

Sampling and Analysis for Public Reporting of Portable X-ray Fluorescence Data Under the 2012 Edition of the JORC Code

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ABSTRACT

There are two discrete aspects to collecting portable X-ray fluorescence (pXRF) data to obtain reliable results and to comply with reporting requirements under the 2012 edition of the JORC Code – sampling method and quality assurance. A robust sampling program is required to obtain representative material for analysis. The appropriate method should be established for a particular project using a small orientation study. A variety of approaches to sampling soils, drill cuttings, rock faces and diamond drill core are discussed. These include using multiple spot analyses, scanning using a single operating beam and the collection of cutting saw pulps. The operator must also be aware of the attenuating effects of analysing through sample bags of different material types for various elements as well as the limitations of current pXRF instruments in reporting reliable data for certain elements. The analysis of the samples must also be accompanied by a quality assurance program in order to generate data that are ‘fit for purpose’. This includes recording X-ray tube resolution on a routine basis, using matrix-appropriate standards for which total elemental concentrations are available, using silica blanks, capturing sufficient duplicate analyses to constrain data precision and obtaining check assays to calibrate pXRF data against laboratory data. Examples of quality control approaches and data are presented. Table 1 of the 2012 JORC Code also recommends that information on instrument make and model, reading times and calibration be provided in any reporting of pXRF data. To this should be added information on operating mode and temperature, software version and moisture content of the samples. 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.

INTRODUCTION

Portable X-ray fluorescence (pXRF) technology is now widely used within the resource industry as it has many clear advantages. Little or no training is required to use the equipment, although appropriate training for operators is certainly recommended. Results are obtained almost immediately and allow rapid decision-making in the field. Making these decisions in a timely manner leads to more efficient and cost-effective exploration and mining practices. XRF is but one of many portable analytical technologies now available to the exploration and mine geologist in order to fast-track the decision-making process in the field. The potential cost savings in screening samples for laboratory analysis are also particularly attractive in times of austerity, and the equipment has the potential to pay for itself very quickly in some situations. In the majority of cases, the pXRF data are used for internal purposes only, and the rigour with which the data are obtained depends on the purpose for which they are to be used (ie the data are ‘fit for purpose’). However,

once data on commodity elements becomes available for an early stage exploration project, the question then arises as to whether they are financially material and should be released publicly. This paper attempts to summarise some of the issues that should be considered before embarking on a pXRF program where the data are likely to become public. It is neither exhaustive nor prescriptive in its approach and further develops some of the recommendations made by Arne *et al* (2014). Each application demands its own careful consideration, but there are common elements that should be included in Table 1 for reporting purposes under the 2012 edition of the JORC Code (hereafter referred to as ‘JORC Table 1’). Many of the recommendations proposed here are equally relevant to reporting codes in other jurisdictions.

While many of the limitations and recommendations on the public reporting of pXRF data presented here have always been applicable, the introduction of the 2012 edition of the JORC Code places a greater emphasis on ensuring that sampling

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has been representative and that the quality of the data is adequate. Explicit statements addressing these issues are now required in JORC Table 1. This responsibility lies with the Competent Person, as it always has, but the care and expertise needed to ensure the quality of pXRF data extends into the realm previously occupied by the independent laboratory. The Competent Person need only maintain a monitoring role on data quality through the use of an independent quality assurance (QA) program, where analyses are undertaken externally by a commercial laboratory. However, where pXRF data are to be reported publicly, the onus of producing representative pXRF data of good quality falls squarely on the shoulders of the Competent Person reporting the data. This extension of the definition of competence into the analytical realm has no doubt caught some geologists unprepared, as evidenced by the occasional public dissemination of pXRF results that are at the very least erroneous and at the worst intentionally misleading.

A review on the state of pXRF technology has recently been undertaken by the Canadian Mining Industry Research Organization Exploration Division (Hall, Buchar and Bonham-Carter, 2011; Hall, Page and Bonham-Carter, 2012). These studies highlighted some of the limitations of the technology available at the time and reviewed the analyses of a variety of certified reference materials (CRMs) using a number of commonly available instruments. A summary of Phase 1 of this work has recently been provided by Hall, Bonham-Carter and Buchar (2014) in a thematic series of papers on pXRF within the journal *Geochemistry: Exploration, Environment, Analysis*. In addition to assessing the performance of five different analytical devices, Hall, Bonham-Carter and Buchar (2014) also provide a brief history of the technique and a series of references for various pXRF applications. The reader is referred to this thematic series of papers in general, and the review by Hall, Bonham-Carter and Buchar (2014) in particular, for further background. Most of the papers included in this thematic set discuss applications of direct interest to mineral exploration and are referred to in the following discussion.

