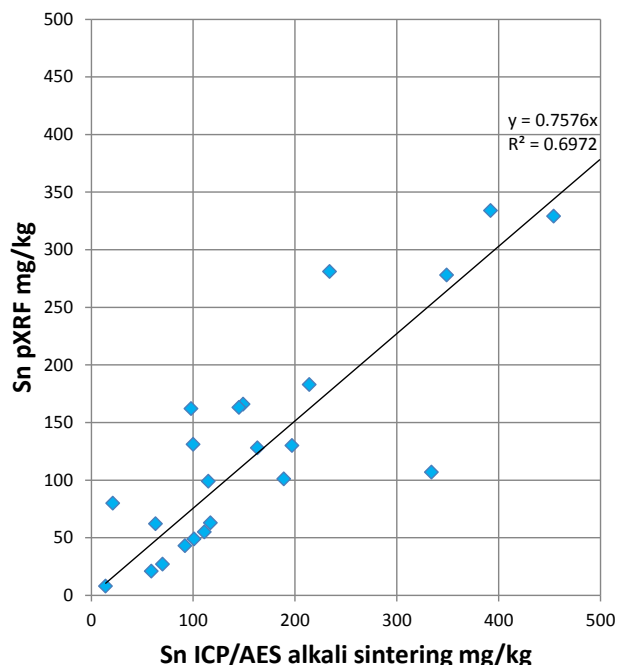


Figure 5: Correlation between alkali sintering ICP and pXRF data

### pXRF quality and exploration

The introduction of robust procedures and QA/QC schemes (Hall et al., 2013, Gazley & Fisher, 2014) helped pXRF analytical method to overcome its controversial reliability issues. A critical review of expedited but inadequate field practice is also given by Durance et al. (2014).

Unlike laboratory analyses, which may be produced by a single instrument, field analyses are often produced by several instruments within one team. This may lead to minor drift between instruments, and even between batteries (Chang & Yang, 2012). This issue is easily dealt with using instrument traceability procedures and standards. Durance et al. (2014) recommended the use of site-specific calibrations rather than general purpose CRMs and warned against measurements through paper bags.

Matrix specific issues may also require geochemical expertise for the reliable interpretation of field data.

Close cooperation between the field analysis team and the laboratory tends to improve significantly the quality of the former and the cost-effectiveness of the latter, with an improved performance of geochemical surveys as a result.

QA/QC good practice is the condition for field measurements gaining acceptance in press releases with respect to JORC or NI 43-101 regulations. These aspects were investigated by Arne & Jeffress (2014) and Arne et al. (2014) who concluded on the acceptability of pXRF under strict QA/QC conditions: "A robust sampling methodology with a suitable quality assurance/quality control program should produce pXRF data of sufficient quality for public reporting purposes, provided that the data are presented using appropriate cautionary language and adequate supporting information". Besides common sense evidence on sample preparation and sample containers, these authors insisted on the necessity of implementing a QA/QC scheme similar to that used by laboratories, and on the relevance of pXRF data for supporting exploration results as long as QA/QC results were satisfactory. Stoker & Berry (2015) showed through two examples that reporting of exploration results, mineral resources and ore reserves based on pXRF were acceptable, as long as pXRF use complied with good laboratory practice.

Field-generated analyses under QA/QC good practice should be considered at least as valuable complements to laboratory analyses. They may offer better relevance in specific cases. Laboratory analyses often overlook potential issues on sample representativeness, sample heterogeneity and sample digestion, while field measurements offer representativeness monitoring, and physical analyses without digestion. Discrepancies between field and laboratory results obtained with the standard aqua regia digestion may point to unexpected refractory mineral phases and suggest the use of total digestion techniques instead.

## **THE PLACE OF ON-SITE TECHNOLOGIES IN EXPLORATION TOMORROW**

In the early 2000s, most on-site technologies were not offering the level of reliability, and thus confidence, required for making sound exploration decisions. Despite the advantage of quick analysis, they were not often developed, or even used. They became increasingly popular after 2007 in exploration camps and even at mine sites, despite some reluctance within the industry to deploy these innovative methods.

Use of on-site analytical methods in site operational automation depends on the physical characteristics of the

technique. pXRF and pXRD need a proximal contact with the sample and cannot be easily adapted to a material flow analysis process, unless an automatic sample preparation scheme is considered. XRF and XRD sensors implemented over conveyor belts are usually heavier and more powerful than handheld analysers. These sensors are therefore modified laboratory devices. LIBS, pFTIR and  $\mu$ Raman accept greater distances and may be incorporated in a sample monitoring scheme if a signal processing chain is used. Water samples cannot yet be analysed in-situ in most cases, this requires subsampling from a flow derivation.

Exploitation of complex spectra (especially for FTIR and  $\mu$ Raman) may need mathematical techniques such as chemometrics rather than direct calibration with standards. Alternative approaches to analytical calibration may be based on comparative or differential techniques, but they will require further critical reviews. Direct quantification of minerals by pFTIR and  $\mu$ Raman are not yet available routinely, as is the case for pXRF. They are not however out of reach, and we may hope to see mineral quantification reach the market before Exploration'27. This quantification is expected to be based on larger databases, with pure mineral and alteration assemblage spectra. It will also require patient research using chemometrics and possibly other approaches (e.g., machine learning) to unlock the apparent complexity of spectra. Calculation capabilities implemented in the field instruments can be an attractive option - in the same way as for Positive Material Identification, but it may lead to "black box" machines with little user control on the diagnosis. On the other hand, increasingly easier and more powerful calculation capabilities will offer advanced exploration staff the opportunity to maximise the value of their data with post-processing and data integration. The "black box" approach is often favoured by manufacturers, while the "big data" approach gives users a better control of their results.

Most of the further development of on-site analysis is expected to be based on its integration with lab methods and on sound QA/QC practice, allowing a precise evaluation of its confidence level and uncertainties.

This is applicable to elemental analyses, on which official exploration results are based. The constraints on mineralogical analyses, used mainly to guide exploration campaigns, are not as restrictive.

It will be also possible to reach better global confidence levels using large data sets generated by field instruments than with budget-restricted laboratory programs. In order to increase the role of field analyses in exploration, the efforts must be focused on increasing the level of confidence in field results. This can be achieved through a stricter application of laboratory principles to field analyses, and through the development of robust and reproducible sampling and measurement protocols. Such protocols can be shared between exploration geologists, mining engineers and field analysis technicians/chemists, with large benefits for data consistency.

Instrument performance will improve too, but it is more likely to improve detection limits or element selectivity, to overcome interferences. New instruments may appear, either from less documented spectral areas or from a different approach to processing the spectra, like in Raman analysis.

This wealth of field-generated information also has to be taken in consideration by laboratory-based programs.

Far from being a cheap alternative to traditional laboratory-based analytical programs, field analytical methods offer an effective complement to them, increasing global efficiency. The best option is to maximise collaboration and synergy between field and laboratory; to extend laboratory QA/QC to field techniques and to use field methods to improve sample representativity and minimise sampling uncertainty. This can be carried out while providing decision making with real time data.

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