

A Review of pXRF (Field Portable X-ray Fluorescence) Applications for Applied Geochemistry

Bruno Lemiere

► **To cite this version:**

Bruno Lemiere. A Review of pXRF (Field Portable X-ray Fluorescence) Applications for Applied Geochemistry. Journal of Geochemical Exploration, Elsevier, 2018, 10.1016/j.gexplo.2018.02.006 . hal-01740950

HAL Id: hal-01740950

<https://hal-brgm.archives-ouvertes.fr/hal-01740950>

Submitted on 22 Mar 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

A Review of pXRF (Field Portable X-ray Fluorescence) Applications for Applied Geochemistry

Bruno Lemière

BRGM, F-45060 Orléans, France – b.lemiere@brgm.fr - Tel +33695902134 – Fax +33238643963

Abstract

In the last thirty years, portable X-ray fluorescence (pXRF) has grown from prototypes to being a key technique for field geochemical analyses, especially for mining and environmental applications. This technology provides real-time or near real-time decision support for operational field decisions (exploration, mining, site remediation or waste management), provides a cost-saving alternative to classical laboratory analysis programs, and deals efficiently with remote or harsh field conditions. The ability to rapidly collect a large number of samples and replicate analyses facilitates acquisition of higher data density compatible with geostatistics.

pXRF can be used profitably for sample screening and selection tasks, dynamic sampling plans based on field observations and measurements, grid mapping of a site and determining relative element abundance. In waste management and remediation, pXRF is used to identify unknown waste composition, and verify waste loads before disposal or treatment.

In all applications, having robust QA/QC plans and systematic laboratory controls on selected samples are essential for ensuring reliable measurements. The best overall results are usually achieved through a clever combination of field (pXRF) and lab data, with pXRF providing the bulk of the data at low cost, on larger data sets and potentially with better reliability than lab-based campaigns based on a limited number of samples.

Keywords

pXRF; FPXRF; HHXRF; exploration geochemistry; environmental geochemistry; field portable; on-site analysis; mining exploration; mining waste; soil contamination; diagnosis; remediation.

Introduction

This paper reviews the story of portable X-ray fluorescence spectrometry, or hand-held XRF, (pXRF) and how it has been developed for applied geochemistry (mainly for the mineral industry and environmental activities). It also reviews its current potential and limitations, and how to make the most of this flexible technology while avoiding common pitfalls. Research from which these conclusions are drawn is available elsewhere and quoted as references. Instrument suppliers provided technical support for this research, but the author has no direct link with them.

History

The early days

pXRF began its life as prototypes in the late 1970s and early 1980s, and was tested for exploration (Glanzman and Closs, 2007, Kalnicky and Singhvi, 2001, Rhodes and Rautala, 1983). This was followed by small-scale production of heavy commercial devices, but with no documented success or usage (Glanzman and Closs, 2007). Early instruments used radon detection technology (Bosco, 2013), hence the name of one of the pioneers and market leaders.

Outside the USA, one of the earliest documented exploration applications of pXRF used a pioneering instrument developed in Russia, the RRK-103 "Poisk". In that study, Konstantinov and Strujkov (1995) identified buried Au-Ag mineralisation by analysing tracer elements (As, Cu, Pb, Zn, Sn) in crosscutting dikes.

Between 1984 and 2000, a Chinese team developed the IED-2000P pXRF analyser incorporating a ^{238}Pu isotope source (Ge, in Potts and West, 2008). Zhou (1992, quoted by Ge, *ibid.*) used it in a copper prospecting area in China, with Pb and Zn as associated elements.

It was first used as a detection tool for lead paint in housing (Bero et al., 1993), but was able to find many elements due to its XRF technology. However, detection had to be simplified in order to be miniaturised and able to run on batteries. In the early 1990s, spectrometers with multi-element capabilities were developed, based on radioactive isotope source emitters: ^{109}Cd , ^{241}Am and sometimes ^{55}Fe , built into the instrument (Piorek, 1994a; US-EPA, 2007; Fig. 1). These constraints limited pXRF applications practically to elements with atomic numbers higher than potassium. Due to the presence of radioactive sources, pXRF instruments were submitted to demanding procedures by nuclear authorities. Despite that, the multielement capability and field performance allowed them to enter the environmental geochemistry field (Bernick et al., 1995b; Shefsky, 1995, 1997). Applications were soon found with contaminated soil (Kuharic et al., 1993; Piorek, 1994b, Shefsky, 1995), continental and marine sediments (Stallard et al., 1995, Kirtay et al, 1998), and even airborne particles (Bernick and Campagna, 1995). The first successes led to standard recognition (US-EPA, 1998a) and to Environmental Technology Verification (ETV) program scrutiny (US-EPA, 1998b). When the EPA introduced Standard Method 6200, that opened the first path to breaching the monopoly that laboratory analyses had held.

The easy, handheld operation led to early use for scrap metal sorting for recycling purposes. This is beyond the scope of geochemistry but was a key driver for the development of lightweight analysers. This broader market offered cheaper units for exploration or environmental purposes.

pXRF's introduction in applied geochemistry

The ability of early instruments to reliably analyse Pb, Zn, Cu and As meant they could be used at contaminated sites as well as mining areas. In both applications, they were used as a screening and fast mapping tool. In mining, they were used for regional exploration first, and applications for grade recognition came later. In environmental studies, they were first used for scoping investigations on soil and sediment. However, their qualitative identification abilities were soon used for waste management (Bosco, 2013). Later, with better understanding of how results depend on sample preparation, they began to be used for

quantitative analysis (Shefsky, 1997; US-EPA, 2004) in both mining and environmental applications (Bernick et al., 1995b).

Early examples of pXRF in mining

Applications of pXRF in mineral exploration before 2000 were rarely reported, either for confidentiality reasons or because of reluctance by the exploration geochemists. There were instances of investigation and publication though (Konstantinov and Strujkov, 1995).

A successful attempt at using pXRF for exploration purposes was made at Mt Lyell (Houlahan et al., 2003), but it was not actually implemented in operations. The reasons for this pullback were not clearly expressed. Thalanga Copper Mines later applied the strategy at the VHMS Highway Reward Copper Mine. They became the first mining operation in Australia to purchase and commission a pXRF for use as the primary analytical grade control tool (ibid.).

Glanzman and Closs (2007) describe a case study in Northern Colorado, unpublished at the time, where the spatial geochemical structure of the explored area was recognised in an extremely short time.

pXRF was investigated for its potential for grade control (Houlahan et al., 2003) to improve extraction, without much application. However, the authors shed light on why this promising technology – in decision support terms – was initially dismissed for internal reasons. The main client for ore grade analyses was not extraction but ore processing. They were not ready to consider possible biases or shifts in decision-making thresholds. The manufacturers' claim that pXRF results could easily replace lab results did not help, and pXRF needed an extra 5 or 10 years to gain mining acceptance. Glanzman and Closs (2007) evaluated this and highlighted its time benefits.

Silicate rock analysis, a strong domain for laboratory XRF at the time, was not really developed in the early pXRF period, though the pioneering work of Potts et al. (1995a) proved it was feasible. Litho geochemistry applications for exploration came later.

Similarly, no example of pXRF application in mine waste management and closure works is known before 2000, despite this technology being used for solid waste management elsewhere.

Application of pXRF in mineral exploration using surficial sediments is also quite young. One of the first publications using till was presented and published by Sarala (2009) and Sarala and Mäkikyrö (2012). Others reported applications based on different sediments, such as stream sediments from arid areas and other transported cover (Bowell et al., 2012; Plourde et al., 2013).

Early examples of pXRF in environmental geochemistry

Bernick et al. (1995a), in one of the earliest published pXRF contaminated site surveys, noticed that cost-effective measurements allowed sampling density to be increased compared to laboratory analyses. They surveyed soil and wet sediment, recognising a 20% maximum moisture limit. They set the bases of quality assurance protocols for field analyses.

McDonald et al. (1999) adapted a pXRF sensor on a cone penetrometer (SCAPS), which allowed fast multiparametric surveys of contaminated soil with depth.

Stallard et al. (1995), Rathbun et al. (1996) and Kirtay et al. (1998) broadened the scope of pXRF to marine sediments. The former's focus was on metal pollutant detection and quantification, while the others showed the value of multiple measurements for anomaly screening. Rathbun et al. (1996) were to our knowledge the first to describe the benefits of field analysis enabling efficient selection of samples to be submitted to the laboratory, within a fixed budget.

Argyrazi et al. (1997) investigated Pb soil contamination at a historic smelting site. They were able to identify sample preparation issues and to demonstrate that, despite significant bias, the results could be validly used for site mapping. Laperche and Hammade (2002) used pXRF to delineate the extent of airborne Pb-Zn soil pollution around a smelter. Maps drawn from their data are given as Fig. 2. We did not find documented examples in remediation work support or post-remediation control, though this application was suggested by Raab et al. (1991), who estimate its cost-benefit.

Kalnicky and Singhvi (2001) summarised the findings of these early years and provided a summary of XRF principles and technology available at that time. They provided an extensive review of calibration methods.

pXRF in a geochemist's life today

pXRF was the first analytical technique able to provide relevant information on-site to field geochemists, and in so doing broke the time barrier between sampling, results and decisions, first in environmental investigations, then in mineral exploration (Wiedenbeck, 2013; Lemiere, 2015). Besides its time efficiency, pXRF was also identified as a non-invasive, low environmental footprint technology (West et al., 2013), therefore eligible for "Green analytical chemistry" status (Garrigues and de la Guardia, 2013) and for living material investigations (Sacristán et al., 2016).

The technology picture today

X-ray emission

The introduction of X-ray tubes as a substitute for source emitters (Woo, 1996, Thomsen and Schätzlein, 2002) led to debate about performance (Kilbride et al, 2006; Cl:aire, 2008), but the next decade saw very fast pXRF development for environmental, mining and waste management applications, all based on X-ray tube instruments. This was boosted by rapid technology developments on detectors (Potts et al., 2003). Radioactive source emitters are still used for lead paint applications, due to the deeper sample penetration required for housing inspection. Thomsen and Schätzlein (2002) described both technologies. Most portable analysers are based on 40 or 50 kV X-ray tubes, with better performance on the latter, but with higher constraints on radiation emission mitigation. Higher tension tubes are used mainly on laboratory instruments.

Operator safety and qualification

Modern instruments provide a high level of operator safety, due to built-in controls, but they are nevertheless radiation emitting devices. Their possession and operation is strictly regulated in many countries, even with variable standard operating procedures between countries. Operator training and certification is often mandatory, and always recommended. Since X-ray tubes are used as sources, the spectrometers emit only when operated. The high level of absorption provided by target solids implies that hazards occur only if operated

in the air, with a poor contact surface, improper shooting angle, or with defective instruments. This implies periodic maintenance and emission controls.

Elemental range and lower analytical limits

pXRF is now a routine analytical method for elements with medium to high atomic mass (K to Pb, and Th and U, Fig. 3) at concentrations between a few mg/kg and a few %. It has more limitations for lightweight elements than laboratory XRF, due to instrument constraints, but recent instruments explored lighter elements (Al, Mg, P, Si) using high performance detectors and/or a helium flow to cope with X-ray absorption. Calibration data on light elements provided by Young et al. (2016) show that accuracy and dispersion are poorer for Al, Mg and P than for heavier elements (Ti, Ca, Zr), while Si results are nearly as good.

The effective element range and limit of detection varies between analysers, depending mainly on tube voltage and anode (Rh, Ag, W), detector technology (a better range is achieved with large area Silicon Drift SDD detectors than with traditional Si-PIN detectors), beam collimation and filtration.

The lower analytical limits (or limits of detection, LOD) vary with tube and detector specification and analyser geometry, but also with sample matrix composition. Higher abundance of heavier major elements, especially iron, negatively affects trace element detection. The best instruments are now capable of LOD in the 5 to 100 mg/kg range for elements with Z between 19 (K) and 68 (Pb). LOD vary between elements with emission lines and possible interferences. Each instrument has therefore its own specific element range, to be considered before selecting an analyser for a specific application.

Calibration and normalisation

On most instruments, pXRF calibration is not the same for trace (soil mode) and major (mining mode) concentrations. These modes are not based on the same calibration principles (fundamental parameters for mining mode, Compton normalisation for soil mode). So this overcomes the "broken line" calibration issues observed on very large concentration ranges (data from Hall et al, 2014). The former provides broad and easy coverage of low concentrations, and is often used for scanning and detection. However, the best approach for high concentrations and quantification is user calibration using the mining mode. Some instruments provide a hybrid mode (Geochem) which provides semiquantitative data over a larger range. This mode is useful for fast screening. Some elements may be available through only one mode, according to the manufacturer's calibration scheme.

If both trace and major level concentrations are desired, a change of mode is needed without moving the analyser between two measurements. This is longer and not very easy, but it improves accuracy.

pXRF calibration techniques were reviewed by Markowicz (2008) and further refined since then (Kenna et al., 2011). Hall et al. (2014) demonstrated that standard factory calibration does not provide full instrument performance or optimal accuracy. An empirical user calibration, using matrix-matching CRMs, or a custom calibration, based on standard addition of elements of concern to a matching matrix, are necessary to get the most of pXRF.

Operation modes and measurement

Various operation modes are available with pXRF spectrometers (Table 1). They can be used independently at a given site provided that results are properly documented and not

mixed during data processing. In all cases, the instrument nose must be kept in direct contact with the sample to minimise air space.

