

Handheld XRF

Portable XRF Analysis in Archaeology – Examining Ceramics with the TRACER

Application Note XRF 473

Introduction

Ceramics are the most common artifacts found in archaeological excavations and represent a valuable cultural heritage spanning over thousands of years. These findings range from everyday cooking utensils to means of transportation and storage to writing substrates. As such, ceramics document human travel and cultural exchange like no other material.

One of the most important areas of research in ceramics is provenance studies, which usually require invasive and time-consuming analytical methods. These approaches are limited not only in terms of the number of samples that can be analyzed, but also in terms of the selection of samples, as unique cultural heritage objects often cannot be damaged or destroyed. However, XRF-based techniques may offer a solution for non-destructive elemental analysis.

Instrumentation

The TRACER 5g is a handheld XRF spectrometer for non-destructive elemental analysis. Unlike typical handheld XRF analyzers, it provides cleaner spectra and is ideal for spectral analysis and the quantification of elements in the sample.

The TRACER 5g offers the ease of use for which handheld XRF instruments are known, while also giving the user an unparalleled degree of flexibility in fine-tuning all relevant measurement parameters.

Complete user control of measurement conditions

- Excitation current and voltage
- Automated and manual filters
- Collimator size
- Atmosphere (vacuum, helium or air)

Fast and accurate spot positioning

- Internal camera with displayed target area and crosshairs for precise positioning
- Long-distance projection for demanding object positioning

Features

- 50 kV / 4 W Rh excitation source
- High-resolution SDD detector with graphene window for optimal light element sensitivity
- SharpBeam™ geometry for minimized focal distance
- Exchangeable 3 mm and 8 mm collimators
- Automated 5-position filter wheel and additional manual filter slot
- Integrated operating and analysis software with remote control capability
- ARTAX advanced spectrum analysis software
- USB, Wi-Fi, and Bluetooth connectivity
- Secure, encrypted data storage
- Low weight (1.9 kg / 4.1 lbs incl. battery)

Semi-quantitative pXRF analysis

Provenance analysis has typically been performed using invasive analytical methods, which are time-consuming and limit the number and selections of samples that can be analyzed, as unique cultural heritage objects are often too valuable to be subjected to invasive analysis. Non-destructive XRF-based elemental analysis offers a solution to this dilemma.

Figure 1 illustrates how regions of interest assist in semi-quantitative analyses by grouping samples based on their element intensities. To further improve the determination of net peak intensities, the deconvolution function of the ARTAX spectrum analysis software can be used to account for overlaps between element lines.

Quantitative pXRF analysis

The short X-ray path and large solid angle of the TRACER, combined with the ability to increase sensitivity by using different filters, result in industry-leading limits of detection (LODs, see Figure 2).

The TRACER 5g uses empirical factory calibrations to quantify element (or oxide) weight fractions from spectra. The calibrations are matrix-specific. Optimal homogeneity of bulk samples is achieved by grinding and preparing packed powder cups. Certified powder standards in nano or micro sizes (Figure 3) are available for fine-tuning a factory calibration through type standardization (Figure 4).

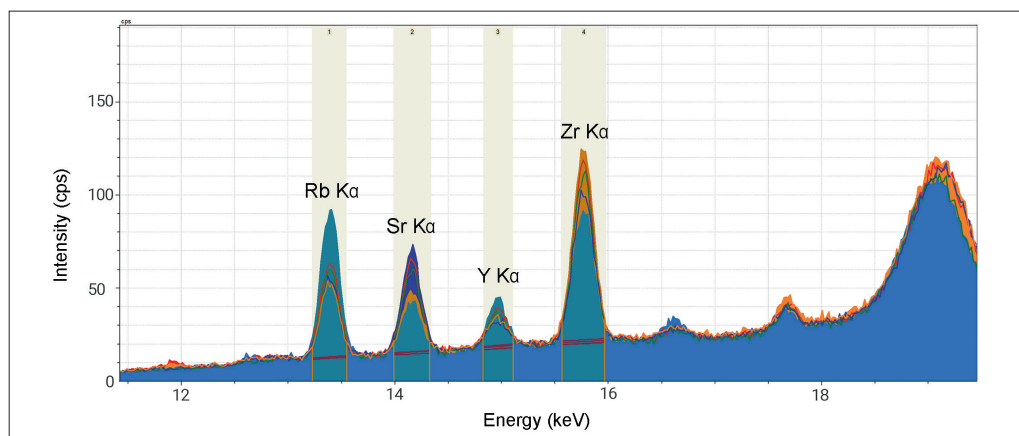


Figure 1

Spectra of four ceramic samples measured at 50 keV and Ti/Al filter, with elemental regions of interest (ROI). The net peak intensities of individual elements can be used to cluster samples from different regions.

