

Field Analytical Techniques for Geochemical Surveys

Bruno Lemière

BRGM - D3E Environment & Water - BP 36009, 3 Av. C. Guillemin - 45060 ORLEANS Cedex 2, France, and

Environmental & Mining Consultant, 36 venelle des Vaupulents, 45000 ORLEANS, France, +33 6 95 90 21 34

Introduction

Obtaining geochemical results on the field has been a persistent dream for exploration geologists in the last century, and a few practical tests were developed, but shipping samples to faraway labs and waiting weeks for results was the rule. This remained a dream until around 1990, when technology developments of portable instruments allowed on-site measurement of the first key metals in solids. This development was very fast and by 2010, most geochemists could have access to field methods, if they decided so. These instruments were soon used for environmental investigations too. In the same time, field instruments for water analysis were developed too, and found applications in the environmental, process and exploration domains.

Results

The present communication is based upon our own work (Negrel et al., 2007, Liakopoulos et al., 2010, Lemièrre et al., 2014), and, more important, upon major contributions by field geochemists since 1995 (Kalnicky & Singhvi, 2001; CL:AIRE, 2008; Hall et al., 2012). An important set of papers was published in GEEA in 2014 (thematic papers on pXRF, vol. 14) and a review paper is currently in preparation, which will provide a comprehensive set of references.

Field analytical techniques cannot provide the level of optimisation laboratory analyses do. They are recommended where there is no other option, where they offer flexibility, where they offer reactivity and, obviously, where they cooperate with the laboratory.

Current validated applications for solids (mostly pXRF, Fig.1 & 2) comprise:

- fast decision-making measurements and analyses: mining rock face evaluation, ore processing monitoring, soil remediation and waste management operations, etc.),

- site recognition grids (mainly on soil, both for environmental and mineral exploration surveys),

- fast drill-hole logging and drilling decisions,
- screening of samples to select which ones will be analysed in the lab,
- identification of potential resources from waste.

Elements for pXRF analysis																	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

	cannot be analysed by pXRF
	difficult analysis with pXRF
	can be analysed by pXRF if abundant
	can be analysed by pXRF in most cases
	can be detected but cannot be analysed