Mode	Description	Precision and limitations
"Point and shoot"	The nose of the instrument is placed in contact with a flat surface of the media (rock face, soil surface) without preparation	Sensitivity altered by air space between media and window. Representativity hampered by heterogeneous mineral grains. No quantitative analysis possible except for naturally fine grained homogeneous media
Field preparation ("mole heap")	Loose media (soil, sediment, tailings) is roughly homogenised and flattened to receive the nose	Air space between grains and moisture causes bias in analyses. Element ratios, abundances and sample ranking usually good
Field preparation (mill or mortar)	Hard media (rock, ore, waste) is fragmented and milled to less than 200 µm	Lower reproducibility and higher scatter due to expedited preparation. Element ratios, abundances and sample ranking usually good. Pellet compression improves analysis quality
Lab-type preparation	Hard or loose media is dried, milled and homogenised according to laboratory procedure (on site or at lab)	Quantitative analyses are possible within the instrument's performance limits

Table 1: pXRF operation modes and sample preparation

Spectrometer nose contact with sample can be made more reproducible using measurement stands, but this is only possible near the site, not on the site itself.

Competing technologies for portable elemental analysis

Laser induced breakdown spectroscopy (LIBS) (Fortes and Laserna, 2010), appeared in 1996. This rapid chemical analysis technology uses a short laser pulse to create a micro-plasma on the sample surface. It offers a broad elemental coverage, including lighter elements, such as H, Be, Li, C, N, O, Na, and Mg. It did not breakthrough in the same way as pXRF but it provides complementary applications for light elements (Harmon et al., 2013; Zorba et al., 2016) and through its remote detection capabilities (Kuhn et al., 2016).

Proton induced X-ray emission (PIXE), despite promising attempts (Wis, 1989; Melquiades and Appoloni, 2004) has not yet been much developed beyond laboratory use. One of its drawbacks – or applications – is its depth of investigation, even more superficial than XRF (Willis, 1988). Its preferential application is now aerosols (Przybyłowicz and Pineda-Vargas, 2015).

What can we expect from pXRF?

Absolute significance of pXRF measurements

pXRF measurements were soon compared to laboratory results, with variable success. Reasons for observed discrepancies included sample preparation (point-and-shoot measurements vs. laboratory homogenised samples, see Table 1), chemical matrix effects (especially for samples with high Fe contents), unchecked element interference, and sample matrix heterogeneity. All of these cast suspicion on pXRF. Sample matrix heterogeneity is statistical (it results from the variable composition of mineral grains within the sample) and not chemical (matrix composition, in the analytical sense).

Conversely, correct pXRF measurements compared to mild digestion analyses were unfairly suspected of high bias. This is easily explained because most digestion techniques extract only a part of the analyte, while pXRF, a physical technique, analyses the whole element contents, regardless of chemical bonds.

The first ETV studies and standard (US-EPA, 1998b and a) showed that pXRF could provide accurate analyses if the sample preparation scheme was the same as for the laboratory. This has been continuously confirmed since then (Radu and Diamond, 2009; Hall et al., 2012; Higuera et al., 2012; Parsons et al., 2013).

Recently, dedicated sample preparation equipment for the field (Fig. 4) was made available by instrument manufacturers. This makes it easier to obtain homogeneous powder samples – and more accurate results. Provisions for user calibration adjustment to minimise matrix composition effects are now available on most instruments.

Faster measurements, such as point-and-shoot on soil or roughly prepared media, cannot usually provide accurate absolute concentrations, because they do not provide any compensation for sample matrix heterogeneity, granularity, porosity or moisture. However, when media are naturally fine grained and homogeneous, this limitation may be removed. In the case of till, the homogeneous matrix is naturally suitable for pXRF analyses, without being very sensitive to moisture and structural changes. For example, in Finland a very good correlation between pXRF, labXRF and AR based ICP-OES and ICP-MS results using till was reported by Sarala et al. (2015), Sarala & Houlihan (2015) and Sarala (2016). In any case, fast pXRF measurements are extremely useful for field observation screening (screening in the sense given by Valcarcel et al., 1999), for mapping and laboratory sample selection (Gałuszka et al., 2015) as they provide reliably comparable results as long as the matrix is the same.

Another approach to mineral grain-size heterogeneity is multiple shooting of a clean rock face, such as a split core (Le Vaillant et al., 2014 on mineralised komatiites; Simandl et al., 2014 for rare element minerals) or an abraded rock face (Holding, 2014). This statistical approach to averaging rock composition was found to be effective at the decision-making level, even if not for quantitative analyses. It can be compared to the traditional point counter under the microscope.

Detailed investigations of heterogeneous samples

Given the improvements in analytical precision, one of the most critical parameters in analytical uncertainty is now matrix homogeneity. This cannot be assessed through lab samples, unless multiple samples are collected for each point. Heterogeneity is best quantified on site before selecting the lab sample, or on each subsample if a composite sample is to be analysed.

Matrix heterogeneity is a challenge for pXRF measurements, as they deal with very small sample volumes. However, this apparent limitation may be turned into an asset, as repeated pXRF measurements across a sample provide a quantitative assessment of its heterogeneity and scale. So pXRF's spot measurement capabilities, instead of being a drawback, can be profitably used for detailed investigations of heterogeneous samples. This was first noticed by Potts et al. (1997) and subsequently used:

- for mineralogical and geochemical observations on ore and mineralised rocks, on hydrothermal alteration patterns, to investigate their geometry, mineral and genetic processes (Yuan, Cheng et al., 2014; Lawley et al., 2015), and
- for soil and waste heterogeneity, to investigate pollution sources and pathways for dispersion (Ramsey et al., 2013).

More practically, repeated pXRF measurements on a sample prior to packing for the laboratory significantly improve sample representativeness. Estimations of sample heterogeneity can be made easily and inexpensively by performing repeated shoots at short distance, either in situ or on the sampling bag (Crumbling, 2008; Sarala et al., 2015; Sarala, 2016).

In other geological applications, Jones et al. (2005) and Gazley et al. (2011) used the sensitivity of pXRF to variations of trace element chemistry to recognise volcanic stratigraphy patterns. The availability of such information on the field has valuable applications for mapping and mineral exploration (Hoatson et al., 2006; Partington, 2010).

Using pXRF as a decision-making tool

pXRF results and threshold values

Sensitivity to trace element variations in a common matrix is one of pXRF's strong points. Therefore absolute precision is not strictly necessary for decision-making, for instance in soil remediation, ore extraction or waste management. Measurement uncertainty reporting and regular lab calibration on a small number of samples provide confidence level estimates and safety margins (Melquiades and Appoloni, 2004).

Samples with large concentration differences from the threshold values for given elements allow on-site decisions to be made without having to wait for laboratory results. Unexpected or ambiguous results will prompt immediate complementary measurements, according to dynamic work plans (Robbat, 1997) or Adaptive Sampling and Analysis Programs (US-DOE, 2001, Horta et al., 2015).

Systematic reporting of uncertainty data means that pXRF measurements can be used routinely for geostatistical or geometallurgy purposes, with better data density and significance than sparse accurate lab results (Crume, 2000; Crumbling, 2001b). The high cost of laboratory analyses implies in most cases that the decision will be based on a small number of samples. Sampling errors or uncertainties exceed by far the analytical uncertainties, often by an order of magnitude. Ramsey and Argyraki (1997) report around 50% uncertainty compared with the result of variations in sampling protocols and sampling point selection.

If this small number of samples is replaced by a large number of pXRF measurements, even with a higher analytical uncertainty (i.e. 10 or 20%, depending on the sample preparation protocol), the confidence level of the decision will be actually higher than with a small number of lab samples (Fig. 5), as long as pXRF measurement accuracy is monitored.

Laboratory monitoring of pXRF measurement accuracy

pXRF measurement accuracy can be improved by running lab controls on a selection of samples based on analyte distribution:

- laboratory sample selection should cover the whole range of abundances for the elements of concern, to monitor their accuracy throughout the range. This may allow the development of site-specific calibration of pXRF measurements,
- laboratory sample selection may focus on samples near the decision level for the elements of concern.

Best practices for cooperation between the field geochemist using pXRF and the laboratory include:

- an exploratory study with pXRF on various facies or media, along with the collection of carefully selected lab samples,
- a tailored field protocol and matrix-adapted calibration, based on the expected element ranges,
- screening samples for laboratory controls being regularly collected and screened on pXRF element distribution or location criteria,
- regular pXRF analyses on the residual fraction of samples returned by the laboratory.

Blind replicate lab analyses and analysis of standards are helpful too, as with any survey.

The most suitable laboratory tests are physical techniques (ED-XRF, INAA). When wet chemical techniques (ICP-AES, ICP-MS, GFAAS) are used for refractory elements (W, Sn, Ti, Zr, Ta, Nb, etc.), the digestion method has to be the most comprehensive possible: alkali sintering followed by multi-acid digestion, i.e. a total dissolution method, to ensure full mineral dissolution.

Decision-making based on pXRF grids

Ramsey (2004) discussed the financial impact of reducing measurement uncertainty versus the cost of a wrong decision. Unlike laboratory analyses, measurement uncertainty is reported by pXRF instruments for each point. By reporting each point's estimated measurement uncertainty along with the measurement, pXRF instruments facilitate confidence level and data quality objective (DQO) calculations. Using systematic pXRF grids will further optimise investigation costs, due to increased data density and low measurement costs.

An additional recent feature of interest for such operations is GPS embedding in analysers, or GPS communication. Pairing pXRF data with GIS devices, while working with scanned site blueprints on screen, allows for instantly obtaining elemental maps (Carr et al., 2008).

The relationship between data density and uncertainty must especially be considered when using the Triad approach (US-EPA, 2008: "the Triad approach to decision-making for hazardous waste sites (...) refers to three primary components, systematic planning, dynamic work strategies, and real-time measurement systems"). pXRF supports the purposes of this approach (optimised investigations and clean-up strategies using immediate and on-site data, in view of significant economies on clean-up costs).

Due to its low operating costs, denser data sets can be collected with pXRF, either by more closely spaced measurements, or by repeated measurements over time. This significantly

reduces the sampling uncertainty issues related with the selection of small numbers of laboratory samples (Crume, 2000; Ramsey and Ellison, 2007; Ramsey and Boon, 2010).

Decision making and real-time measurements

In both mining and environmental projects, many decisions are based on chemical analysis results. While project evaluation or feasibility is based on certified laboratory results and on threshold values, to limit investigation costs many operational decisions have to be taken at the site as quickly as possible. Results from pXRF are available within minutes, while laboratory results come after days or weeks, especially at remote sites.

In conventional practice, decisions are based on a given or calculated threshold value, with a safety margin for sampling errors and uncertainty. This is made easier when uncertainty is directly reported by the instrument, and when sampling error can be constrained by repeated on-site measurements (Jones et al., 2005). This is improved by matrix-specific calibrations using repeated measurements (Rouillon and Taylor, 2016; Steiner et al., 2017).

There are many operational situations in which the delay between sampling and receiving laboratory results entails significant costs. In mining exploration, this obviously applies to whether to drill further or not, but also to deciding where to drill or to sample, while field teams and equipment are mobilised. This is even more obvious in remote locations, far away from laboratory logistics. Potentially large cost savings can be made from not waiting for laboratory results, and orientating exploration resources (ground teams, drilling rigs, and more) towards the most promising targets.

In environmental investigations, the sampling plan will be more cost-efficient if it can be carried out without returning to the field. During remediation options, relevant decisions can often be made on batches of soil or waste without storing them while waiting for results. For such situations, the confidence level of on-site pXRF results has to be carefully monitored by a QA/QC program, to assess the confidence level for operational decisions. This incorporates a sampling and analysis plan, hence quantified sampling errors, and sample-specific analytical uncertainties. It is also used for systematic planning and for performance-based measurement systems (Lesnik and Crumbling, 2001).

If compliance has to be based upon this type of measurement, a correlation has to be determined between field and laboratory measurements. Bias or systematic shift are acceptable as long as the dispersion stays within accepted limits (Figs. 6 and 7).

Decisions can be made safely as long as the uncertainty on the pXRF result, including instrumental uncertainty and a provision for bias, is smaller than the difference between the result and the compliance value (Fig. 8), as long as pXRF measurements are monitored by proper QA/QC schemes. This has not yet been legally challenged, to the best of our knowledge. In the event of a challenge, it would be probably necessary to demonstrate that pXRF can be traceably related with the accuracy of a legally approved technique. This is similar to how alternative techniques are qualified when a classic technique is recommended by a standard. This demonstration is usually done for each new technique.

Reliability of decisions based on lab or portable XRF

For a long time, the issue of the reliability of pXRF data was considered mainly from the absolute accuracy point of view. So lab-based XRF decisions were safer, and pXRF use was restricted to screening tasks. With improved equipment, and the increasing reference base, it

became clear that even if pXRF measurements on field samples provided less accurate data, these data sets were nevertheless consistent for sample ranking, for geochemical signatures and for spatial distribution, since most of the inaccuracy was only bias. The impact of loose sampling density on the reliability of decisions was overlooked, despite the availability of reliability assessment methods such as DQO (US-EPA, 2000).

On a more general basis, within usual budgets, better analytical accuracy is obtained from laboratory analyses, but on fewer samples; while slightly lower accuracy is obtained from pXRF field analysis, but with better known uncertainty and far larger data sets (Crumbling, 2001a). For both methods, sampling errors exceed analytical errors by far (Malissa and Riepe, 2000; Esbensen and Wagner, 2014). In many cases, the quality of pXRF data sets is actually better than the quality of data sets based on laboratory analyses alone, if the elements of concern are within the range of pXRF (Fig. 3).