Mg	Al	Si	P	S	K	Ca	Ti	V	Cr	Mn	Fe	Co
0.3	896	394	137	18.7	65.9	55.3	44.3	5.9	12.2	19.8	18.6	0.1
Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Ba
3.9	2.2	3.2	3.2	0.3	1.5	1.7	1.4	2.0	2.1	11.6	1.0	1.4

Figure 2

TRACER 5g LODs of all the elements commonly present in ceramics given in wt.% for Mg and ppm for all other elements.

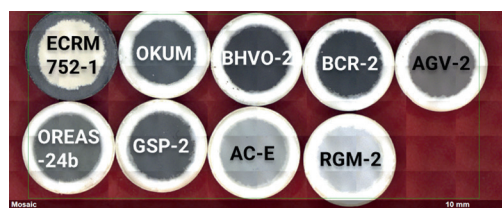
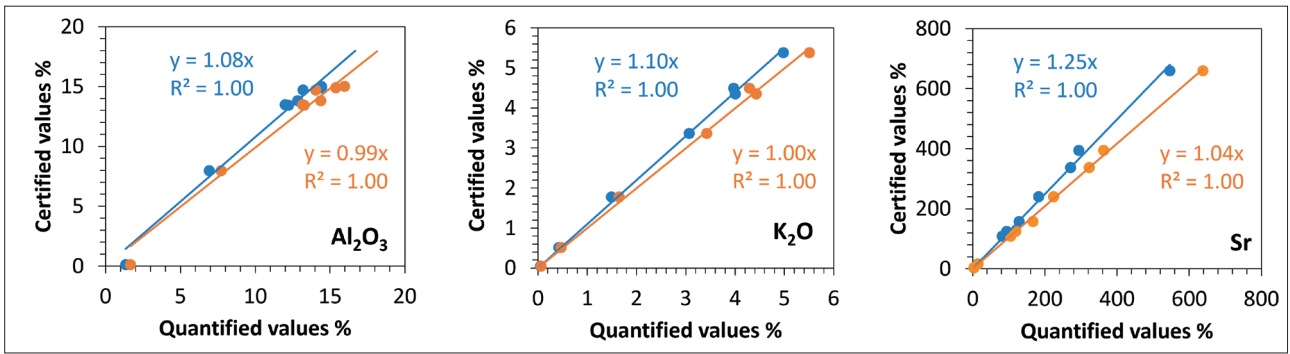


Figure 3

Nanopowder standards (μ Standards) for advanced type standardization (left). The XRF element distribution maps show their excellent homogeneity (right).



In-situ pXRF analysis

Unlike homogeneous powder samples, untreated ceramics usually have a heterogeneous composition. In addition, their surface may be irregular or enriched or depleted with certain elements due to alteration (e.g., patina) or even decorative materials such as paint. For such samples, quantitative analysis cannot provide reliable results for non-destructive ceramic provenance research.

In contrast, semi-quantitative or qualitative approaches are more promising. It is important to select the right elements for interpreta-

tion for these analyses. Elements with low energy lines such as Mg, Al, or Si are not ideal because their representativeness for the overall composition of the sample is limited due to their low information depth and, in addition, due to surface weathering or ornamentation (Figure 5).

In general, elements with energy lines above 8 keV provide the best results for bulk analysis of ceramics, as their high penetration depth compared to elements with energy lines below 8 keV provides information from deeper layers of the sample (above 200 μm to more than 0.5 mm).

Figure 4

Selected TRACER 5g calibration curves before (blue) and after (orange) type standardization using certified nanopowder standards. After type standardization, a significant improvement in accuracy is achieved.