There are fewer publications available on the use of pXRF in mining applications. Houlahan, Ramsay and Povey (2003) emphasised the importance of sample preparation in order to obtain precise and accurate data for grade control purposes. Many of the issues associated with obtaining representative analyses that apply to the grade control setting also have relevance to lithochemical studies on diamond drill core and are discussed by Ross, Bourke and Fresia (2014). Quiniou and Laperche (2014) discuss the application of pXRF in determining Ni and Fe contents of lateritic material from New Caledonia, with particular regard to sample preparation and machine calibration. A common thread through all of these publications is the need for considered sampling and preparation, as well as calibration and a robust QA program where accurate and precise results are desired.

INSTRUMENT SELECTION, ORIENTATION AND CALIBRATION

There are a number of factors to consider before proceeding with a pXRF program for a particular project. There must be a good understanding of the elements to be detected and the levels at which they are likely to be present. An awareness of potential interference problems is also required. The interference between the As, K α and K β lines with the L α and L β lines for Pb is a common problem for some applications. The software on an individual pXRF unit may be designed to handle these common overlaps by using an alternative

emission line, but how effective the treatment is may vary from manufacturer to manufacturer and may also be dictated by the software version. It is also important to be aware that elements with atomic numbers less than 12 are not currently detectable using pXRF.

The anode used in the X-ray tube is also significant because not all elements are available for all X-ray tubes, meaning that the program needs must be discussed with the equipment manufacturers at the pre-purchase stage. For example, a Rh or Ag anode would be required to detect Mg for at least one line of current instrumentation.

It is also important to note in which operating mode the elemental data being reported were obtained. Most devices use either a 'soil' or 'mining' mode, and the two approaches use differing internal calibration methods – Compton normalisation versus fundamental parameters. Although Compton normalisation is most often used to obtain trace element data at the ppm level, a fundamental parameter calibration may be more appropriate for some minor elements and it may be necessary to collect data using both calibrations (Ross, Bourke and Fresia, 2014).

Other variables that may potentially be important include operating temperature (internal and external) and pressure (as a function of altitude) and whether there have been software and/or hardware upgrades of the pXRF device. Instrumental details should be summarised in JORC Table 1.

Knowledge of pathfinder element associations in the case of gold is required because the lower limits of detection (LODs) for gold in most of the currently available instrumentation precludes its reliable use at the levels common in most exploration and mining applications. LODs quoted by equipment manufacturers may be based on a pure silica matrix, in which case they are 'best case' LODs, or on a generic 'soil' matrix, in which case they should be considered indicative only. The LODs for some of the important pathfinder elements for Au – such as Te, Sb and Hg – may be too high to allow these elements to be used effectively for exploration purposes by comparison to inductively coupled plasma mass spectrometry. A review of existing laboratory data may be required to determine what, if any, pathfinder elements associated with Au may be suitable for detection by pXRF. It is also important to recognise that LODs are calculated for individual readings as the matrix corrections can vary slightly from sample to sample, so a collective LOD must be calculated through post-processing of the data if desired for a particular project. An example of LODs calculated for a soil program in ioGAS™ using the three SD errors from a Delta Premium equipped with a Ta anode are given in Table 1. If a value of 2 ppm Sb were to be considered anomalous for a particular Au project, then the use of pXRF data for sample screening in this instance is likely to produce numerous false negatives. Note

TABLE 1

Summary of calculated limits of detection (LOD) values for selected elements from a portable X-ray fluorescence soil program.

Element	LOD value (ppm)	% above LOD
Cu	2.5	99.6
Mo	0.6	54
Sb	6.0	30
Pb	1.2	100
Zn	1.4	100
W	2.0	4

also that the data from the pXRF device needed to make these calculations are not always available using default factory settings, meaning that some adjustment of the device settings may be required in order to obtain the required information.

One factor that must be established before analyses by pXRF can proceed is the optimal count time to be used for data collection. Most devices will rotate through a series of beam filters to generate optimised data for different element suites, so it is the actual time spent counting on the beam relevant for the element of interest that is important. The active count time is generally perceived to affect the precision of the reading, with precision increasing as count time increases. However, the accuracy of the data is also impacted, with short count times less than 30 seconds producing inaccurate (as well as imprecise) results for some elements (Hall, Bonham-Carter and Buchar, 2014; Yuan *et al*, 2014). Optimisation of the active count time for the relevant beams is needed to achieve the best quality data for the shortest possible counting time. This count time needs to be stated in JORC Table 1.

If accurate data are needed for grade control or public reporting purposes, it will be necessary to calibrate the pXRF instrument. Factory calibrations are rarely accurate for a range of sample matrices and are a poor indicator of performance when evaluating an instrument for purchase. Rather, it should be assumed that a project-specific calibration will be required and either matrix-matched CRMs acquired for this purpose (Figure 1) or samples from the project area having a range of concentrations should be analysed at a laboratory. It needs to be kept in mind that the CRMs must be certified for total analyses or a laboratory method selected that will yield a total analysis for the elements of interest in order to be directly comparable to pXRF data.