Beyond the acceptability of pXRF data, Ramsey and Boon (2012) examined whether field data were merely a surrogate for "real" data, or if they could actually bring more value through their higher density, compensating for their lower accuracy. They demonstrated that higher sampling density coped efficiently with matrix heterogeneity and sampling uncertainties, which could be appreciated and understood on-site (Boon and Ramsey, 2012). They developed the "fitness for purpose" concept, which allows to compare how far traditional sampling campaigns and pXRF measurements satisfy the objectives of the investigation. They conclude that within a given budget, field measurements often outperform traditional analyses.

Once these possible pathways are taken into account, a geochemist has the final say, deciding which is best adapted for his or her purpose (taking into account DQO, confidence in the decision, compliance, time and budget) and what the share of field measurements (pXRF) and certified laboratory analyses should be in the investigations.

pXRF in mining and mineral exploration projects

Ore elements, associated elements and indirect approaches

pXRF is able to analyse many commodity elements down to a few mg/kg in rocks, soil or stream sediment. It can also determine associated elements (tracer) elements for certain types of ore deposits (e.g., As, Sb, Se, Bi; Cu for Au, Arne et al., 2014), and determine some characteristic elements of alteration aureoles (K, Rb, Ba, Sr, P) or lithology (Ca, Fe, K, Ti, Zr).

Access to sub-mg/kg elements (Nb, Hf, Ta, Ag, Au, PGEs) and to rare earth elements (REE) is more challenging, but manufacturers are pushing instrument limitations further every day through improvement of detectors. However, the X energy and detection constraints for some elements (individual REEs, for instance) still require heavier instruments that are transportable but not hand-held (Hall et al., 2014).

XRF's limitations have until now precluded its use with elements lighter than Mg, elements for which LIBS may provide an alternative (Harmon et al., 2013). Despite recent progress, analyses of Si, Al and P are still difficult and controversial, and Mg even more so. Simandl et al. (2012) demonstrated that pXRF could reliably analyse P from a phosphate deposit (exploration for phosphate \pm yttrium and REE), and provide a quantitative but biased, or semi-quantitative estimation for Nd, Ce, La, Zr, W, and Al.

Clever combinations of elements allowed Brand and Brand (2016) to use pXRF for Li exploration, despite this light element being out of reach of pXRF. A similar approach was used by Zhang et al. (2017) at the Mount Pleasant deposit (Fire Tower Zone, W-Mo-Bi, and North Zone, Sn-Zn-In). They deduced mineralisation signatures (As and Mo, along with K, Rb, Fe, and Mn depletion, interpreted as the W-Mo mineralisation; and Sn, Zn, Cu, and S with slightly depleted Sr and Ba, representing Sn-Zn mineralisation) from principal component analysis (PCA) of the multi-element pXRF data.

Lithochemistry and hydrothermal alteration

A good example of multielement application is given by Benn et al. (2012): pXRF's major and trace element capabilities were both efficiently used for lithology discrimination, similarly to lithochemical exploration methods. Marsala et al. (2012) used major elements to calculate the mineral composition of drill-hole cuttings, similar to petrographic norms, and found this approach to be more accurate than visual examination.

Le Vaillant et al. (2014) investigated the direct use of pXRF as a lithochemical discrimination tool to distinguish potentially mineralised and barren komatiites, using geochemical criteria developed for laboratory analyses, and extended it to hydrothermal alteration mapping (Le Vaillant et al., 2016). More general applications of pXRF in geological reconnaissance and mapping were reviewed recently (Young et al., 2016).

Durance et al. (2014) used pXRF for lithochemistry at gold camps and it enabled precise identification of host formations. Gazley et al. (2014) used pXRF in gold exploration for the recognition of host lithologies in drill-cores, but also for the quantification of sulfide content and of hydrothermal alteration with associated elements (As, Cu, K, V).

The recognition of hydrothermal alteration zones is often possible using Ca, Fe, K or Al, even though the analysis of some other elements is difficult or impossible (Mg, B, Li, Na).

Before field

Because pXRF performs fast and inexpensive measurements with good reproducibility it can usefully be used to scan old sample collections for new purposes such as identifying targets for new commodities and quickly selecting prospects. This is applicable also to core libraries, with the added benefit of dynamic sampling around observed anomalies.

Matrix heterogeneity issues

An important limitation of pXRF for rare or precious elements results from nugget distribution, which is poorly accounted for by the small beam diameter and investigation depth of the X-rays, since these are usually submillimetre and vary with atomic weight (Potts et al., 1995b, 2006, Jones et al., 2005, Brand and Brand, 2014; Gazley and Fisher, 2014). This is addressed in the laboratory by milling and splitting large amounts of sample, but is not applicable to field pXRF measurements.

More generally, the small X-ray beam size makes pXRF sensitive to spot sample heterogeneity (Potts and West, 2008) but this can be turned to an advantage to evaluate matrix heterogeneity (Glanzman and Closs, 2007; Gałuszka et al., 2015). Repeating measurements at several spots on a sample may reduce the uncertainty inherent to beam size, yet offer an alternative to sample milling.

For till samples, Sarala et al. (2015) and Sarala (2016) used three repeated measurements to increase accuracy and to diminish matrix and heterogeneity effects. Bourke and Ross

(2016) reported that repeating measurements (3 to 7 times) at the surface of a core produced the same accuracy as milling, for fine to medium-grained metavolcanics.

pXRF capabilities in microanalysis allow mapping of elemental distributions related to mineralogy at the macroscopic scale (core, outcrop). This may provide valuable insights on ore texture, ore-forming processes and hydrothermal alteration (Ross et al., 2014a and b; Yuan, Cheng et al., 2014). However, matrix specific issues may require geochemical expertise for the reliable interpretation of field data.

Relationship with wet chemical analyses

Several factors converge into systematic bias, in which raw pXRF results are lower than laboratory analyses on the same sample. These include:

- additional air in the sample due to simpler preparation, and to less controlled distance between sample and window,
- moisture, which attenuates the signal (Lemiere et al., 2014; Ussath et al., 2017),
- instrument features, including different fundamental parameter calibration and less powerful sample excitation.

This bias does not affect all elements evenly and it depends on matrix composition. It cannot be easily corrected unless a site-specific calibration is performed using trustworthy laboratory analyses. However, its rate (usually 10 to 30% provided that the right analytical mode is selected, e.g. Hall et al. 2014 § 4.3.2) and reproducibility at the site scale do not significantly affect interpretation of results.

However there are some opposite types of case, where pXRF was found to provide higher, but more accurate results than laboratory wet chemical techniques, especially ICP-AES or ICP-MS, for more refractory elements such as Cr or Ti (Rouillon and Taylor, 2016), Sn (Hall et al., 2014) and W (Knésl et al., 2015). For W, Nb and Ta, the intrinsic advantage of XRF as a physical technique is balanced by poor standard accuracy (Hall et al., 2014), which may require matrix-specific correction factors (Knésl et al., 2015). The same bias is observed between laboratory XRF and wet techniques. It results from the physical nature of XRF analysis, which does not rely upon digestion procedures. The digestion bias in wet chemical methods is not widely documented because most exploration is based on them, and many geochemists believe that pXRF overestimates these elements. However, a good correlation between wet geochemistry and pXRF for several elements (particularly for base metals), even if biased, allowed application in mineral exploration due to good comparability of pre-existing (wet chemical) datasets and new pXRF results. This was demonstrated in glaciated terrains using till by Sarala (2016). This was also discussed by DiScenza et al. (2014) for environmental analysis of soils.

Ge et al. (2005a) proposed procedures for the systematic use of pXRF in mineral exploration but the current practice is to develop site-specific strategies, making the most of continuous technology innovation by providers, and paying attention to QA/QC and to possible pitfalls (Brand, 2014; Brand and Brand, 2014).

Reporting pXRF results

Despite these limitations, pXRF data have been used for demonstrating exploration results. This was made possible through the application of robust procedures and QA/QC schemes such as those recommended by Hall et al. (2013), Fisher and Gazley (2014) or Gazley and Fisher (2014). A critical review of expedited field practice, suitable for reconnaissance but inadequate for reporting, was given by Durance et al. (2014), who recommended the use of site-specific calibrations rather than general purpose CRMs. They also warned against measurements through paper bags. Unlike laboratory analyses, field analyses are often produced by several instruments. This may lead to minor drift between instruments, and even between batteries (Chang and Yang, 2012), but is easily dealt with using traceability procedures and standards.

The suitability of pXRF data for exploration results reporting under JORC or NI 43-101 regulations was discussed by Arne and Jeffress (2014) and Arne et al. (2014). They 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". Published reports show that pXRF analyses are gradually becoming accepted (Bosc and Barrie, 2013; Stoker and Berry, 2015). Reporting of exploration results, mineral resources and ore reserves based on pXRF are acceptable, as long as pXRF use complies with good laboratory practice.

Mining and exploitation

In many cases, testing ore grade on the pit or gallery wall can be attempted, but it always needs site-specific calibration, depending on the commodity's concentration range (Quiniou and Laperche, 2014), on the host rock matrix, and on specific elements occurring at high concentrations (for instance, iron: Jinsung et al., 2012).

Waste management and mine closure

The main issue with waste management is predicting acid drainage, but another issue is identifying potentially toxic elements that may be released by acid leaching. pXRF may effectively detect Pb, Zn, As, Cu and many other elements (V, Cr, Mn, Co, Ni, Ge, Se, Nb, Mo, Pd, Ag, Cd, In, Sn, Sb, Te), directly or indirectly (for instance, sub-ppm Cd through Zn) in leachable waste. Examples were given for Pb, Zn, Cu, Cd and As by Kovacs et al. (2006) and by Druzbecka and Craw (2013) for As and Sb. Continuous monitoring of these data contributes to safe waste management.

pXRF has many applications in accelerated environmental assessment of closed mining and metallurgy sites (Meza-Figueroa et al., 2009; Peinado et al., 2010; Jang, 2010; Weindorf et al., 2013), ranking sites for management (EPA Ireland, 2009), detailed site investigations (Hürkamp et al., 2009) or while designing monitoring or closure plans (Liakopoulos et al., 2010; González-Corrochano et al., 2014).

After closure, pXRF can be used for the reassessment of waste for reprocessing (Bellenfant et al., 2013), for waste management (Parbhakar-Fox et al., 2014) and for monitoring site clean-up and recovery, including metal contents in plants (Tamás and Kovács, 2005).

pXRF in environmental projects

Site diagnosis, contamination detection and mapping

pXRF was immediately successful for the analysis of fine-grained homogenous media (soil, sediment) and for the elemental characterisation of coarser media (metal scrap, residual waste). It was also tested on water (Melquiades and Appoloni, 2004; Melquiades et al., 2011) but its detection limits restrict direct application to highly contaminated water.

pXRF provides invaluable help at the reconnaissance stage of a site diagnosis (Weindorf et al., 2013). It identifies most of the elements of concern, delineating the contaminated zones, for instance, airborne soil contamination (Paulette et al., 2015), and mapping their degree of contamination with dense grids (Puckett and Takasaki, 2004). The resulting image may be slightly biased or shifted in concentration, but its topology (Fig. 2) will reflect accurately what a similar map with classic lab analyses would have shown. The systematic multielement approach of pXRF allows extended use of multivariate statistics to discriminate anthropogenic from natural background variations (Yuan, Sun et al., 2014; Ran et al., 2014).

The cost and delay for large sets of lab analyses precludes that alternative in most cases. The amount of information obtained from pXRF grids is much better than what can be obtained from a limited set of analyses on composite samples. Besides this, samples for laboratory analysis can be selected in an optimal manner using these data.

Rouillon et al. (2017) demonstrated that for contaminated site assessment, the biggest part of measurement uncertainties was sampling (>95% variation), and that the large data sets allowed by pXRF increased the confidence level of decisions (representativeness, mapping contrast and reduced uncertainty), and the cost effectiveness.

The ultimate recognition of pXRF ability to screen soil is its recent election to ISO standard status (2013). ASTM does not yet provide any standard for field use.

Drake et al. (2003) proposed air pollution monitoring. Van Grieken et al. (2005) updated recognition procedures.

Soil contamination applications were recently extended to metal monitoring in crops (Sacristán et al., 2016). Non-destructive applications of pXRF on plants, developed for agronomy purposes (Reidinger et al., 2012), might be used in the future for site diagnosis or verification purposes, alone or combined with infrared (Wang et al. 2015). The author's own experience on vineyards and copper contents of trunks (unpublished) supports this.

Remediation

Most remediation operations require immediate, on-site data for management decisions. This is especially true for ex situ operations. Precise determination of uncertainty means batches are kept controlled under regulatory values with an acceptable confidence level. On-site analyses will support decisions in a more cost-effective way, and within the required time frame (Ridings et al. 2000, Schuck et al., 2002, Takasaki and Pitre, 2006).

During the remediation of a former gold mine (Bodenan et al., 2004), As-contaminated waste and soil were identified. The high As concentrations required an expensive hazardous waste management plan. Field measurements by pXRF determined that the hazardous fraction was in fact less 200 m³, a much reduced portion of the whole.

One of the issues of real-time monitoring is the need to deal with dry samples, for soil or for dredged sediments. Direct measurements were known to be biased for moisture levels

above 20% (US-EPA, 1998b and 2007), and simple correction procedures were useful only under 20% (Ge et al., 2005b, Bastos et al., 2012). The quantification of water contents was first attempted to allow quantitative analysis of wet sediments by XRF scanners (Kido et al., 2006), but was applied then to pXRF instruments. Pressure dewatering, quicker than oven drying, was later found to be a viable option for decision-making on wet materials (Lemiere et al., 2014).