Figure 1. Elements that may be currently analysed by pXRF

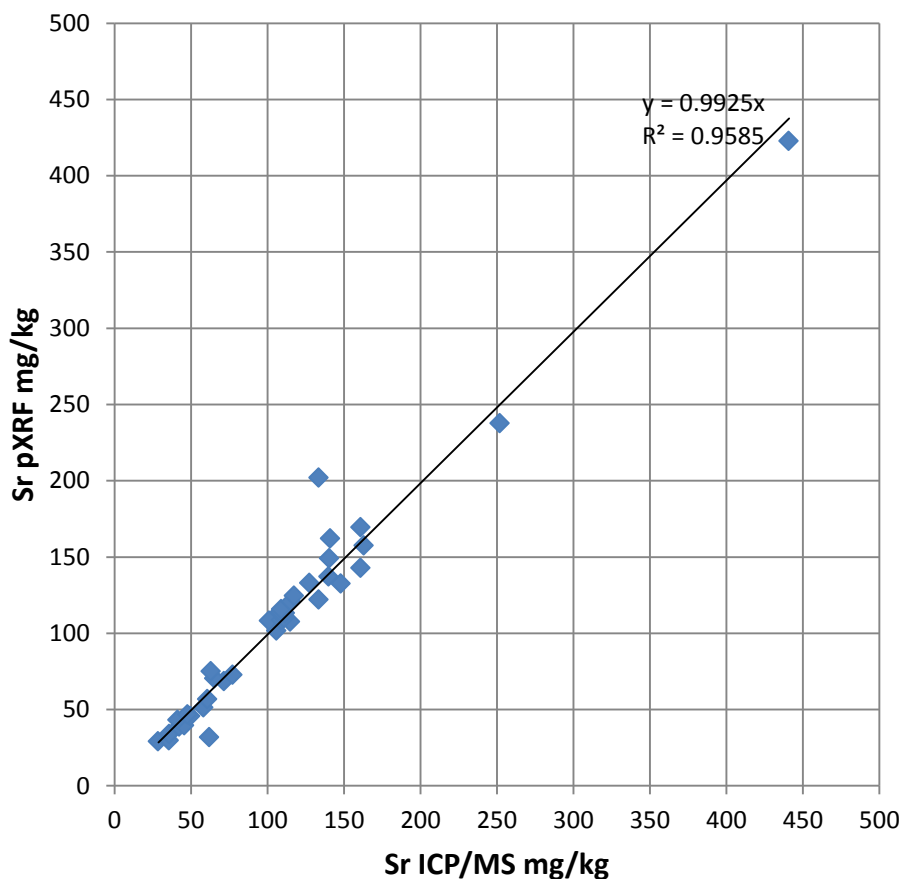


Figure 2. pXRF vs laboratory correlation in well-prepared sandstone samples

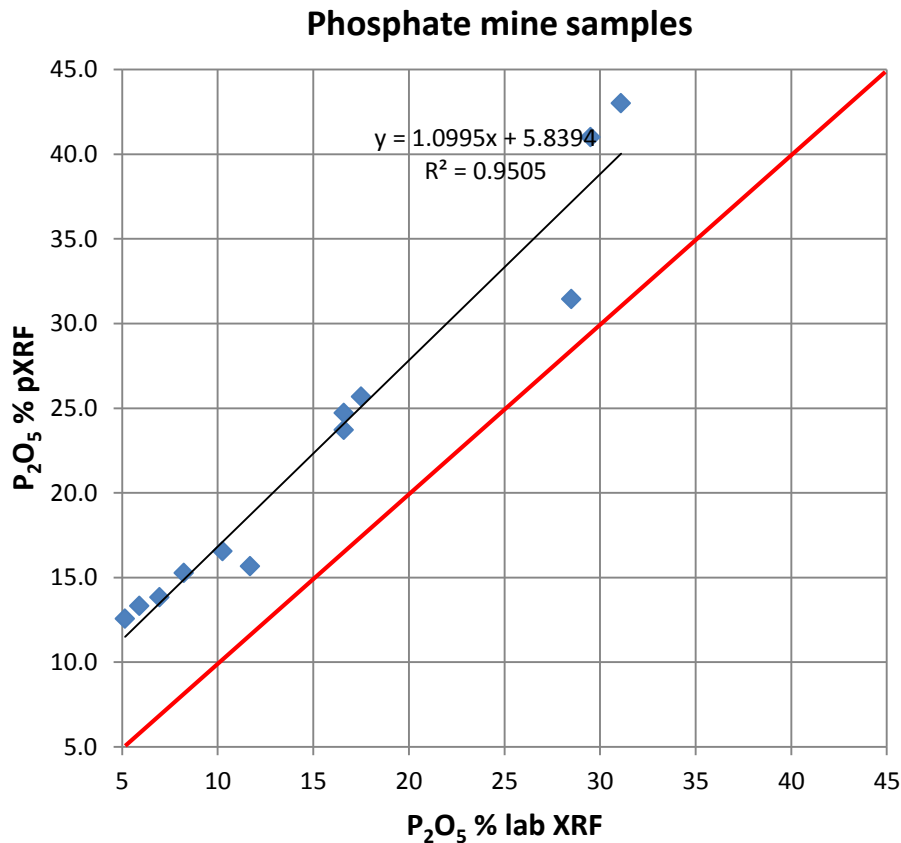


Figure 3. pXRF vs laboratory correlation in roughly prepared samples

Some of the most important issues with field analytical techniques for solids lie in sampling and sample preparation techniques. If samples are prepared on site as required by the laboratory, there are better chances to obtain reliable analyses with field methods. Measurements obtained on raw or roughly prepared samples may provide useful and meaningful results, but will usually show large bias or uncertainty (Fig. 3).

Experimental but promising developments are ongoing for lighter elements (LIBS), organic substances (FTIR), and for minerals (pXRD, FTIR, μ Raman).

Current validated applications for water (mostly ASV and ISE along with physicochemical sensors) comprise:

- accurate measurement of geochemical properties that are not stable with time and transport,
- fast decision-making measurements and analyses: wastewater treatment or discharge monitoring, including process monitoring and alarm networks,
- catchment mapping and reconnaissance (both for environmental and mineral exploration surveys),
- screening of samples to select which ones will be analysed in the lab,

- improved measurements and analyses for site investigations: catchment or pit lake reconnaissance and monitoring, groundwater logging and monitoring.

