Archeological Artifacts Analysis, Field Analysis of Majors and Traces With One Instrument

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Introduction

Portable X-Fluorescence Analysis (PXRF) is a non-destructive technique for measuring elemental composition. It has been used with great success in archaeological provenance studies of obsidian artifacts, (Phillips and Speakman 2009). PXRF is also more and more used as geochemical Exploration and Mapping tool (Cameron & Cordier, 2009). Advances in detector design enable spectral resolution of 145 eV at high count rates of 150 000 cps with the XFlash® SDD technology. PXRF's Light element (Mg, Al, Si) detection is hampered by their high absorption in air. The TRACER series have very close optical coupling and the air in the snout can be removed by using the patented NASA portable vacuum system.

Category	Laboratory XRF	Portable XRF
Sample Preparation	Significant sample preparation is required. Usually fused beads or pressed pellets for powders.	Minimal sample preparation required, depending on accuracy needs. Usually powders in sample cups (see EPA 6200).
Location	Large XRF equipment must be used in a controlled and equipped laboratory.	Instruments are used in the field, often with batteries. Samples can be measured in-situ, without the need to transport offsite.
Limit of Detection	The laboratory environment allows greater excitation power, use of high vacuum, multiple monochromators, and other improvements that often allow very low detection limits.	Detection limits are generally higher than for laboratory equipment, especially for lower-Z elements, which have short penetration depths in the samples and in air.
Accuracy	Careful sample preparation allows high accuracy because of homogeneity. This accuracy can be particularly important at low levels.	The amount of sample preparation is related to the accuracy obtained. Varying levels of accuracy are acceptable for different applications, ranging from semiquantitative to quantitative.
Turnaround time	Turnaround time is often long because of transportation to the laboratory and time needed for adequate sample preparation	Turnaround time is very short because of minimal sample preparation and no need for sample transport.
Training	Generally, well-trained, skilled laboratory technicians are required to run the equipment and prepare samples.	Normally less training and laboratory skill is needed to use the portable equipment and to prepare the samples.
Cost	The initial cost of the equipment is higher than for a portable device. Also, the sample transfer and preparation, and the maintenance of a laboratory can add to the cost of measurement.	The initial cost of the equipment is lower, as are sample preparation and transportation costs. When accuracy is important, often the lowest overall cost is for a laboratory analyzer to be used in conjunction with the portable device. The majority of samples are measured in the field by the portable analyzer and the laboratory analyzer is used to verify the accuracy of the portable device, requiring only a fraction of the samples to be sent and prepared for laboratory analysis.

Fig. 1 Comparison PXRF with Laboratory XRF

PXRF Method

XRF is a non destructive method and ideally suited for the analysis of artifacts: Challenges in the analysis are the absorption of the light elements as well as the sample homogeneity. Additionally, for quantification, it is required to correct for inter compositional matrix effects, which either requires approximation or the measurement of the "full" major composition:

Element	Air (cm)	Silica (microns)
O	0.147	2.1
Na	0.595	3.1
Mg	0.986	5.1
Si	2.46	12.4
Ti	40.1	47.3
Fe	115.6	128
As	517	544
Zr	1601	1765
Sn	4552	6577

Average density of air = 0.0012g/cm3, Density of SiO2 = 2.6g/cm3-Depths are for 90% absorption of the Ka1 line for each element *Shaded cells are elements that have a path length too short to be measured using portable XRF.

Fig. 2 Penetration Depths of Various Elements in SiO2 and Air

Figure 2 shows the challenges based on the physics of the emission lines for the analysis of majors. Using a spot size of 6 mm, it integrates over a comparatively large sample volume 24-40mm3 minimizes the potential effects of sample heterogeneity, mainly for the "trace" elements important for sourcing: Rb, Sr, Y, Nb, Zr. Using a specially developed "green" excitation filter the background can be reduced and signals optimized to achieve single digit detection limits for these elements. For the major element detection it is imperative to use the technique within the limitations of to the analyzed sample layer.

Fig. 3 Portable, field and stationary use of the TRACER PXRF systems

Advanced PXRF can be used in three ways:

- With PC control but mobile in the field
- in point and shoot mode as data logger (including GPS integration)
- in bench top mode, identical to a laboratory instrument

Data acquisition/evaluation:

- Trace element profile only: using customized conditions (current, excitation, filter) for desired trace element group. Evaluation via ratios or dedicated user empircal calibration using absorption correction on unit or offline
- Major element profiling using portable vacuum system or unit with large XFlash® detector. Evaluation with the built in GEO-QUANT™ or a user made fundamental parameter calibration in point and shoot mode or offline mode.
- Major and Traces with full FP matrix correction or FP user calibration in a dual mode, user selectable switching of the conditions. Evaluation the built in GEO-QUANT™ or a user made fundamental parameter calibration in point and shoot mode or offline mode
- Direct spectral investigation and area of interest comparisons. Evaluation either directly or using multivariate statistical methods (PCA, PCR) on either whole spectra or extracted net intensities from deconvoluted spectra.
- Fast qualitative ID in the field to determine rock , mineralization type

Results

Sourcing elements Rb,Sr, Y, Zr and Nb are well resolved and show excellent Signal to Noise enabling low detection limits and high selectivity (Fig. 4).