Site verification

Once remediation work is completed, it is more efficient to check if remediation objectives were met using pXRF screening, similar to the initial diagnosis. It may be especially efficient for checking before official inspection. Another similar type of application is hazard mapping in populated areas, for agricultural use (Weindorf et al., 2012a), residential use (Dixon et al., 2006; Carr et al., 2008) or source identification (Yuan, Sun et al., 2014).

Other uses of pXRF for geochemists

The properties of pXRF, described above for exploration and environmental geochemistry, can be applied in almost any area of geochemistry: lithofacies or alteration identification in geomapping (Young et al., 2016), mineral or industrial processing monitoring (Healy et al., 2016), drill-hole logging (on cuttings or on cores), reservoir characterisation and delineation, oil and gas exploration applications, archaeology (e.g. Frahm and Doonan, 2014; Newlander et al., 2015), meteoritics and planetary science (Zurfluh et al., 2011; Young et al., 2016), and many others. Specific calibration procedures for litho-geochemistry were proposed by Steiner et al. (2017).

Indirect applications of pXRF were widely extended to other soil properties for agricultural uses and soil functionality, using its multivariate capabilities (Zhu et al. 2011; Weindorf et al., 2012b, 2012c and 2012d; Sharma et al., 2014; Sharma et al., 2015, Brevik et al., 2016). They were used to investigate pedogenesis and soil derivation from bedrock (Stockmann et al., 2016).

pXRF applications for industrial waste (scrap metal, plastics, treated wood), for archaeological purposes (non-destructive in situ analysis) and for testing industrial products are not described here, as they are beyond the domain of geochemistry.

pXRF do's and don'ts

The major feature of pXRF is that it can provide data on most geologic materials in almost any situation. But, in spite of the apparent simplicity of readings, the kind of information produced depends totally upon the level of sample preparation. Direct point-and-shoot counting on raw surfaces will provide only semi-quantitative information, and in many cases nothing more than an abundant/present/absent classification for most elements. This might provide useful trend analyses at a site scale, and valuable insights on mineral processes (ore genesis, alteration, waste segregation) that complement bulk sample analyses. On the other hand, measurements performed on lab-ready samples, properly milled, dried and homogenised, often compare satisfactorily with laboratory analyses.

1. Do keep the analyser in contact with the sample.

Any air layer between the sample and the instrument window will affect analysis results, especially for lighter elements. Avoid shooting samples through sample bag or protector

films, unless you use the same bag or film for all the samples, and you are ready to accept the resulting bias.

2. Don't mix point-and-shoot results and pXRF analyses on prepared samples.

The strong points of pXRF are its ability to deliver usable results within minutes, to provide large numbers of measurements or analyses for a fraction of the cost of laboratory analyses, and, even better for decision-making, its unequalled ability to fit into dynamic sampling plans (Robbat, 1997), Triad (Crumbling, 2001a) or adaptive sampling (US-DOE, 2001) strategies. Many applied geochemistry programs are actually better documented if pXRF is used on a large scale, because information density is improved. Absolute accuracy may require the same sample preparation as for the laboratory, especially for ores and rocks. This can be achieved within a few hours, which is still good in terms of operational delays. However, for soil and sediment, in most cases, a simpler preparation (sieving, homogenisation) will provide results that compare satisfactorily with laboratory results.

3. Don't mix pXRF field results and lab analyses on maps or in tables.

Even though pXRF results can compare reliably and allow ranking, their absolute values may differ from lab results, especially if they are obtained from roughly prepared samples. Mixing lab and field results can lead to misclassification or erroneous topologies. Separate maps have to be drawn when results for both analysis types are available (Fig. 2), unless a careful analysis of their correlations demonstrates they are statistically similar.

4. You can use geochemical maps drawn from pXRF measurement grids, but don't report them with absolute values unless a representative subset was also analysed in the laboratory.

Measurements obtained with a rough sample preparation, or even no preparation, can be compared together and show a good sensitivity to element variations, even if the absolute concentrations are biased. The resulting map will show an accurate topology, but the scale has to be relative (Fig. 2).

5. Do select the right analytical mode carefully.

You need to take into consideration the expected concentration range and the study's objectives. In most cases, the soil mode offers an adequate coverage of trace level elements, while the mining mode is required for more accurate determinations of higher concentrations. A change of mode may thus be needed without moving the analyser between two measurements. If screening at various levels is only needed, the geochemistry mode, available on some analysers, is faster.

6. Do have to hand a selection of certified reference materials (CRMs) for regular measurement.

Besides the necessary double-check of performing laboratory analyses on selected samples, selected certified reference materials (CRMs) should be regularly measured, and those results incorporated into the instrument's QA/QC scheme (IAEA, 2005, p. 3).

7. Do make your own internal standards that match matrix composition better.

CRMs with matrix compositions similar to studied samples are not always available, so we recommend preparing internal standards from a local sample of known composition (IAEA, 2005, p. 3-4), showing low contents in the elements of concern (ore or pollutants). Precisely known amounts of these elements are added to the local low concentration sample (VanCott et al., 1999; Arne et al., 2014) to create a range of internal standards covering the expected range of the monitored elements.

8. Do only use custom calibration on homogeneous matrix samples.

Calibrating pXRF instruments with specific factors calculated from laboratory analyses may significantly improve accuracy (Bourke and Ross; 2016, Rouillon and Taylor 2016) but only if this is applied to a lot of samples with a homogenous matrix composition - for instance, the same geological formation). If applied to heterogeneous rock types, this strategy may lead to significant errors, as matrix effects generate variable regression factors (Rowe et al., 2012; Hall et al., 2013).

9. Do verify calibrations for each instrument if several pXRF analysers are used.

These instruments provide a robust framework for analysis, but variations may be observed between them (Hall et al., 2012, Brand and Brand, 2015a).

10. Do ensure traceability of results for instrument and operating parameters.

When several instruments are used within a project, regardless of whether they are identical or different models or brands, measurements such as counting time by filters should be traceable to their instrument and its operational parameters. Instrument cleanliness and battery life are also important.

11. Do perform an orientation survey with laboratory analyses before using pXRF extensively in a project.

A preliminary orientation study is required for any large project based on pXRF data. This identifies matrixes and element ranges, and defines a suitable sampling protocol. An early comparison between field results and laboratory analyses provides an insight on possible biases and elements for a QA/QC frame.

12. Do ensure systematic QA/QC monitoring of pXRF results.

This is required if pXRF field measurements have to be used as data by the project. This is even more essential if operational decisions are based on them. QA/QC protocols are the same as in the laboratory, with blanks, CRMs and standards, systematic and random duplicates, and careful performance monitoring of each instrument (Hall et al., 2013, 2014).

Conclusion

The current status of pXRF in applied geochemistry encompasses several situations in the mining and environmental sectors:

- Providing a cost-saving alternative to classical laboratory analysis programs. Based on this sole criterion, pXRF is a risky bet for junior exploration or remediation companies, unless an experienced operator and adequate procedures are involved,
- Dealing with remote or harsh field conditions, and providing geologists with decision support information of key importance for exploration planning by diminishing laboratory sample lots and without waiting for shipping and laboratory delays (Brand and Brand, 2015b),
- Providing real-time or near real-time decision support for operational decisions (exploration and drill-hole management, ore extraction and processing, site remediation or waste management),
- Optimising data quality and data density in the perspective of a full site information system (geometallurgy, environmental) by providing 2D and 3D grids compatible with geostatistics, and controlled by lab analyses on selected samples,
- Providing higher sampling density data sets and therefore achieving better fitness for purpose than lab-only data sets (Ramsey and Boon, 2012), with less concerns with sampling uncertainties (Boon and Ramsey, 2012).

Besides these ambitious applications, pXRF can be used profitably by most geochemists for sample screening and selection tasks:

- Quick ranking of samples on site, and selection for laboratory analysis of a smaller number of relevant samples,
- Dynamic sampling plans based on field observations and measurements, allowing better investigations than blind field work completed before laboratory analyses are available,
- Grid mapping of a site, using relative element abundance classes, and laboratory confirmation of the absolute abundance values.

Both in the mining and environmental worlds, pXRF is an important technology for:

- Accelerated site diagnosis,
- Investigating anomalies,
- Input and output material monitoring,

In waste management, pXRF is used profitably for:

- Identifying unknown waste,
- Selecting samples for the lab, and selecting the substances to be analysed,
- Verifying waste loads before disposal or treatment.

To summarise these findings, pXRF is now a fundamental tool for the geochemist in exploration, mining and in environmental geochemistry. It does not substitute laboratory analyses (Ridings et al., 2000), but it offers a wide range of possibilities for site investigations that could not be provided by laboratory analyses for an acceptable cost (Higuera et al., 2012; Paulette et al., 2015). pXRF is highly recommended for extensive field surveys and lab sample selection, using a robust protocol (West et al., 2015; Fisher et al., 2014) and to complement these surveys by systematic control analyses in the laboratory.

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

The best results are usually achieved through a well-planned combination of field and lab data, with pXRF providing the bulk of the data at low cost, allowing large data sets and better reliability than exclusively lab-based campaigns based on a limited number of samples.

Acknowledgments

This research was supported by various projects with funding by the European Union (Regional Policy and Enlargement Directorates), the French Ministry for Research, the French post-mining safety institute (GEODERIS), the French North Pas de Calais and Belgian Walloon regions, and the French Waterways Agency (VNF). We are grateful to instrument suppliers for technical support. We also gratefully acknowledge discussions with other pXRF users, in BRGM and the Association of Applied Geochemists, valuable comments and suggestions by Dr. Pertti Sarala and one anonymous reviewer, and manuscript proofreading by Dr Karen M. Tkaczyk.

References

- Argyrazi A, Ramsey MH, Potts PJ (1997) Evaluation of portable X-ray fluorescence instrumentation for in situ measurements of lead on contaminated land. *Analyst* 122: 743-749
- Arne, D.C. and Jeffress, G.M. (2014) Sampling and Analysis for Public Reporting of Portable X-ray Fluorescence Data Under the 2012 Edition of the JORC Code. *Sampling 2014 / Perth, WA*, 29–30 July 2014.
- Arne, D.C., Mackie R.A., and Jones, S.A. (2014) The use of property-scale portable X-ray fluorescence data in gold exploration: advantages and limitations. *Geochemistry: Exploration, Environment, Analysis* 14, 233-244.
- Bastos, R. O., Melquiades, F. L. and Biasi, G. E. V. (2012) Correction for the effect of soil moisture on in situ XRF analysis using low-energy background. *X-Ray Spectrom.* 41, 304–307.
- Bellenfant, G., Guezennec, A.G., Bodenan, F., D’Hugues, P., and Cassard, D. (2013) Reprocessing of Mining waste: combining environmental management and metal recovery? in *Mine Closure 2013*, Cornwall, UK - M. Tibbett, A.B. Fourie and C. Digby (eds), Australian Centre for Geomechanics, Perth, ISBN 978-0-9870937-4-5, p. 571-.
- Benn, C., Jones, N., Weeks, D., Bell, J., and Mugerman, K (2012) Lithological Discrimination in Deeply Weathered Terrains Using Multielement Geochemistry – An Example from the Yanfolila Gold Project, Mali. *Explore*, 156.

Bernick, M.B., and Campagna, P.R. (1995) Application of field-portable X-ray fluorescence spectrometers for field-screening air monitoring filters for metals. *Journal of Hazardous Materials*, 43 (1-2), p.91-99.

Bernick, M.B., Getty, D., Prince, G., and Sprenger, M. (1995a) Statistical evaluation of field-portable X-ray fluorescence soil preparation methods. *Journal of Hazardous Materials* 43, 1–2, 111–116.

Bernick, M.B., Kalnicky, D.J., Prince, G., and Singhvi R. (1995b) Results of field-portable X-ray fluorescence analysis of metal contaminants in soil and sediment. *Journal of Hazardous Materials*, 43, 1–2, 101–110.

Bero, B.N., Von Braun, M.C., Knowles, C.R., and Hammel, J.E. (1993) The use of X-ray fluorescence to detect lead contamination of carpeted surfaces. *Environmental Monitoring and Assessment* 27: 17-33.

Bodenan, F., Baranger, P., Piantone, P., Lassin, A., Azaroual, M., Gaucher, E., and Braibant, G. (2004) Arsenic behaviour in gold-ore mill tailings, Massif Central, France: hydrogeochemical study and investigation of in situ redox signatures. *Applied Geochemistry* 19, 1785–1800.

Boon, K.A., and Ramsey, M.H. (2012) Judging the fitness of on-site measurements by their uncertainty, including the contribution from sampling. *Science of the Total Environment* 419, 196–207.

Bosc, R. and Barrie, C.T. (2013) Douvray porphyry copper deposit mineral resource estimate, Somine project, Northeast mineral district, Republic of Haiti. NI 43-101 Technical Report, MAJESCOR Resources Inc. Retrieved on 07/02/2017 at [http://www.majescor.com/uploads/43-101%20douvray%20majescor%2020130228%20\(2013-03-01\)-1.pdf](http://www.majescor.com/uploads/43-101%20douvray%20majescor%2020130228%20(2013-03-01)-1.pdf) .

Bosco, G.L. (2013) Development and application of portable, hand-held X-ray fluorescence spectrometers. James L. Waters Symposium 2012 Report. *Trends in Analytical Chemistry*, 45, 121-134.