Note that not all pXRF instruments are created equal and there will be significant differences in performance and calibration between the same model from a single manufacturer (Brand and Brand, 2014; Ross, Bourke and Fresia, 2014). Separate calibrations are therefore required for each unit used on a project. Operating and calibration details should be included in JORC Table 1, and the operating conditions during calibrations should be the same as those used during analysis of unknown samples.

SAMPLING METHOD

As with all geochemical sampling, care must be exercised in order to obtain representative data. The situation is

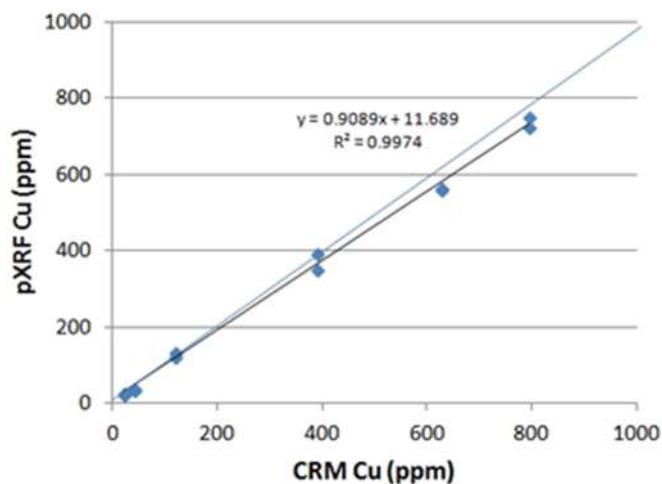


FIG 1 – Example of a calibration for Cu derived from commercially available certified reference materials (CRMs).

exacerbated in the case of pXRF data, because the detector area is in the order of 1 cm² for most instruments and the depth of penetration even less. It is therefore very easy, either intentionally or unintentionally, to bias a reading towards heterogeneities in the sample (eg blebby sulfide).

There are a number of approaches to obtaining representative data for pXRF. In the case of soil samples, this might involve the use of sieves to reduce the grain size of the sample. For analysis of drill chips, the fines collected in the bottom of a sample bag potentially provide more homogeneity than the coarser material.

The purpose for which the data are being collected defines how rigorous the sample preparation should be. Where the identification of relative enrichments of certain elements is the aim of the pXRF program, analysis of unsieved but dry soil samples directly through a sample bag can produce percentile element plots that are remarkably similar to laboratory data for some elements (eg Arne, Mackie and Jones, 2014) (see Figure 2). A similar conclusion was reached by Plourde *et al* (2013), although in that study, samples were sieved to less than 2 mm and were not analysed through sample bags.

What does appear to be important is to ensure a consistent dryness of the sample during analysis as high water content can dilute elemental concentrations. An extreme example of this is presented by Lemiere *et al* (2014) for lake sediments, where dehydrating the samples to a consistent water content of between 50 and 30 per cent was sufficient to allow correlation of the pXRF data with laboratory results. Where moisture is incorporated into the instrument calibration, this should be made clear in JORC Table 1.

The greatest challenge for sampling is presented by pXRF analysis of rock, either in trenches, across rock faces or in drill core. In such instances, some degree of sample preparation may be required that involves pulverisation of sample material on-site or the use of diamond saw cuttings. Somarin *et al* (2012) generated pXRF results from pulp samples filleted from diamond drill core using a modified angle grinder that have a very high coefficient of determination for Cu, Pb, Zn, Ag and Fe when compared to laboratory results for the traditional half core assays. An alternative to using a file saw would be to capture diamond saw cuttings if the core is to be halved for laboratory analysis. These cuttings can be dried and mounted in a plastic cup for analysis and should provide a fairly representative sample of the drill core, but the process is time consuming.

Direct scanning of the sawn surface by dragging the pXRF detector over the core can also produce acceptable results, but these were inferior to those obtained using the filleting approach in the study by Somarin *et al* (2012). A key requirement of scanning drill core with a pXRF is to ensure that only one beam is active during the analysis or else data will be collected on different beams over different portions of the core. There are also challenges associated with maintaining a constant rate of scanning and close contact with the surface of the core, as well as complications associated with dealing with broken core and discontinuous sample intervals. Simandl *et al* (2014) also assessed the use of core scanning and found it superior to averaging multiple spot analyses in a study of Nb mineralisation in a carbonatite. The coefficient of variation (CV, also known as the relative standard deviation) was used to assess the homogeneity of particular elements within the carbonatite based on a set number of spot analyses. This approach can be turned to advantage by selecting a maximum allowable CV for the sampling strategy and then determining the number of spot analyses required to achieve it. It may not be possible to obtain data of sufficient quality through the use