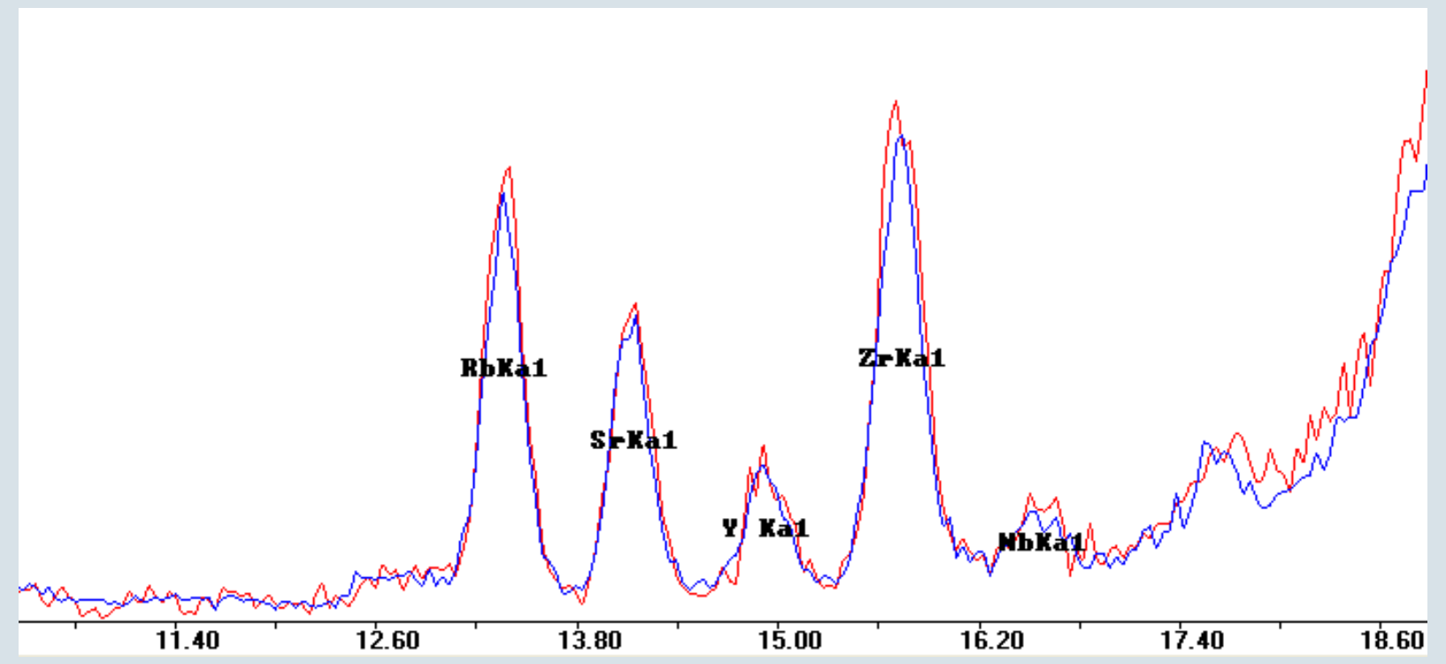

Fig. 4 Comparison PXRF with Laboratory XRF

Data collected in the field is processed either with the PDA and reports concentrations or the data is processed using spectral deconvolution and then ratioed. The ratios can then be related to known rock sources by using statistical methods.

Major element analysis accuracy using a factory calibration will be affected greatly by the mineralogical composition as well as the surface state of the sample (e.g. weathering, roughness). Fig. 2 shows the implication grain size has on the analysis. If a sample can be "powered" and analyzed in benchtop mode as either powder or pellet this will increase the accuracy. Using "intype" standards previously run and then analyzed with a reference method it is possible to measure directly the rock with better accuracy.

Summary

The new TRACER IV series was developed to enable cross over analysis capabilities for both field based and stationary analysis. The SPECTRA^{edx} software package allows the user to modify factory calibrations or create own FP or empirical calibrations. Data can be logged in the field and then reprocessed in camp allowing the use of spectral de convolution methods for complex mineralizations such as high REE containing intrusions of high current economic interest. The use of the portable vacuum pump and/or use of a large Xflash® SDD detector greatly enhance the light element capabilities.

Conclusions

- Single digit ppm detection for Rb, Sr, Y, Zr, Nb for sourcing
- Major and Trace element analysis in one go
- SPECTRAedx software allows for FP and empirical user calibrations identical to conventional benchtop EDXRF.

Technology

For research use only. Not for use in diagnostic procedures.