Bourke, A. and Ross, P.-S. (2016) Portable X-ray fluorescence measurements on exploration drill-cores: comparing performance on unprepared cores and powders for ‘whole-rock’ analysis. *Geochemistry: Exploration, Environment, Analysis* 16, 147–157.

Bowell, R.J., Egorova, L., Gurevick, D., Sedov, V., Holwell, D.A., Mikhailov, A. & Kordi, P. (2012). Grass roots exploration in remote areas: An example from the Kuene region, Namibia. *CIM Journal*, 3, 33–46.

Brand, N., and Brand, C. J. (2014) Performance Comparison of Portable XRF Instruments: A Mineral Exploration Prospective. Australian X-ray Analytical Association Workshops, Conference, and Exhibition, 9 to 13 February 2014, Perth, Australia. Accessed on 2014/12/02 from http://www.pxrf.com.au/wp-content/uploads/2014/09/pXRF_performance_Feb-2014_talk.pdf

Brand, N. (2014) Performance comparison of portable XRF instruments. *Geochemistry: Exploration, Environment, Analysis*, v. 14:125-138, first published on February 4, 2014, doi:10.1144/geochem2012-172

Brand N. W and Brand C.J. (2015a) Finding a needle in a haystack: performance evaluation of portable XRF instruments from three manufacturers. 27th IAGS, Tucson, AZ, April 2015. www.appliedgeochemists.org/index.php/events/aag-events/2-uncategorised/139-27th-international-applied-geochemistry-symposium

Brand N. W and Brand C.J. (2015b) The portable XRF experience. Application of Portable X-Ray Fluorescence in Exploration and Mining, short course, 27th IAGS, Tucson, AZ, April 2015. Ibid.

Brand N. W and Brand C.J. (2016) Detecting The Undetectable Lithium By PXRF. Retrieved at <https://www.pxrf.com.au/news-posts/detecting-undetectable-lithium-pxrf/#> on 2017/01/27.

Brevik, E.C., Calzolari, C., Miller, B.A., Pereira, P., Kabala, C., Baumgarten, A., and Jordán, A. (2016). Soil mapping, classification, and pedologic modeling: History and future directions. *Geoderma* 264, 256–274.

Carr, R., Zhang, C., Moles, N. and Harder, M. (2008) Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. *Environ Geochem Health* 30:45–52.

Chang, Z., Yang, Z., (2012) Evaluation of inter-instrument variations among Short Wavelength Infrared (SWIR) devices. *Econ. Geol.* 107, 1479–1488.

Claire (2008) Field Portable X-ray Fluorescence (pXRF): A rapid and low cost alternative for measuring metals and metalloids in soils. *Research Bulletin* 7, 4 p. Retrieved from <http://www.claire.co.uk> on April 2012.

Crumbling, D. M. (2001a) 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

Crumbling, D. M. (2001b) Applying the Concept of Effective Data to Environmental Analyses for Contaminated Sites. USEPA report 542-R-01-013. Retrieved in 2012 from www.epa.gov/tio/download/char/effective_data.pdf

Crumbling, D.M. (2008) Advanced Design Application and Data Analysis for Field-Portable XRF. Example of an XRF MIS Strategy. NEMC Conference, Aug 12, 2008. Retrieved on 02/04/2013 from www.clu-in.org.

Crume, C. (2000) The Business of Making a Lab Field-Portable. *Environmental Testing and Analysis*, November/December 2000.

DiScenza, D.J., Keimowitz, A.R. and Fitzgerald, N. (2014) Calibration and Evaluation of an X-Ray Fluorescence Method for the Determination of Lead and Arsenic in Soils. *J Environ Anal Chem* 1:103. doi: 10.4172/2380-2391.1000103

Dixon, S.L., McLaine, P., Kawecki, C., Maxfield, R., Duran, S., Hynes, V, and Plant, T. (2006) The effectiveness of low-cost soil treatments to reduce soil and dust lead hazards: The

Boston lead safe yards low cost lead in soil treatment, demonstration and evaluation. *Environmental Research* 102 113–124.

Drake, P.L., Lawryk, N.J., Ashley, K., Sussell, A.L., Hazelwood, K.J. and Song, R. (2003) Evaluation of two portable lead-monitoring methods at mining sites. *Journal of Hazardous Materials* 102, 29–38.

Druzicka, J., and Craw, D. (2013) Evolving metalloid signatures in waters draining from a mined orogenic gold deposit, New Zealand. *Applied Geochemistry* 31, 251–264.

Durance, P, Jowitt, S. M., and K. Bush (2014) An assessment of portable X-ray fluorescence spectroscopy in mineral exploration, Kurnalpi Terrane, Eastern Goldfields Superterrane, Western Australia. Institute of Materials, Minerals and Mining and The AusIMM, *Applied Earth Science (Trans. Inst. Min. Metall. B)*, 123, 3, 150-163.

EPA Ireland (2009) *Historic Mine Sites - Inventory and Risk Classification Volume 1*. 170 p, accessed on 2014/02/18 from http://www.epa.ie/pubs/reports/land/mines/#.Vsd73PnhC_6 . ISBN: 1-84095-318-3.

Esbensen, K.H., and Wagner, C. (2014) Theory of sampling (TOS) versus measurement uncertainty (MU) – A call for integration. *Trends in Analytical Chemistry* 57, 93–106.

Fisher, L., Gazley, M.F., Baensch, A., Barnes, S.J., Cleverley, J. and Duclaux, G. (2014) Resolution of geochemical and lithostratigraphic complexity: a workflow for application of portable X-ray fluorescence to mineral exploration. *Geochemistry: Exploration, Environment, Analysis*, 14(2), 149–159.

Fortes, F.J. and Laserna, J.J. (2010) The development of fieldable laser-induced breakdown spectrometer: No limits on the horizon. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 65, 975–990.

Frahm, E. and Doonan, R.C.P. (2013) The technological versus methodological revolution of portable XRF in archaeology. *Journal of Archaeological Science* 40, 2, 1425-1434.

Gałaszka, A., Migaszewski Z.M., and Namieśnik, J. (2015) Moving your laboratories to the field – Advantages and limitations of the use of field portable instruments in environmental sample analysis. *Environmental Research* 140, 593–603.

Garrigues, S. and de la Guardia, M. (2013) Non-invasive analysis of solid samples. *Trends in Analytical Chemistry* 43, 161-173.

Gazley, M.F., Vry, J.K., du Plessis, E., and Handler, M.R. (2011) Application of portable X-ray fluorescence analyses to metabasalt stratigraphy, Plutonic Gold Mine, Western Australia. *Journal of Geochemical Exploration* 110, 74–80.

Gazley, M.F., and Fisher, L.A. (2014) A review of the reliability and validity of portable X-ray fluorescence spectrometry (pXRF) data. *Mineral Resource and Ore Reserve Estimation–The AusIMM Guide to Good Practice*, The Australasian Institute of Mining and Metallurgy Melbourne, 69-82.

Gazley, M.F., Tutt, C.M., Fisher, L.A., Latham, A.R., Duclaux, G., Taylor, M.D., and de Beer, S.J. (2014) Objective geological logging using portable XRF geochemical multi-element data

at Plutonic Gold Mine, Marymia Inlier, Western Australia. *Journal of Geochemical Exploration* 143, 74–83.

Ge, L., Lai, W., Lin, Y. and Zhou, S. (2005a) In situ applications of FPXRF techniques in mineral exploration. In IAEA (2005), p 61-120.

Ge, L., Lai, W. and Lin, Y. (2005b) Influence of and correction for moisture in rocks, soils and sediments on in situ XRF analysis. *X-Ray Spectrom.* 2005; 34: 28–34.

Glanzman, R.K. and Closs, L.G. (2007) Field Portable X-Ray Fluorescence Geochemical Analysis – Its Contribution to Onsite Real-time Project Evaluation. *Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration*, 291-301.

González-Corrochano, B., Esbrí, J.M., Alonso-Azcárate, J., Martínez-Coronado, A., Jurado V., and Higuera, P. (2014) Environmental geochemistry of a highly polluted area: The La Union Pb–Zn mine (Castilla-La Mancha region, Spain). *Journal of Geochemical Exploration* 144, 345–354.

Hall, G., Buchar, A. and 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.

<https://www.appliedgeochemists.org/index.php/publications/other-publications/2-uncategorised/106-portable-xrf-for-the-exploration-and-mining-industry>

Hall, G., Page, L. and Bonham-Carter, G. (2013) Quality Control Assessment of Portable XRF Analysers: Development of Standard Operating Procedures, Performance on Variable Media and Recommended Uses. Phase II. Canadian Mining Industry Research Organization (Camiro) Exploration Division, Project 10E01 Phase I Report.

<https://www.appliedgeochemists.org/index.php/publications/other-publications/2-uncategorised/106-portable-xrf-for-the-exploration-and-mining-industry>

Hall, G.E.M., Bonham-Carter, G.F. and Buchar, A. (2014) Evaluation of portable X-ray fluorescence (pXRF) in exploration and mining: Phase 1, control reference materials. *Geochemistry: Exploration, Environment, Analysis*, 14, 99–123.

Harmon, R.S., Russo, R.E., and Hark, R.R. (2013) Applications of laser-induced breakdown spectroscopy for geochemical and environmental analysis: A comprehensive review. *Spectrochimica Acta Part B* 87, 11–26.

Healy, M.G., Fenton, O., Forrestal, P.J., Danaher, M., Brennan, R.B. and Morrison, L. (2016) Metal concentrations in lime stabilised, thermally dried and anaerobically digested sewage sludges. *Waste Management* 48, 404–408.

Higuera, P., Oyarzun, R., Iraizoz, J.M., Lorenz, S., Esbrí, J.M., and 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.

Hoatson, D.M., Jaireth, S., and Lynton Jaques, A. (2006) Nickel sulfide deposits in Australia: Characteristics, resources, and potential. *Ore Geology Reviews*, 29, 3–4, 177-241.

Holding, M.C. (2014) Improved Field hXRF Analysis - The critical role of representative training set selection (geology), spectral acquisition (sensor sampling), proper calibration/validation (chemometrics). Bachelor project in Geology-Geoscience, Univ. Copenhagen, 110 p. Retrieved on 2017-02-21 from [https://dl.dropboxusercontent.com/u/13542010/Martin C Holding BSc report 060614 official version.pdf](https://dl.dropboxusercontent.com/u/13542010/Martin%20C%20Holding%20BSc%20report%20060614%20official%20version.pdf)

Horta, A., Malone, B., Stockmann, U., Minasny, B., Bishop, T.F.A., McBratney, A.B., Pallasser, R. and Pozza, L. (2015) Potential of integrated field spectroscopy and spatial analysis for enhanced assessment of soil contamination: A prospective review. *Geoderma* 241–242, 180–209.

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. Australasian Institute of Metallurgy. 377–385.

Hürkamp, K., Raab, T., and Völkel, J. (2009) Two and three-dimensional quantification of lead contamination in alluvial soils of a historic mining area using field portable X-ray fluorescence (pXRF) analysis. *Geomorphology*, 110, 28–36.

IAEA (2005) In Situ Applications of X Ray Fluorescence Techniques. IAEA-TECDOC-1456 (ISBN:92-0-107105-1), retrieved from <http://www-pub.iaea.org/books/IAEABooks/7212/In-Situ-Applications-of-X-Ray-Fluorescence-Techniques> on 15/09/2014.

ISO (2013) Soil quality -- Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument. ISO standard 13196:2013.

Jang, M. (2010) Application of portable X-ray fluorescence (pXRF) for heavy metal analysis of soils in crop fields near abandoned mine sites. *Environ Geochem Health*, 32:207–216.

Jinsung An, Ki-Hyun Kim, Hye-On Yoon, Jungju Seo (2012) Application of the wavelength dispersive X-ray fluorescence technique to determine soil fluorine with consideration of iron content in the matrix. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 69, 38-43

Jones, M.C., Williams-Thorpe, O., Potts, P.J., and Webb, P.C. (2005) Using Field-Portable XRF to Assess Geochemical Variations Within and Between Dolerite Outcrops of Preseli, South Wales. 29, 3, 251-269.

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

Kenna, T.C., Nitsche, F.O., Herron, M.M., Mailloux, B.J., Peteet, D., Sritrairat, S., Sands, E., and Baumgarten, J. (2011) Evaluation and calibration of a Field Portable X-Ray Fluorescence spectrometer for quantitative analysis of siliciclastic soils and sediments. *Journal of Analytical Atomic Spectrometry*, 26, 395–405.

Kido, Y., Koshikawa, T., Tada, R. (2006) Rapid and quantitative major element analysis method for wet fine-grained sediments using an XRF microscanner. *Marine Geology* 229, 209–225

Kilbride, C., Poole, J., and Hutchings, T.R. (2006) A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses. *Environmental Pollution* 143, 16-23

Kirtay, V.J., Kellum, J.H., and Apitz, S.E. (1998) Field-portable X-ray Fluorescence Spectrometry for metals in marine sediments: Results from multiple sites. *Water Science and Technology* 37, 6–7, 141–148.

Knésl, I., Jandová T., Rambousek P., and Breiter, K. (2015) Calibration of Portable XRF Spectrometer in Sn-W Ore-Bearing Granites: Application in the Cínovec Deposit (Erzgebirge/Krušné Hory Mts., Czech Republic)

Konstantinov, M.M. and Strujkov, S.F. (1995) Application of indicator halos (signs of ore remobilization) in exploration for blind gold and silver deposits. *Journal of Geochemical Exploration* 54, 1, 1–17.

Kovács, E., Dubbin, W.E., and Tama's, J. (2006) Influence of hydrology on heavy metal speciation and mobility in a Pb-Zn mine tailing. *Environmental Pollution* 141, 310-320.