Possible issues about sample preparation are less important for water samples than for solid samples, as lab-ready preparation on site is mandatory in most cases, and homogeneity is easier to ensure.

Discussion

Impassioned debate followed development about the quality of field analyses vs. laboratory analyses, with often non-neutral contributions from instrument suppliers and from the laboratory profession. Beyond instrument limitations, it appeared soon that sample preparation and sample representativeness were key issues to interpret field analysis results. This is still the case today, even if documented evidence of field-lab concordance is frequently published – by geochemists which paid attention enough to sample preparation and representativeness. The late apparition of relevant standards, to the notable exception of EPA 6200 (1998), did nothing for a smooth acceptance of field methods or their beneficial introduction in the analytical toolbox of applied geochemists.

Conclusions

Benefits of field analysis comprise in-situ analysis, without transport issues; ASAP, DSP or Triad (adaptation of sampling strategy along results collection or dynamic sampling plans: Robbat, 1997; Crumbling, 2001; US-DOE, 2001), increase of data density and quality (through larger data sets) and better representation of transient phenomena.

Possible pitfalls include improper interpretation of field data as a result of insufficient understanding of the sampling and measurement processes, use of heterogeneous data sets collected by different methods, and the lack of critical examination of data.

Current developments of new or adapted technologies cover mineralogy (portable XRD, micro Raman, IR spectroscopy), light inorganic elements (LIBS, pXRF), organic substances (IR spectroscopy, GC, GC/MS) and more focused applications.

References

CL:AIRE, 2008. Field Portable X-ray Fluorescence (PXRF): A rapid and low cost alternative for measuring metals and metalloids in soils. Research Bulletin, 7, 1–4. [Retrieved from www.claire.co.uk on April 2012.]

Crumbling, D.M. 2001. Using the Triad approach to improve the cost-effectiveness of hazardous waste site clean-ups. US-EPA report 542-R-01–016. [Retrieved in 2001 from www.clu-in.org]

Hall, G., Buchar, A. & Bonham-Carter, G., 2012. Quality Control Assessment of Portable XRF Analysers: Development of Standard Operating Procedures, Performance on Variable Media and Recommended Uses. Canadian Mining Industry Research Organization (Camiro) Exploration Division, Project 10E01 Phase I Report.
<http://www.camiro.org/exploration/r-ecently-completed-projects>

Higuera, P., Oyarzun, R., Iraizoz, J.M., Lorenz, S., Esbrí, J.M. & Martínez-Coronado, A. 2012. Low-cost geochemical surveys for environmental studies in developing countries: Testing a field portable XRF instrument under quasi-realistic conditions. *Journal of Geochemical Exploration*, 113, 3–12. Downloaded from <http://geea.lyellcollection.org/> at Bureau De Recherches Geologiques Et Minières BRGM, FRANCE on July 18, 2014

Kalnicky, D.J. & Singhvi, R. 2001. Field portable XRF analysis of environmental samples *Journal of Hazardous Materials*, 83, 93–122.

Lemiere, B., Laperche, V., Haouche, L. and Auger, P., 2014. Portable XRF and wet materials: application to dredged contaminated sediments from waterways. *Geochemistry: Exploration, Environment, Analysis* 2014, v.14; p 257-264.

Liakopoulos, A., Lemiere, B., Michael, C., Crouzet, C., Laperche, V., Romaidis, I., Drougas, I., Lassin, A, 2010. Environmental impacts of unmanaged solid waste at a former base metal mining and ore processing site (Kirki, Greece). *Waste Management & Research*, 28(11) 996–1009

Négrel, Ph., Lemièrre, B., Machard de Grammont, H., Billaud, P., Sengupta, B., 2007. Hydrogeochemical processes, mixing and isotope tracing in hard rock aquifers and surface waters from the Subarnarekha River Basin, (East Singhbhum District, Jharkhand State, India). *Hydrogeology Journal*, 15, 8, pp.1535-1552.

Robbat, Jr., A., 1997. *Dynamic Workplans and Field Analytics: The Keys to Cost-effective Site Investigations*, Tufts University, Case Study.

US-DOE, 2001. Adaptive Sampling and Analysis Programs (ASAPs). Report DOE/EM-0592.

US-EPA, 1998. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Vol IA, SW-846, Method 6200, Revision 0.