Lab Report XRF 437

ARTAX / TRACER III-V
Provenance Studies on Ceramics with Portable (Micro-)XRF Spectrometers

Objective and approach

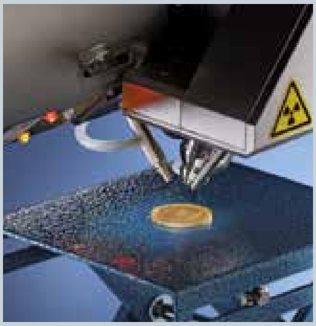
Characterization and regional allocation of ceramics require fast and non-destructive analytical methods. This report describes the application of XRF spectrometry and explains a fast and reliable method for provenance studies.

The analytical approach focused on the determination of the elements Rb, Sr, Y, Zr, and Nb (K lines) by means of (Micro-) XRF spectrometry. **Why these elements?** The palette of inorganic pigments contains a large number of different compounds with exact stoichiometric compositions. Each pigment is characterized by its color and elemental composition. Some pigments have natural as well as synthetic origins. In addition to the analysis of the main components, the exact determination of the trace elements and contamination indicates whether a pigment is artificial or of natural origin.

- The strong geochemical heterogeneity of these elements ensures a large variation in the composition of the ceramics depending on their origin.
- XRF shows high detection sensitivity for sought after elements with detection limits in the low ppm range.
- XRF delivers a large information depth up to 1 mm to obtain representative results with few measurements.
- Quantification is simple and reliable due to negligible matrix effects.

Instruments

ARTAX



TRACER III-V

Measurement conditions

- Micro-XRF spectrometer ARTAX 800:
  X-ray tube, Rh target, collimator with 3 mm spot size, 50 kV, 700 µA, 5 points, 60 s each.
- Handheld XRF spectrometer TRACER III-V:
  X-ray tube, Rh target, 5 mm spot size, 40 kV, 10 µA, Ti-Al filter, 300 s.

Intensity comparison

A polychromatic sherd from Petén (Guatemala) was used for comparison of the handheld XRF and the Micro-XRF spectrometer (figure 1). The quantitative data in table 1 documents a 4 times higher intensity for the ARTAX measurement (measuring time = 360 s). Nevertheless, all elements of interest could be detected by both technologies. In a second experiment the Petén ceramic was measured on the colored side and the backside. Figure 2 shows severe surface effects in the low energy range of the spectrum. For heavy elements from Rb to Nb the composition remains almost unchanged, which confirms the element selection for provenance studies.

Elemental composition

Figures 3 and 4 show the element spectra of the samples from Yucatán and Anáhuac Valley. Zr is the dominant element in the analyzed Yucatán ceramics. The average composition spectrum is compared to the spectra of three samples that show small compositional variations (A, C, B).

Anáhuac ceramics were very homogenous. With the exception of sample AT-LEG (sample I on the right), the variations of all other ceramics are almost negligible.

Ceramic objects

Selection of ceramics analyzed with (µ)XRF

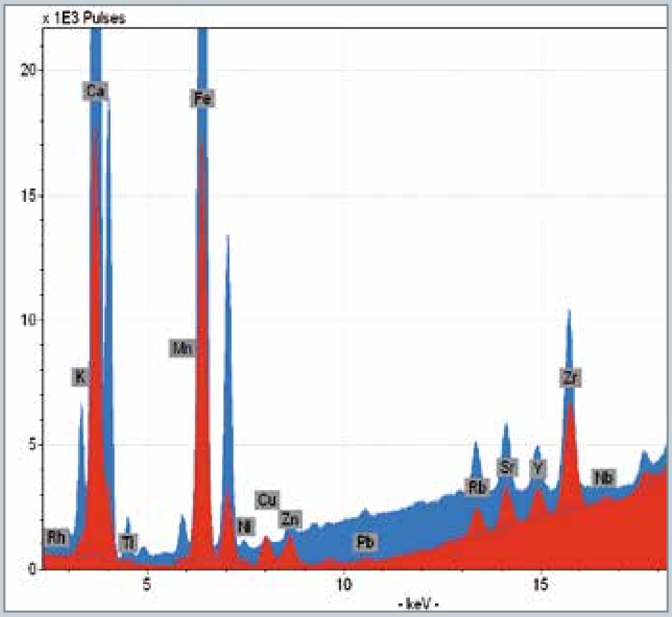


Figure 1: Comparison of a TRACER (red) and an ARTAX (blue) spectrum of the polychromatic sherd from Petén