Kuharic C.A., Cole W.H., Singh, A.K. and Gonzales D. (1993) An X-Ray Fluorescence Survey of Lead Contaminated Residential Soils in Leadville, Colorado: A Case Study, US-EPA report EPA/600/R-93/073.

Kuhn, K., Meima, J.A., Rammilmair, D. and Ohlendorf, C. (2016) Chemical mapping of mine waste drill cores with laser-induced breakdown spectroscopy (LIBS) and energy dispersive X-ray fluorescence (EDXRF) for mineral resource exploration. *Journal of Geochemical Exploration*, 161, 72-84.

Laperche, V. and Hammade, V (2002) Diagnostic rapide sur site - Utilisation de méthodes d'évaluation de la teneur en métaux de sols pollués par mesure de leur susceptibilité magnétique et par fluorescence X. Report CNRSSP/02/08.

Lawley, C.J.M., Dubé, B., Mercier-Langevin, P., Kjarsgaard, B., Knight, R., and Vaillancourt, D. (2015) Defining and mapping hydrothermal footprints at the BIF-hosted Meliadine gold district, Nunavut, Canada. *Journal of Geochemical Exploration*, 155, 33–55.

Le Vaillant, M., Barnes, S.J., Fisher, L., Fiorentini, M.L. and Caruso, S. (2014) Use and calibration of portable X-Ray fluorescence analysers: application to lithochemical exploration for komatiite-hosted nickel sulphide deposits. *Geochemistry: Exploration, Environment, Analysis* 14, 199-209.

Le Vaillant, M, Barnes, S.J., Fiorentini, M.L., Santaguida, F. and Törmänen, T. (2016) Effects of hydrous alteration on the distribution of base metals and platinum group elements within the Kevitsa magmatic nickel sulphide deposit. *Ore Geology Reviews* 72, 128–148.

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* 14, 257-264.

Lemiere, B (2015) Field Analytical Techniques for Geochemical Surveys. Keynote conference, 27th International Applied Geochemistry Symposium, Tucson, Az, USA

https://www.appliedgeochemists.org/images/stories/IAGS_2015/Abstracts/27th%20IAGS_Lemiere_Keynote_Field%20Analytical%20Techniques.pdf).

Lesnik B., Crumbling D. (2001) Guidelines for Preparing SAPs Using Systematic Planning and PBMS. Environmental Testing and Analysis, January/February 2001.

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 and Research, 28, 11, 996–1009

McDonald, B.J., Unsell, C.W., Elam, W.T., Hudson, K.R. and Adams, J.W. (1999) A cone penetrometer X-ray fluorescence tool for the analysis of subsurface heavy metal contamination. Nuclear Instruments and Methods in Physics Research A 422, 805-808.

Malissa, H. and Riepe, W. (2000) Statistical evaluation of uncertainty for rapid tests with discrete readings — examination of wastes and soils. In: De Bièvre, Paul, Günzler, Helmut (Eds.) (2003) Measurement Uncertainty in Chemical Analysis. Springer, Verlag, Heidelberg, 207-210.

Marsala, A.F., Loermans, T., Shen, S., Scheibe, C. and Zereik, R. (2012) Portable energy-dispersive X-ray fluorescence integrates mineralogy and chemostratigraphy into real-time formation evaluation. Petrophysics, 53, 102–109.

Markowicz, A. (2008) Quantification and Correction Procedures. In: Potts, P.J. and West, W. (eds) Portable X-ray fluorescence spectrometry – capabilities for in situ analysis. RSC Publishing, Cambridge, Chapter 2, 13–38.

Melquiades, F. L., and Appoloni, C. R. (2004) Application of XRF and field portable XRF for environmental analysis. Journal of Radioanalytical and Nuclear Chemistry, 262, 2, 533-541.

Melquiades, F.L., Parreira, P.S., Appoloni, C.R., Silva, W.D., and Lopes, F. (2011) Quantification of metals in river water using a portable EDXRF system. Applied Radiation and Isotopes 69, 327–333.

Meza-Figueroa, D., Maier, R.M., de la O-Villanueva, M., Gómez-Alvarez, A., Moreno-Zazueta, A., Rivera, J., Campillo, A., Grandlic, C.J., Anaya, R., and Palafox-Reyes, J. (2009) The impact of unconfined mine tailings in residential areas from a mining town in a semi-arid environment: Nacozari, Sonora, Mexico. Chemosphere 77, 140–147.

Newlander, K., Goodale, N., Jones, G.T. and Bailey, D.G. (2015) Empirical study of the effect of count time on the precision and accuracy of pXRF data. Journal of Archaeological Science: Reports 3, 534–548.

Parbhakar-Fox, A.K., Edraki, M., Hardie, K., Kadletz, O. and Hall, T. (2014) Identification of acid rock drainage sources through mesotextural classification at abandoned mines of Croydon, Australia: Implications for the rehabilitation of waste rock repositories. Journal of Geochemical Exploration 137, 11–28.

Parsons, C., Margui Grabulosa, E., Pilic, E., Floor, G.H., Roman-Ross, G, and Charlet, L. (2013) Quantification of trace arsenic in soils by field-portable X-ray fluorescence

spectrometry: Considerations for sample preparation and measurement conditions. *Journal of Hazardous Materials* 262, pp. 1213–1222.

Partington, G. (2010) Developing models using GIS to assess geological and economic risk: An example from VMS copper gold mineral exploration in Oman. *Ore Geology Reviews*, 38, 3, 197-207.

Paulette, L., Man, T., Weindorf, D.C., and Person, T. (2015) Rapid assessment of soil and contaminant variability via portable x-ray fluorescence spectroscopy: Copşa Mică, Romania.

Peinado F.M., Morales Ruano S., Bagur González M.G., Estepa Molina C. (2010) A rapid field procedure for screening trace elements in polluted soil using portable X-ray fluorescence (PXRF). *Geoderma* 159 76–82.

Piorek, S. (1994a) Modern, PC based, high resolution portable EDXRF analyzer offers laboratory performance for field, in-situ analysis of environmental contaminants. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 353, 1–3, 528-533

Piorek, S. (1994b) Principles and applications of man-portable X-ray fluorescence spectrometry. *TrAC Trends in Analytical Chemistry* 13, 7, 281-286.

Plourde, A.P., Knight, R.D., Kjarsgaard, B.A., Sharpe, D.R. & Lesemann, J.-E. (2013) Portable XRF spectrometry of surficial sediments, NTS 75-I, 75-J, 75-O, 75-P (Mary Frances Lake – Whitefish Lake – Thelon River area), Northwest Territories. Geological Survey of Canada, Open File 7408.

Potts, P.J., Webb, P.C., Williams-Thorpe, O. and Kilworth, R. (1995a) Analysis of Silicate Rocks Using Field-portable X-ray Fluorescence Instrumentation Incorporating a Mercury (II) Iodide Detector: A Preliminary Assessment of Analytical Performance. *Analyst*, 120, 1273-1278.

Potts, P.J., Bowles, J.F.W., Reed, S.J.B. and Cave, M.R. (1995b) *Microprobe Techniques in Earth Sciences*. Chapman and Hall, London

Potts, P.J., Williams-Thorpe, O. and Webb, P.C. (1997) The bulk analysis of silicate rocks by portable X-ray fluorescence: Effect of sample mineralogy in relation to the size of the excited volume. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 21, 29–41.

Potts, P.J., Ellis, A.T., Kregsamer, P., Marshall, J., Strel, C., Weste, M., and Wobrauschek, P. (2003) Atomic spectrometry update. X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.*, 18, 1297–1316.

Potts, P.J., Bernardini, F., Jones, M.C., Williams-Thorpe, O. and Webb, P.C. (2006) Effects of weathering on in situ portable x-ray fluorescence analyses of geological outcrops: dolerite and rhyolite outcrops from the Preseli Mountains, South Wales. *X-ray Spectrom.* 35, 8–18.

Potts, P.J. and West, M. (2008) *Portable X-ray Fluorescence Spectrometry: Capabilities for In Situ Analysis*. The Royal Society of Chemistry, Cambridge.

Przybyłowicz, W.J., and Pineda-Vargas C. (2015) 14th International Conference on Particle Induced X-ray Emission (“PIXE 2015”). Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 363, p.1-3.

Puckett, G. and Takasaki, K. (2004) Use of Field Portable X-Ray Fluorescence (FP-XRF) and the Triad Approach To Investigate the Extent of Lead Contamination at a Small Arms Training Range, Fort Lewis, WA. Triad Profile retrieved on 2014/12/02 at http://www.triadcentral.org/user/includes/dsp_profile.cfm?Project_ID=5

Quiniou, T. and Laperche, V. (2014) An assessment of field-portable X-ray fluorescence analysis for nickel and iron in laterite ore (New Caledonia). *Geochemistry: Exploration, Environment, Analysis Online First*, <http://dx.doi.org/10.1144/geochem2012-159>.

Raab G.A., Enwall R.E., Cole W.H., Kuharic C.A., Duggan J.S. (1991) Fast Analysis of Heavy Metals in Contaminated Soils Using Field-Portable X-Ray Fluorescence Technology and Geostatistics. In: Pawlowski L., Lacy W.J., Dlugosz J.J. (eds) *Chemistry for the Protection of the Environment*. Environmental Science Research, vol 42. Springer, Boston, MA.

Radu, T., and Diamond, D (2009) Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. *Journal of Hazardous Materials* 171 1168–1171.

Ramsey M.H. and Argyraki A. (1997) Estimation of measurement uncertainty from field sampling: implications for the classification of contaminated land. *Science of the Total Environment*, 198, 243–257.

Ramsey, M.H. (2004) Sampling the Environment: Twelve Key Questions That Need Answers. *Geostandards and Geoanalytical Research*, 28, 2, pp . 251-261.

Ramsey M.H. and Ellison S.L.R. (editors) (2007) Eurachem / EUROLAB / CITAC / Nordtest / AMC Guide: measurement uncertainty arising from sampling: a guide to methods and approaches. Retrieved from http://www.eurachem.org/guides/pdf/UfS_2007.pdf on 14/09/2014.

Ramsey, M.H., and Boon, K.A. (2010) New Approach to Geochemical Measurement: Estimation of Measurement Uncertainty from Sampling, rather than an Assumption of Representative Sampling. *Geostandards and Geoanalytical Research*, 34, 3, pp . 293–304.

Ramsey, M.H., and Boon, K.A. (2012) Can in situ geochemical measurements be more fit-for-purpose than those made ex situ? *Applied Geochemistry* 27, 969–976

Ramsey, M.H., Solomon-Wisdom, G. and Argyraki. A. (2013) Evaluation of In Situ Heterogeneity of Elements in Solids: Implications for Analytical Geochemistry. *Geostandards and Geoanalytical Research*, 37, 4, pp . 379–391.

Ran, J, Wang, D, Wang, C, Zhang, G and Yao L. (2014) Using portable X-ray fluorescence spectrometry and GIS to assess environmental risk and identify sources of trace metals in soils of peri-urban areas in the Yangtze Delta region, China. *Environ Sci Process Impacts* 16(8),1870-7.

Rathbun, J.E., Huellmantel, L.L., Tracy, M., Elliott Smith, V. and Ahlgren, K. (1996) Rapid Sediment Assessment: Indicator Analysis and Screening Analysis Approaches. *J. Great Lakes Res.* 22(3):523-533.

Reidinger, S., Ramsey, M.H., and Hartley, S.E. (2012) Rapid and accurate analyses of silicon and phosphorus in plants using a portable X-ray fluorescence spectrometer. *New Phytol.* 195(3):699-706.

Rhodes, J.R., and Rautala, P. (1983) Application of a microprocessor-based portable XRF analyzer in minerals analysis. *The International Journal of Applied Radiation and Isotopes*, 34, 1, 333-343.

Ridings, M., Shorter, A.J. and Bawden-Smith, J. (2000) Strategies for the investigation of Contaminated Sites using Field Portable X-Ray Fluorescence (FPXRF) Techniques. *Communications in Soil Science and Plant Analysis* 31, 11-14, 1785-1790

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

Ross, P. -S., Bourke, A. and Fresia, B. (2014a) Improving lithological discrimination in exploration drill-cores using portable X-ray fluorescence measurements: (1) testing three Olympus Innov-X analysers on unprepared cores. *Geochemistry: Exploration, Environment, Analysis*, first published February 4, 2014; doi 10.1144/geochem2012-163

Ross, P. -S., Bourke, A. and Fresia, B. (2014b) Improving lithological discrimination in exploration drill-cores using portable X-ray fluorescence measurements: (2) applications to the Zn-Cu Matagami mining camp, Canada. *Geochemistry: Exploration, Environment, Analysis*, first published February 4, 2014; doi 10.1144/geochem2012-164

Rouillon, M., and Taylor, M.P. (2016) Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research? *Environmental Pollution* 214, 255-264.

Rouillon, M., Taylor, M.P. and Dong, C. (2017) Reducing risk and increasing confidence of decision making at a lower cost: In-situ pXRF assessment of metal-contaminated sites. *Environmental Pollution*, In Press, Corrected Proof, <https://doi.org/10.1016/j.envpol.2017.06.020>

Rowe, H., Hughes, N., and Robinson, K. (2012) The quantification and application of handheld energy-dispersive x-ray fluorescence (ED-XRF) in mudrock chemostratigraphy and geochemistry. *Chemical Geology* 324–325, 122–131.