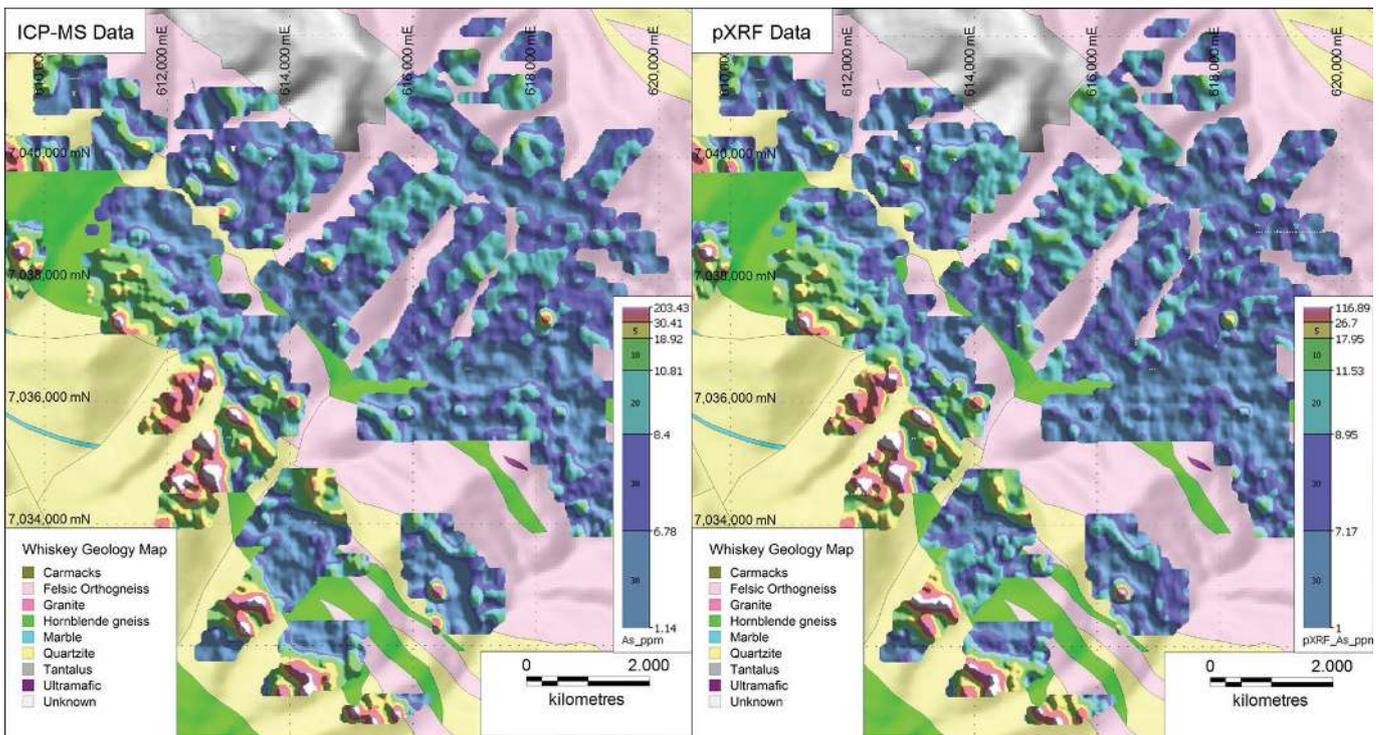


FIG 2 – Comparison of As data obtained using portable X-ray fluorescence (pXRF) from unsieved soil samples and inductively coupled plasma mass spectrometry (ICP-MS) data from the sieved (-100 mm) fraction following an aqua regia digestion (modified from Arne *et al*, 2014).

of multiple spot analyses, in which case another sampling strategy must be adopted. The sampling strategy used should be clearly described in JORC Table 1 and may require an orientation study to optimise.

Analysis of material directly through sample bags can successfully be used to generate relative concentration maps for some elements (Arne, Mackie and Jones, 2014), although it is advisable to be aware of how much attenuation of secondary X-rays may result from this approach (Figure 3). There is an increasing amount of attenuation of secondary X-rays with the lighter elements, to the extent that the film used to make sample mounts can cause significant attenuation of X-rays for light elements such as P (Hall, Bonham-Carter and Buchar, 2014). This attenuation must be corrected for in the calibration process if the objective of the pXRF survey is to report absolute values, but care must be taken not to change sample bag type during a survey as they have variable attenuation and ‘contamination’ properties (Morris, 2009). Whether samples were analysed through sample bags and what the bag material consisted of should be listed in JORC Table 1.