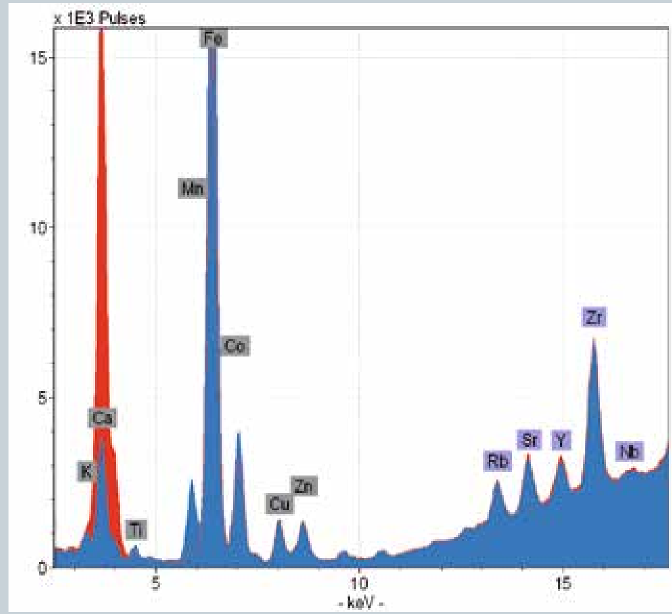


Figure 2: ARTAX spectra of the polychromatic sherd, colored side (red) and the backside (blue)

Table 1: Quantitative results (net area counts) of the Petén sherd measurement

Element	Rb	Sr	Y	Zr	Nb
ARTAX counts	35,717	45,729	22,806	121,635	5,028
TRACER counts	9,005	11,530	7,323	34,081	1,847

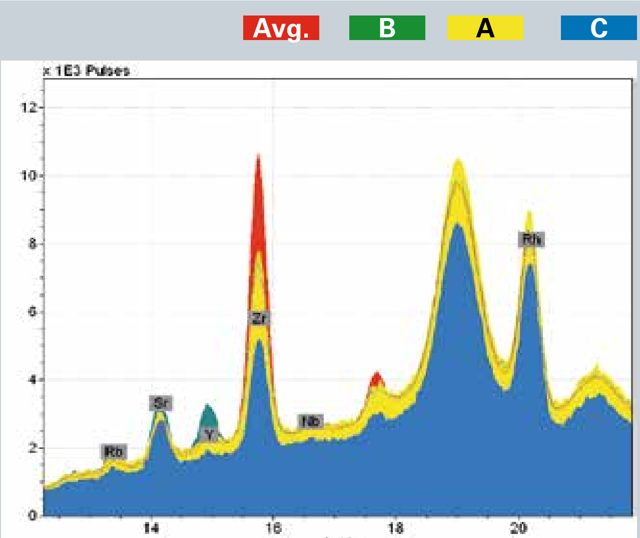


Figure 3: TRACER XRF spectra of representative Yucatán samples (#9, #14, #33) and the average (Avg.) of all samples