Sacristán, D., Viscarra Rossel, R.A., and Recatalá, L. (2016) Proximal sensing of Cu in soil and lettuce using portable X-ray fluorescence spectrometry. *Geoderma* 265, 6–11.

Sarala, P. (2009) New advances in geochemical exploration in glaciated terrain – examples from northern Finland. In: Lentz, D., Thorne, K.G. and Beal, K.-L. (eds.), *Proceedings of the 24th International Applied Geochemistry Symposium*. Fredericton, New Brunswick, Canada, June 1st-4th, 2009. Volume II. The Association of Applied Geochemistry, 565-567.

Sarala, P. & Mäkikyrö, M. (2012) Mobile XRF methods in mineral exploration in glaciated terrain – examples from northern Finland. In: 34th International Geology Congress, Brisbane, Australia, 5-10 Aug 2012. Optical disc (CD-ROM).

Sarala, P., Taivalkoski, A. & Valkama, J. (2015) Portable XRF – Advanced on-site analysis method in till geochemical exploration. Geological Survey of Finland, Special Paper 57, 63-86.

Sarala, P. & Houlahan, T. (2015) Portable XRF for mineral exploration geochemistry in till. Applied Earth Science (Trans. Inst. Min. Metall. B) 124:1, 53-54.

Sarala, P. (2016) Comparison of different portable XRF methods for determining till geochemistry. Geochemistry, Exploration, Environment, Analysis 16, 181-192.

Schuck, R., Gevalt, D., Mullen, J., Menzie, C., and Fogarty, K. (2003) Risk-based remediation of lead and chromium impacted sediments in Lake Waban, Wellesley, MA: a case study. 2nd International Symposium on Contaminated Sediments Case Histories. p. 286-291.

Sharma, A., Weindorf, D.C., Man, T., Aldabaa, A.A.A., and Chakraborty, S. (2014) Characterizing soils via portable X-ray fluorescence spectrometer: 3. Soil reaction (pH). Geoderma 232–234, 141–147.

Sharma, A., Weindorf, D.C., Wang, D., and Chakraborty, S. (2015) Characterizing soils via portable X-ray fluorescence spectrometer: 4. Cation exchange capacity (CEC). Geoderma 239–240, 130–134.

Shesky, S. (1995) Lead in Soil Analysis Using the NITON XL. International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals (A&WMA VIP-47), Las Vegas, Feb. 22-24, 1995, 1106-1117.

Shesky, S. (1997) Comparing Field Portable X-Ray Fluorescence (XRF) To Laboratory Analysis Of Heavy Metals In Soil. International Symposium of Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, Nevada, USA, January 29-31, 1997. Retrieved from <http://www.epa.gov/tio/download/char/dataquality/sshesky02.pdf>

Simandl, G.J., Fajber, Prussin, Paradis, S. and Grattan, K. (2012) Use of Portable XRF in evaluation of REE-bearing Phosphate Deposits, Geofile 2012-01.

Simandl, G.J., Fajber, R., and Paradis, S. (2014) Portable X-ray fluorescence in the assessment of rare earth element enriched sedimentary phosphate deposits. Geochemistry: Exploration, Environment, Analysis 14, 211-221.

Stallard, M.O, Apitz, S.E., and Dooley, C.A. (1995) X-ray fluorescence spectrometry for field analysis of metals in marine sediments. Marine Pollution Bulletin, 31 (4-12), p.297-305.

Steiner, A.E., Conrey, R.M., and Wolff J.A. (2017) pXRF calibrations for volcanic rocks and the application of infield analysis to the geosciences. Chemical Geology, in press, doi: [10.1016/j.chemgeo.2017.01.023](https://doi.org/10.1016/j.chemgeo.2017.01.023).

Stockmann, U., Cattle, S.R., Minasny, B. and McBratney, A.B. (2016) Utilizing portable X-ray fluorescence spectrometry for in-field investigation of pedogenesis. Catena, 139, 220–231.

Stoker, P. and Berry, M (2015) Australian Institute of Geoscientists Friday Seminar Series, Brisbane. https://www.aig.org.au/wp-content/uploads/2015/11/pXRF2015_02_Stoker.pdf

Tamás, J. and Kovács, E. (2005) Vegetation Pattern and Heavy Metal Accumulation at a Mine Tailing at Gyöngyösoroszi, Hungary. *Z. Naturforsch.* 60c, 362-367.

Takasaki, K, and Pitre, E. III (2006) Use of Field Portable X-ray Fluorescence (FPXRF) and the Triad Approach To Remediate Lead Contamination at a Small Arms Training Range Fort Lewis, WA. Triad Profile retrieved on 2014/12/02 at http://www.triadcentral.org/user/includes/dsp_profile.cfm?Project_ID=21

Thomsen, V. and Schatzlein, D. (2002) Advances in Field-Portable XRF. *Spectroscopy* 17(7), p. 14-18.

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

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

US-EPA (1998b) Environmental Technology Verification Report, Field Portable X-ray Fluorescence Analyzer, Niton XL Spectrum Analyze. Report EPA/600/R-97/150, downloaded from http://www.epa.gov/etv/pubs/01_vr_niton.pdf on 13/09/2014.

US-EPA (2000) - Guidance for the Data Quality Objectives Process. EPA QA/G-4 manual (report EPA/600/R-96/055).

US-EPA (2004) X-ray Fluorescence (XRF) Instruments Frequently Asked Questions (FAQ), downloaded from <http://www.epa.gov/superfund/lead/products/xrffaq.pdf> on 13/09/2014.

US-EPA (2007) Method 6200. Field portable X-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment. Accessed on 2014/12/02 from www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6200.pdf

US-EPA (2008) Demonstrations of Method Applicability under a Triad Approach for Site Assessment and Cleanup — Technology Bulletin, Office of Solid Waste, EPA 542-F-08-006.

Ussath, M., Grimmer, M., Hoth, N. and Alcalde, J. (2017) Hand-held X-ray fluorescence (hXRF) measurements as a useful tool in the environmental and mining sector – Comparative measurements and effects of water content. IMWA 2017 conference, Mine Water and Circular Economy, Lappeenranta, Finland. Wolkersdorfer C, Sartz L, Sillanpää M, Häkkinen A (Editors). Retrieved on 2018/01/05 from http://www.imwa.info/docs/imwa_2017/IMWA2017_Ussath_979.pdf

Valcarcel, M., Cardenas, S. and Gallego, M. (1999) Sample screening systems in analytical chemistry. *Trends in analytical chemistry*, 18, 11, 685-694.

Van Grieken, R., Janssens, K., Van Espen, P., Injuk, J., Padilla, V, Vittiglio, G., and Potgieter, J.H. (2005) Novel quantitative procedures for in situ X-ray fluorescence analysis. in IAEA (2005), p.45-60.

VanCott, R.J., McDonald, B.J., and Seelos, A.G. (1999) Standard soil sample preparation error and comparison of portable XRF to laboratory AA analytical results. *Nuclear Instruments and Methods in Physics Research A* 422, 801-804.

Wang, D., Chakraborty, S., Weindorf, D.C., Li, B., Sharma, A., Paul, S., and Nasim Ali, M. (2015) Synthesized use of VisNIR DRS and PXRF for soil characterization: Total carbon and total nitrogen. *Geoderma* 243–244, 157–167.

Weindorf, D.C., Zhu, Y., Chakraborty, S., Bakr, N., and Huang, B. (2012a) Use of portable X-ray fluorescence spectrometry for environmental quality assessment of peri-urban agriculture. *Environ Monit Assess* 184:217–227.

Weindorf, D.C., Zhu, Y., McDaniel, P., Valerio, M., Lynn, L., Michaelson, G., Clark, M. and Ping, C.L. (2012b) Characterizing soils via portable x-ray fluorescence spectrometer: 2. Spodic and Albic horizons. *Geoderma* 189–190, 268–277.

Weindorf, D.C., Zhu, Y., Haggard, B., Lofton, J., Chakraborty, S., Bakr, N., Zhang, W., Weindorf, W.C. and Legoria, M. (2012c) Enhanced Pedon Horizonation Using Portable X-ray Fluorescence Spectrometry. *Soil Sci. Soc. Am. J.* 76, 522–531.

Weindorf, D.C., Bakr, N. and Zhu, Y. (2012d) Advances in Portable X-ray Fluorescence (PXRF) for Environmental, Pedological, and Agronomic Applications. *X-Ray Spectrom.* 41, 304–307.

Weindorf, D.C., Paulette, L., and Manc, T. (2013) In-situ assessment of metal contamination via portable X-ray fluorescence spectroscopy: Zlatna, Romania. *Environmental Pollution* 182, 92-100.

West, M., Ellis, A.T., Potts, P.J., Strelci, C., Vanhoof, C., Wegrzynekf, D. and Wobrauschek P. (2013) 2013 Atomic spectrometry update - A review of advances in X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.*, 28, 1544-1590.

West, M., Ellis, A.T., Potts, P.J., Strelci, C., Vanhoof, C. and Wobrauschek P. (2015) 2015 Atomic spectrometry update - A review of advances in X-ray fluorescence spectrometry and their applications. *J. Anal. At. Spectrom.*, 30, 1839-1889.

Wiedenbeck, M (2013) Field-portable XRF: A geochemist's dream? *Elements*, February 2013. (retrieved on 02/02/2017 at http://elementsmagazine.org/archives/e9_1/e9_1_dep_theelementstoolkit.pdf)

Willis, J.P. (1988) XRFS and PIXE: Are they complementary or competitive techniques?: A critical comparison. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 35, 3–4, 378-387.

Wis, R.D., Ed. (1989) Particle induced X-ray emission and its analytical applications. *Nuclear Instrum. Methods Phys. Res.* B49.

Woo, R.Y. (1996) Development and characterization of a novel compact x-ray source. Master's thesis, Texas A&M University. Available electronically from: <http://hdl.handle.net/1969.1/ETD-TAMU-1996-THESIS-W662> .

Young, K.E., Evans, C.A., Hodges, K.V., Bleacher, J.E., and Graff, T.G. (2016) A review of the handheld X-ray fluorescence spectrometer as a tool for field geologic investigations on Earth and in planetary surface exploration. *Applied Geochemistry* 72, 77-87.

Yuan G-L., Sun, T-H., Han, P., Li, J., and Lang, X-X. (2014) Source identification and ecological risk assessment of heavy metals in topsoil using environmental geochemical mapping: Typical urban renewal area in Beijing, China. *Journal of Geochemical Exploration* 136, 40-47.

Yuan, Z., Cheng, Q., Xia, Q., Yao, L., Chen, Z., Zuo, R. and Xu, D. (2014) Spatial patterns of geochemical elements measured on rock surfaces by portable X-ray fluorescence: application to hand specimens and rock outcrops. *Geochemistry: Exploration, Environment, Analysis* 14, 265-276.

Zhang W., Lentz D.R. and Charnley, B.E. (2017) Petrogeochemical assessment of rock units and identification of alteration/mineralization indicators using portable X-ray fluorescence measurements: Applications to the Fire Tower Zone (W-Mo-Bi) and the North Zone (Sn-Zn-In), Mount Pleasant deposit, New Brunswick, Canada. *Journal of Geochemical Exploration* 177, 61–72.

Zhu, Y., Weindorf, D.C., and Zhang, W. (2011) Characterizing soils using a portable X-ray fluorescence spectrometer: 1. Soil texture. *Geoderma* 167–168, 167–177.

Zorba, V., Gonzalez, J.J., Chan, G.C.-Y., Mao, X. and Russo, R.E. (2016) Applications of Laser-Induced Breakdown Spectroscopy (LIBS). Reference Module in Chemistry, Molecular Sciences and Chemical Engineering.

Zurfluh, F.J., Hofmann, B.A., Gnos, E. and Eggenberger, U. (2011) Evaluation of the utility of handheld XRF in meteoritics. *X-Ray Spectrom.* 40, 449–463.