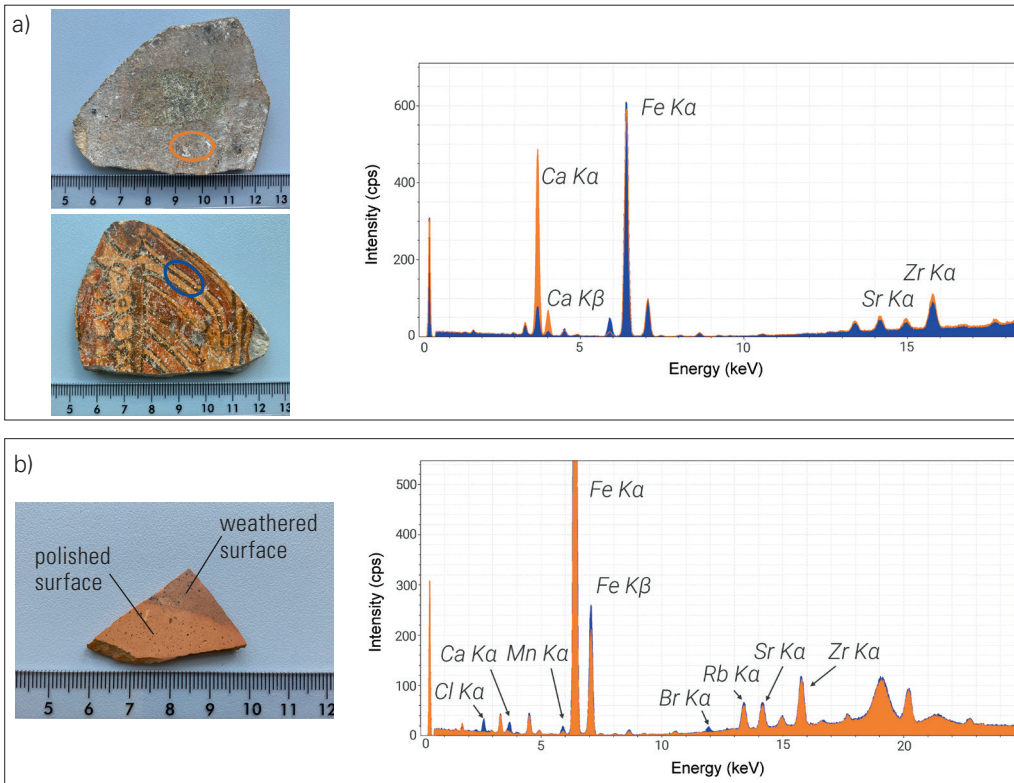


Figure 5

Differences in composition due to paint layers and surface weathering.

a) Painted piece of ceramic, measured on the painted side (blue spectrum) and the unpainted side (orange spectrum) at 50 keV with Ti/Al filter. The painted side shows a lower Ca signal than the unpainted side, because Ca is attenuated by the paint layer.

b) Piece of ceramic, measured on the weathered surface (blue spectrum) and on the polished surface (orange spectrum). The weathered surface shows larger Cl, Ca, and Mn peaks, which probably originate from exposure to sea water.

Provenance studies based on element ratios

The elemental composition of a ceramic piece is like a fingerprint that scientists can use to trace the origin of the raw material. Trace element analysis is particularly helpful when either XRF intensities or element concentrations are used, as the elemental XRF net peak intensities (counts per second) are directly related to the concentrations.

The elemental XRF intensities can be extracted from the raw spectra using the deconvolution method in the Bruker ARTAX software and displayed as ratios in a scatter chart (Figure 6).

Since the net intensity of an element corresponds to its concentration, a scatter chart with concentrations derived from one of the Bruker matrix-matched factory calibrations will show the same trend. It should be noted that this rule of thumb only applies to oxide samples. Metals have more inter-element effects and should only be analyzed with a metal calibration.

Conclusion

The TRACER 5g handheld XRF spectrometer enables the non-destructive elemental analysis of ceramics on site and accurate quantification of bulk samples.

The quantification accuracy can be further improved by type standardization with certified reference materials. For non-destructive provenance analysis in the field, a semi-quantitative approach based on the comparison of trace element ratios with high Z values is the ideal solution.

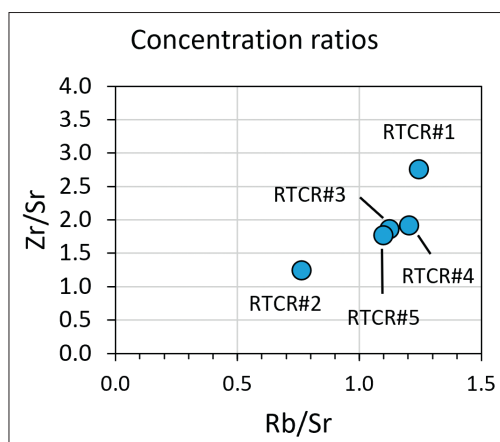
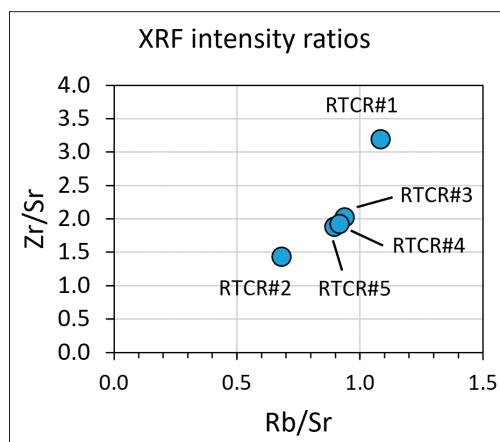


Figure 6

Provenance studies of five ceramic samples based on element ratios. The same clustering of samples can be observed in the ratios based on XRF intensity and concentration.

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