

PROVENANCE STUDIES ON CERAMICS WITH PORTABLE μ -XRF INSTRUMENTS

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Goal and Approach

Fast non-destructive chemical characterization of ceramics

Analytical Method: μ -XRF, focused on the determination of Rb, Sr, Y, Zr, and Nb (K-lines)

Why these elements?

- the strong geochemical heterogeneity of these elements ensures a large variation in the composition of the ceramics with respect to their source region
- high detection sensibility of these elements with XRF (detection limit in the low ppm range)
- large information depth up to 1 mm, allowing to obtain representative results with few measurements
- simple quantification because of negligible matrix effects

Data evaluation: Correspondence analysis

Instruments

ARTAX



TRACER



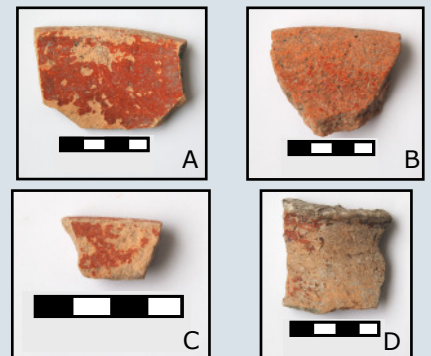
Measurement conditions

TRACER: Rh-Tube, 5 mm spot, 40 kV, 10 μ A, Ti-Al-filter, 300 s

ARTAX: Rh-Tube with collimator, 3 mm Spot, 50 kV, 700 μ A, 5 points 60 s each

Objects

Yucatan (Quintana Roo)



Anahauc Valley (Mexico City)

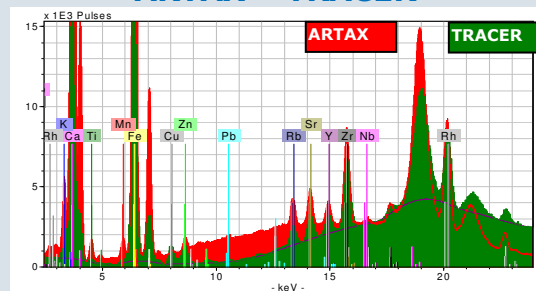


Peten (Guatemala)



Analyzed ceramic samples: 11 fragments from Yucatan, State of Quintana Roo, 10 fragments from the Anahauc Valley, Mexico City, and one polychromatic ceramic fragment from the Peten-Region in Guatemala. Scale = 4 cm.

ARTAX – TRACER



Comparison of a TRACER and an ARTAX spectrum of the polychromatic sherd (Fig. k). Note the well defined peaks for the elements of interest, the net intensities calculated after deconvolution of the spectrum are shown in the table on the right side.

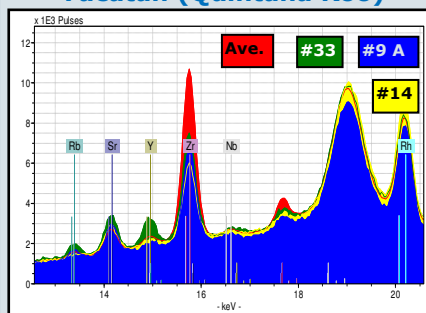
Intensity comparison

A comparison of the net intensity on one sample measured with the ARTAX and TRACER show a ~ 4 times higher intensity for the same measuring time.

Element	ARTAX Net. Int.	TRACER Net. Int.
Rb	35717	9005
Sr	45729	11530
Y	22806	7323
Zr	121635	34081
Nb	5028	1847

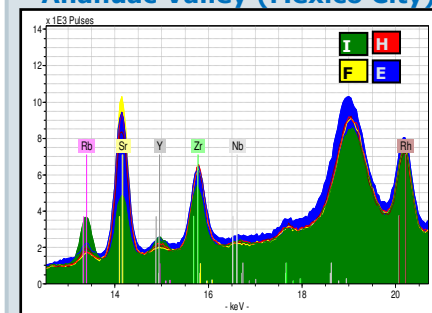
Results

Yucatan (Quintana Roo)



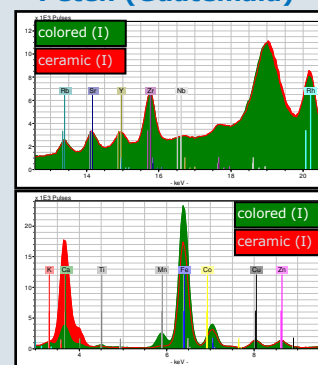
Zirconium is the dominant element in the analyzed Yucatan ceramics. The average composition spectrum is compared to the spectra of three samples that show small compositional variations #14, #9 (Fig. A).

Anahuac Valley (Mexico City)



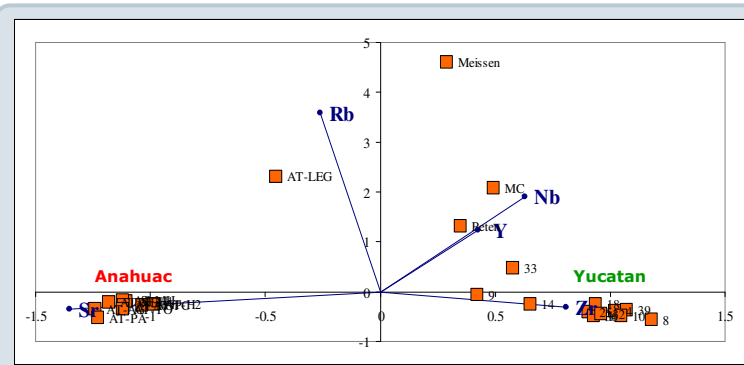
Anahuac ceramics were very homogeneous. With exception of sample AT-LEG (Fig. I), the variations of all other ceramic, shown in figures E to J, are almost negligible.

Peten (Guatemala)



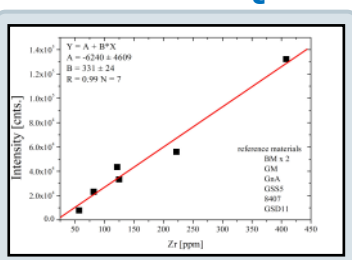
No detectable effects of the ceramic color cover on the composition of the elements Rb to Nb. In the lower energy range, there are severe surface effects in the spectra.

Statistical evaluation



Compositional grouping using correspondence studies of the analyzed ceramic using the net intensities of Rb, Sr, Y, Zr and Nb. Modern ceramic samples as well as Meissen porcelain were plotted for further comparison. The data was obtained with TRACER.

Quantification



Calibration showing correlation between intensity and concentration. Results were obtained using wax-tablets made with international ref. materials BM, GM GSS5, 8407 and GSD11.

The linear regression parameters were used for calculation of the concentrations.

[ppm]	Rb	Sr	Y	Zr	Nb
#9	9	81	13	221	8
#14	<3*	61	16	237	8
#33	11	65	65	223	15
Yucatan Ave.	6	57	26	594	14
s	7	7	7	229	5
Anahuac Ave.	29	456	17	182	§
s	6	31	3	14	
AT-LEG	150	188	22	167	8
Peten	63	88	68	234	10
MC	111	55	29	251	14
Meissen	165	31	32	135	44

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

Conclusion

A fast non-destructive chemical characterization of ceramics can be performed using ARTAX or TRACER!

Short measuring times (~ 60 s to 300 s) per object are sufficient

A correspondence analysis using the net intensities or the concentration can be performed to evaluate the data

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

TRACER: faster measurement, possible to use on the field

ARTAX: higher reproducibility of results because of precise sample positioning and automatic line or area scan