QUALITY ASSURANCE

A QA program is required if data are to be publicly reported, regardless of whether absolute or relative data are obtained, and should be briefly described in JORC Table 1. It is also good analytical practice if the data are for internal use only. An example of a workflow incorporating a QA program with analysis of quality control samples is provided by Fisher *et al* (2014).

Data from either a CRM or a project-specific reference material are needed to demonstrate consistency in the data produced by each individual pXRF device used on the project, as well as for indicating the presence of an analytical bias where accurate data are required (Figure 4). The performances of individual pXRF devices are known to drift over time (Brand and Brand, 2014), and it is important to track this variation so that it may be corrected in the final data set

through levelling of the data. Device performance can also be tracked by recording the beam resolution each time the equipment is turned on to begin analytical work. Significant variations in beam resolution may be a precursor to a failing X-ray tube.

Although cross contamination at the analytical stage is unlikely to be a major problem with pXRF equipment, it is advisable to periodically run a silica blank on at least a daily basis to demonstrate consistency of the device and cleanliness of the analytical window. An upper limit set at three times the calculated LOD is used in the example illustrated in Figure 5. The raw Cu data have been plotted in this diagram, but as all are below the LOD of 2.5 ppm (Table 1), they could have also been plotted as 1.25 ppm Cu or less than 2.5 ppm, following the conventions used with laboratory data.

Data precision is evaluated and monitored using duplicate analyses, including field duplicate and analytical duplicate pairs. The preferred metric for assessing data precision is the CV, as previously discussed, described by Stanley and Lawrie (2007) for duplicate analyses and recommended by Abzalov (2008). Whether an acceptable level of precision is obtained should also be included in JORC Table 1. Examples of what might be considered to be industry best practice and what is acceptable for a variety of common deposit types and mineralisation styles is given in Table 3 of Abzalov (2008). Ultimately, it is a corporate decision as to what level of precision is considered to be ‘fit for purpose’ for a particular project, but the level is quantifiable and should be reported.

It is advisable to send a certain proportion of samples to an independent laboratory for analysis where pXRF forms the main analytical method for a particular program. It is critical to ensure that the laboratory method chosen provides a total value for the elements of interest for direct comparison with the pXRF data where absolute values are important. Relative patterns in elemental concentrations from pXRF can still be compared with laboratory data where partial analytical methods are used to analyse the samples. The main benefit