Fig. 1 An early radioactive source pXRF spectrometer

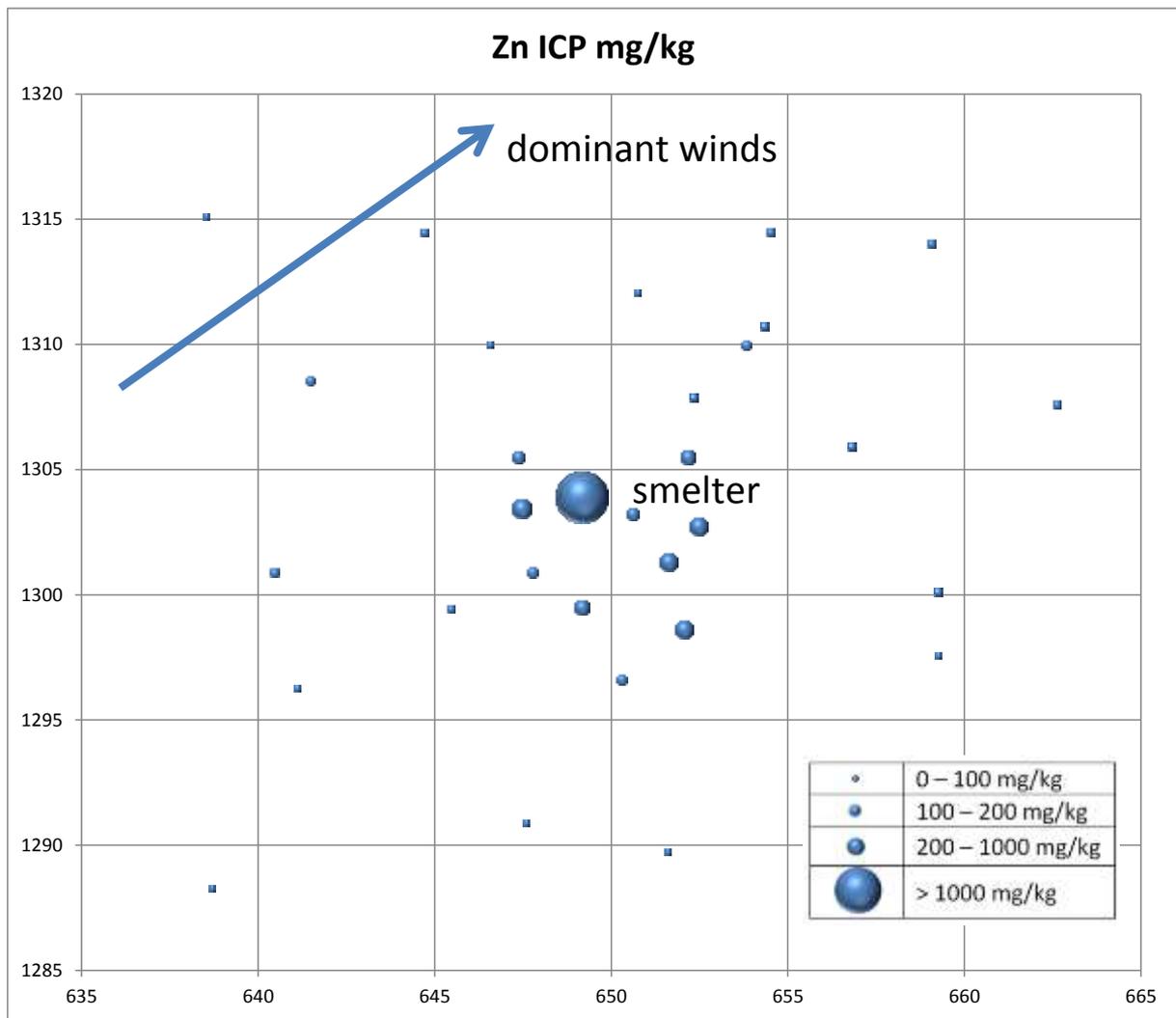


Fig. 3 Elements accessible to pXRF analysis



Fig. 4 Sample preparation equipment running on batteries

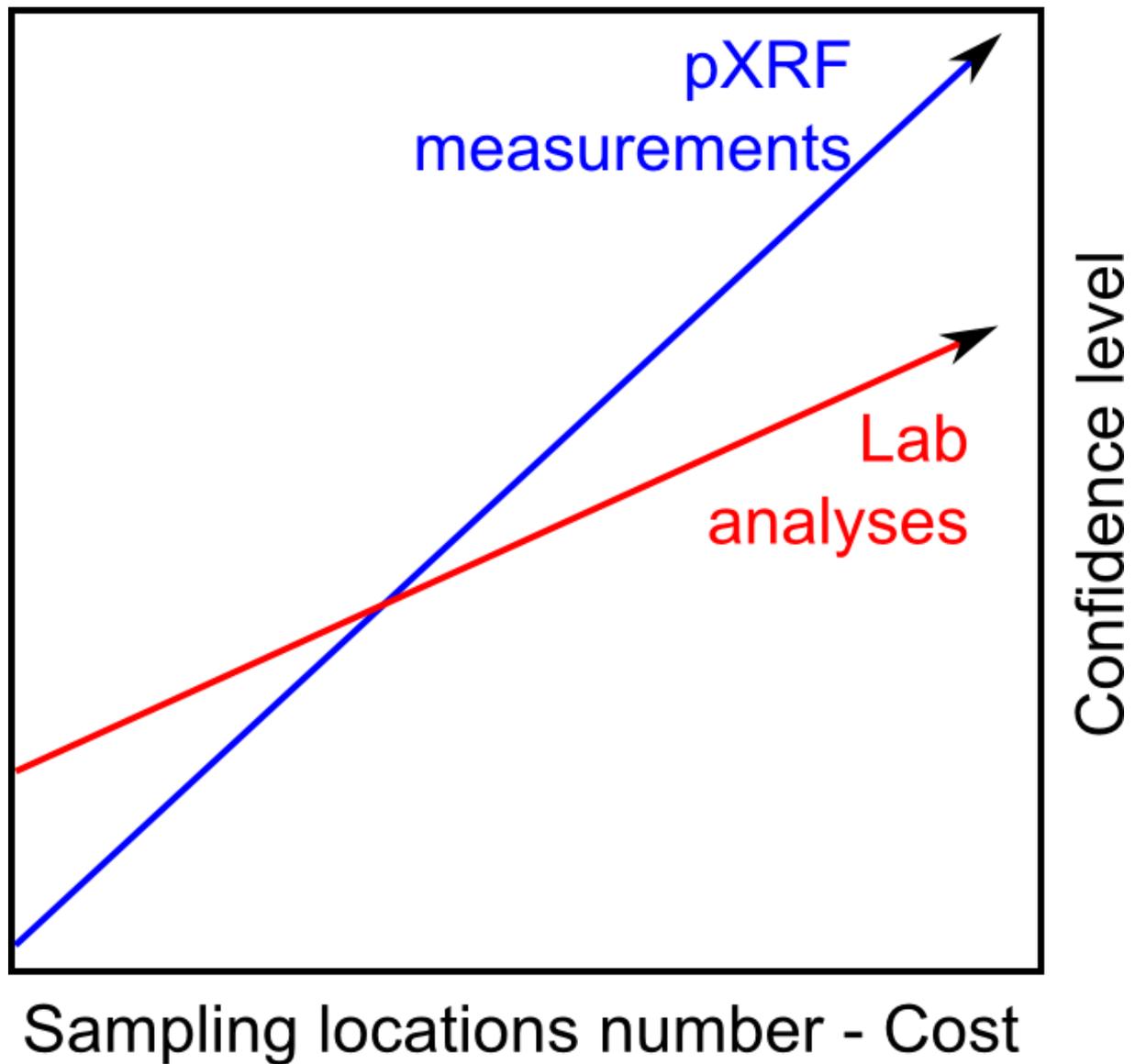


Fig. 5 Relationship between data confidence for a given cost (based on a lower cost by sampling point for pXRF, hence a higher data density for a given cost) (Created with Inkscape)

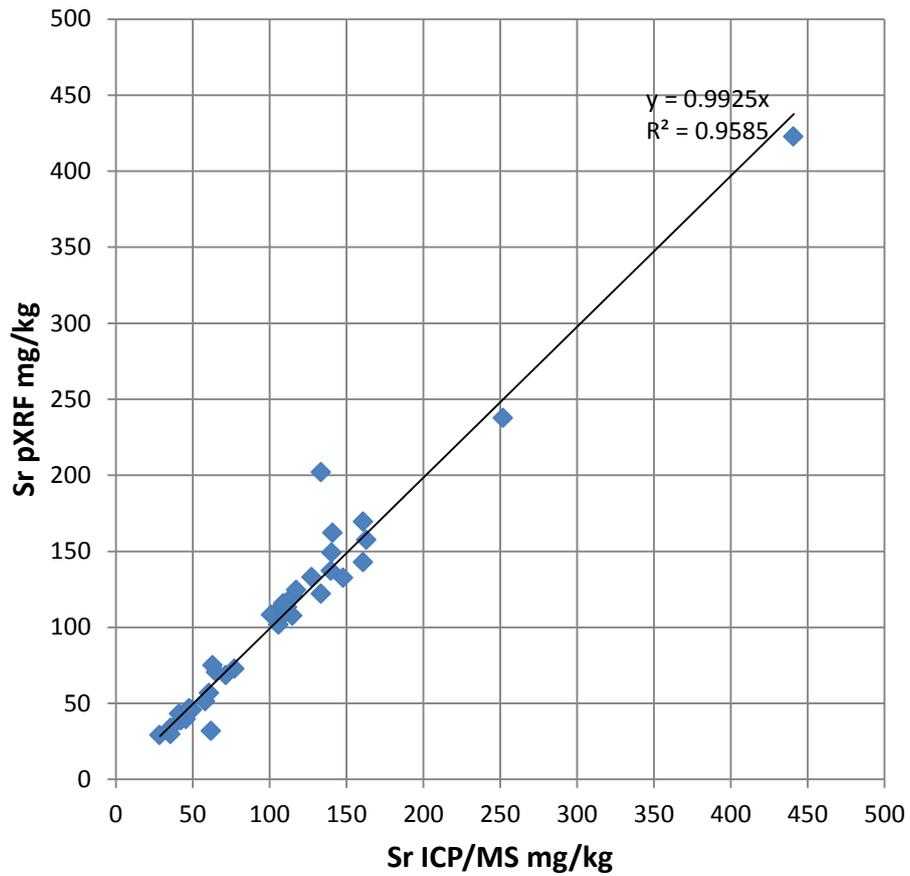


Fig. 6 Correlation between laboratory and pXRF data, on a favourable case (strontium in sandstone, confidential groundwater resource evaluation drill-holes) (Created with MS Excel)

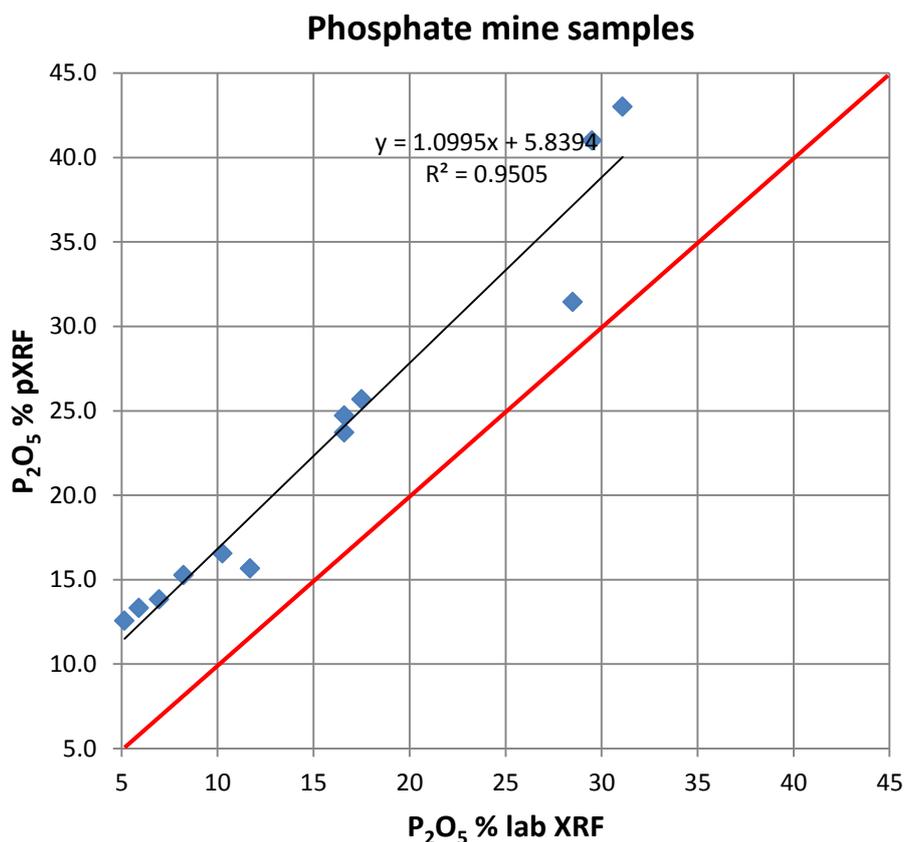


Fig. 7 Correlation between laboratory and pXRF data, on a less favourable but viable case (phosphorus in carbonate sedimentary rocks, confidential exploration data) (Created with MS Excel)

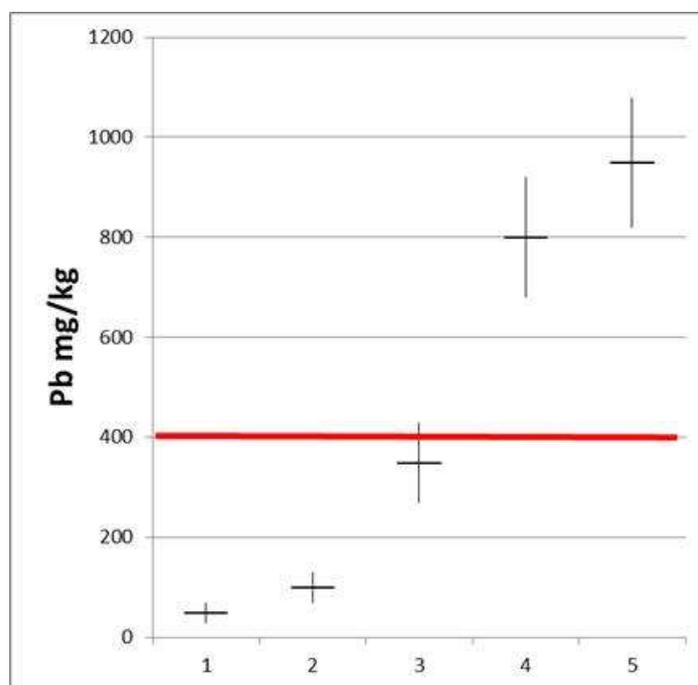


Fig. 8 Relationship between pXRF measurements with uncertainty bars and a compliance limit (lead in contaminated sediments, limit at 400 mg/kg). Points 1, 2, 4 and 5 are unambiguously classified. Point 3 needs laboratory confirmation (Random data with real pXRF bars. Created with MS Excel)