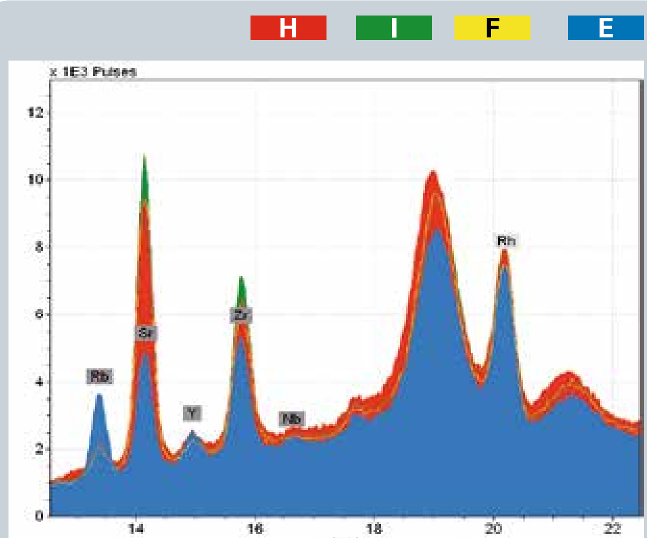


Figure 4: TRACER XRF spectra of representative Anáhuac samples (E, F, H, I)

Statistical evaluation

Based on the concentrations of Rb, Sr, Y, Zr and Nb (table 2) a statistical correspondence analysis for compositional grouping of the ceramics was performed. Figure 5 shows the grouping of historic artefacts. Modern ceramic (MC) samples as well as Meissen porcelain were plotted for further comparison. The data was obtained with the TRACER spectrometer.

Conclusion

A fast non-destructive chemical characterization of ceramics can be performed using the ARTAX or TRACER spectrometers. Short measuring times (~ 60 s to 300 s) per object are sufficient. A correspondence analysis using the net intensities of the elements can be performed to evaluate the data for provenance studies.

The performance of TRACER and ARTAX for this type of provenance analyses is similar. Following special features of the instruments can be highlighted:

- TRACER allows faster measurements, most suitable for use in the field.
- ARTAX offers higher reproducibility, because of accurate sample positioning and automatic line or area scan.

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Table 2: Concentration of selected key elements in ceramics

Sample	Rb	Sr	Y	Zr	Nb
C	9	81	13	221	8
A	< 3*	61	16	237	8
B	11	65	65	223	15
Yucatán avg.	6 ± 7	57 ± 7	26 ± 7	594 ± 229	14 ± 5
Anáhuac avg.	29 ± 6	456 ± 31	17 ± 3	182 ± 14	§
AT-LEG	150	188	22	167	8
Petén	63	88	68	234	10
MC	111	55	29	251	14
Meissen	165	31	32	135	44

* = detection limit 6 sigma;
§ results below detection limit = 4 ppm

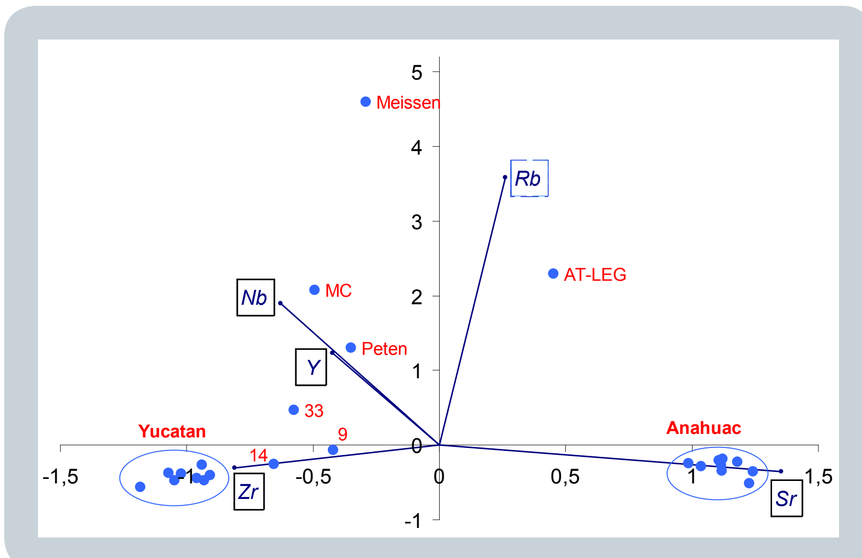

Figure 5: Plot of the correspondence analysis of the analyzed ceramics

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