Standard Oreas 42p

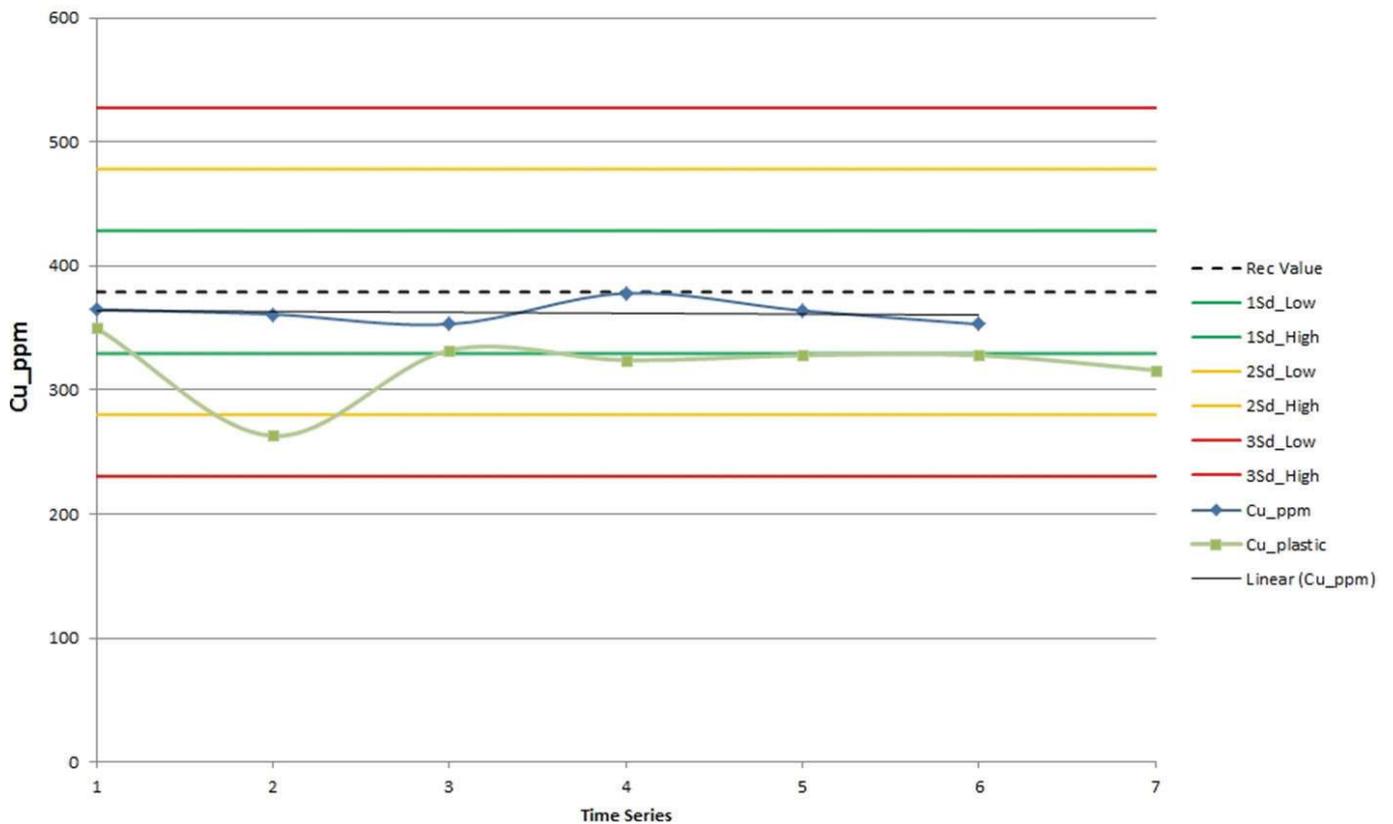


FIG 3 – Attenuation of secondary X-rays from Cu analysed through plastic sample bag material and a Mylar film compared to samples analysed through a thin Mylar film only.

CRM Oreas 42P

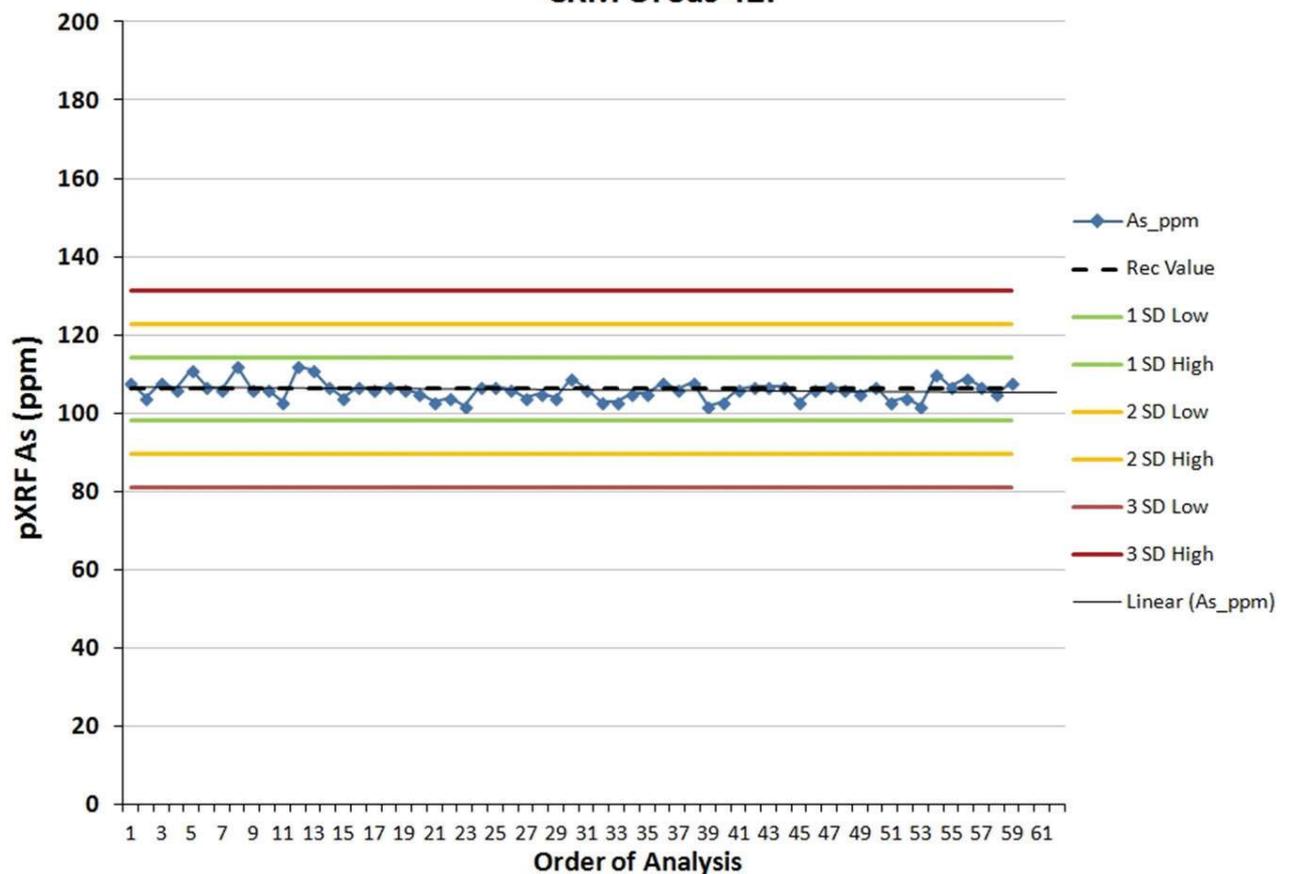


FIG 4 – Example of quality assurance data from a certified reference material (CRM) generated on a portable X-ray fluorescence (pXRF) over a period of several months.

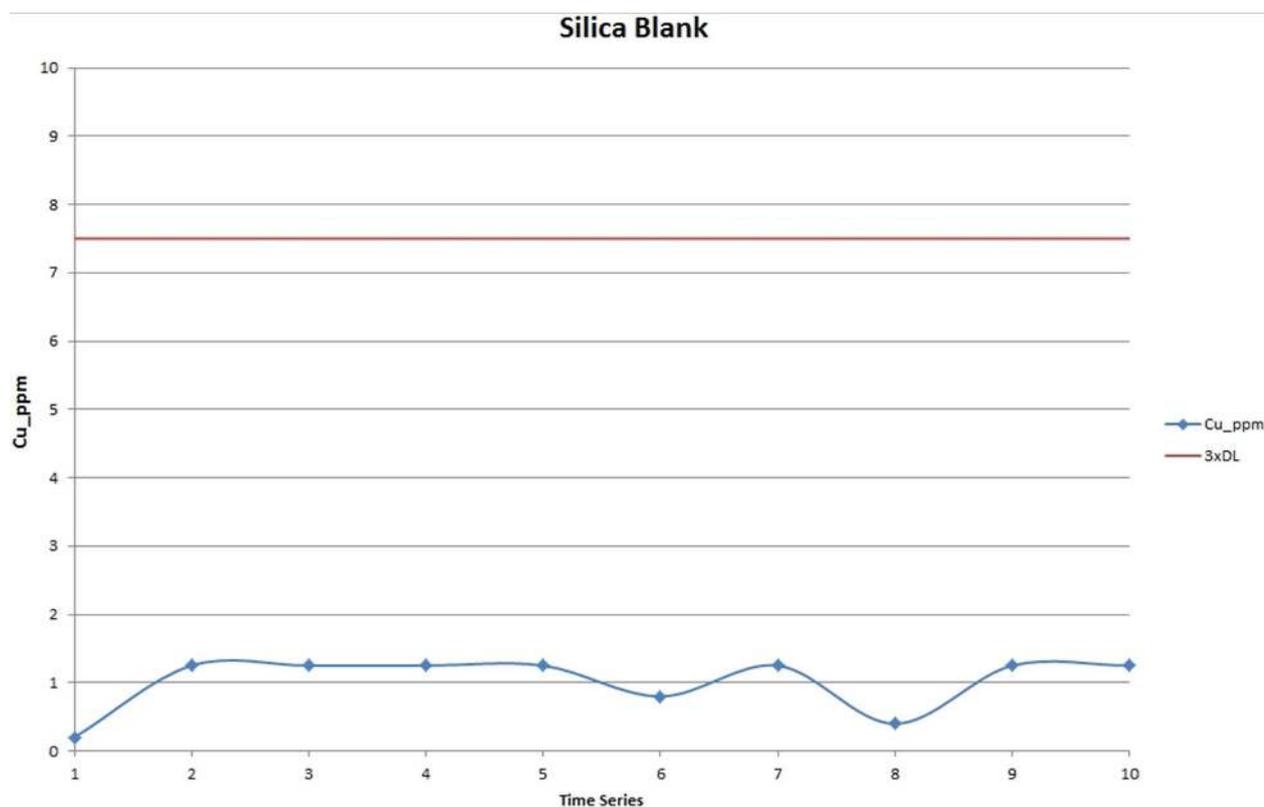


FIG 5 – Repeat analyses of a silica blank for Cu.

of sending check samples to a laboratory for analysis is that it reintroduces the element of independence that is generally lost when the company controlling the project is also generating pXRF data for public dissemination. Notwithstanding the previous discussion, the lack of independence is likely to be the biggest hurdle to the general acceptance of pXRF data by public stock exchanges and will likely limit its use to the reporting of exploration results in most circumstances.

CONCLUSIONS

The use of pXRF technology is now widespread in the resource industry and is only one of many portable analytical instruments likely to become commonplace for field analyses in the coming years. Generation of geochemical data in the field transgresses into the realm that was previously the exclusive domain of the independent laboratory. The Competent Person responsible for pXRF data generation and eventual public dissemination of that data must ensure that it conforms to the requirements of the 2012 edition of the JORC Code. Consideration should be given to whether pXRF data are appropriate to a particular project, and what the interferences and required LODs are likely to be. pXRF data may be used to identify relative concentrations of particular elements, in which case the data are semi-quantitative in nature, or to determine absolute values for grade control or public reporting purposes. In the latter case, calibration of individual instruments is required. A QA program should accompany data collection in both instances to ensure consistency in the data, quantify any analytical bias present and validate a certain proportion of the data independently with laboratory analyses. Information on the instrumentation used, whether and how it was calibrated, how material has been sampled, what QA program was in place during the generation of the data and whether the quality of the data is acceptable must all be summarised in JORC Table 1.

ACKNOWLEDGEMENTS

The authors would like to thank colleagues both past and present for discussions and insights on the use of pXRF in the resource industry. In particular we would like to thank Steve Sugden, Nikita Sergeev, Andrew Margereson, Rob Mackie, Jim Royall, Adrian Fleming, Gwendy Hall, Keith Grattan, Scott Curry, Todd Houlahan, Aaron Baensch and Andrew Summers. Those of us who can see the benefits of applying pXRF in the resource industry are cognisant of the fact that inappropriate usage by a small number of companies damages public confidence in the technology. We hope that this short paper will contribute in some small way to improved practices and reporting of pXRF results in the future. The opinions expressed here are solely those of the authors and do not necessarily reflect the views of JORC or The AusIMM.

REFERENCES

- Abzalov, M, 2008. Quality control of assay data: a review of procedures for measuring and monitoring precision and accuracy, *Exploration and Mining Geology*, 17:131-144.
- Arne, D C, Jeffress, G, Sergeev, N and Margereson, A, 2014. What reporting portable XRF data to the 2012 JORC Code guidelines means, *AIG News*, 115:1-6.
- 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 [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2013-233>>
- Brand, N W and Brand, C J, 2014. Performance comparison of portable XRF instruments [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-172>>

- Fisher, L, Gazley, M F, Baensch, A, Barnes, S J, Cleverly, J and Duclaux, G, 2014.** Resolution of geochemical and lithostratigraphic complexity: a workflow for application of portable X-ray fluorescence to mineral exploration [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-158>>
- 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 [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-241>>
- Hall, G E M, Buchar, A and Bonham-Carter, G F, 2011.** Quality control assessment of portable XRF analysers: development of standard operating procedures, performance on variable media and recommended uses, Canadian Mining Industry Research Organization Exploration Division, Project 10E01, Phase 1.
- Hall, G E M, Page, L and Bonham-Carter, G F, 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 Exploration Division, Project 10E01, Phase 2.
- Houlahan, T, Ramsay, S and Povey, D, 2003.** Use of field portable X-ray fluorescence spectrum for grade control – a presentation of case studies, in *Proceedings 5th International Mining Conference*, pp 377–385 (The Australasian Institute of Mining and Metallurgy: Melbourne).
- Lemiere, B, Laperche, V, Haouche, L and Auger, P, 2014.** Portable XRF and wet materials: application to dredged contaminated sediments from waterways [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-179>>
- Morris, P A, 2009.** Field-portable X-ray fluorescence analysis and its application in GSWA, Geological Survey of Western Australia, Record 2009/7.
- Plourde, A P, Knight, R D, Kjarsgaard, B A, Sharpe, D R and 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.
- Quiniou, T and Laperche, V, 2014.** An assessment of field-portable X-ray fluorescence analysis for nickel and iron in laterite ore (New Caledonia) [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-159>>
- Ross, P-S, Bourke, A and Fresia, B, 2014.** Improving lithological discrimination in exploration drill-cores using portable X-ray fluorescence measurements: (1) testing three Olympus Innov-X analysers on unprepared cores [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-163>>
- Simandl, G J, Paradis, S, Stone, R S, Fajber, R, Kressall, R D, Grattan, K, Crozier, J and Simandl, L J, 2014.** Applicability of handheld X-ray fluorescence spectrometry in the exploration and development of carbonatite-related niobium deposits: a case study of the Aley Carbonatite, British Columbia, Canada [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-177>>
- Somarín, A K, Lopez, R, Herrera, M and Guiza-Gonzalez, S, 2012.** Application of the Thermo Scientific portable XRF analyzer in geochemical exploration: an example from the Francisco I. Madero Zn-Pb-Cu-(Ag) deposit, Zacatecas, Mexico, in *Proceedings Geological Association of Canada/Mineralogical Association of Canada Joint Annual Meeting*.
- Stanley, C R and Lawie, D, 2007.** Average relative error in geochemical determinations: clarification, calculations and a plea for consistency, *Exploration and Mining Geology*, 16:267–275.
- 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 [online], *Geochemistry: Exploration, Environment, Analysis*. Available from: <<http://dx.doi.org/10.1144/geochem2012-173>>

