

Supplementary Electronic Material

The experimental working conditions in the SEM-EDX were:

Operation conditions in the SEM-EDX: A voltage of 20 kV, a current beam of 2×10^{-9} A beam current. X-ray detector operates at a working distance of 15 mm. The electron beam was always disposed perpendicularly to the polished surface of the cross-sections.

X-ray spectra acquisition conditions were: dead time 20 %, minimum number of counts acquired 2000, live time acquisition mode with an acquisition time of 100 s, process time of 5 s, number of channels automatically selected by the instrument that provided a channel width of 10 eV. Pulse pileup correction was active, which automatically performs deconvolution of overlapped peaks.

As the samples prepared are poor conductor, they were carbon coated for avoiding localized charging and any resulting distortion or reflection of the electron beam.

Software Inca (Orsay Physics Kleindiek Oxford Instruments) has been used for controlling the acquisition of digital images and X-ray spectra.

Images were acquired with the backscattered electron detector. A scansize of 1024, dwell time of 34 μ s and frame time of 26.739 s were the image acquisition conditions.

The software Inca automatically considers the C sputtering treatment and automatically re-calculates the intensity of the emission line of the C peak according to a calculated thickness of the external layer of C formed by the sputtering of 10 μ m and density of 2.25 g cm⁻³. Therefore, presence of C-containing minerals and organic matter was established from the rest of analytical techniques applied in this research.

Certificate reference standard materials used for calibrating the instrument:

C: CaCO₃; O: SiO₂; Na: Albite; Mg: MgO; Al: Al₂O₃; Si: SiO₂; P: GaP; S: FeS₂; Cl: KCl; K: MAD-10 Feldspar; Ca: wollastonite; Ti: Ti; Mn: Mn; Fe: Fe.

Qualitative measurements:

LOD: a theoretical averaged LOD for SEM-EDS measurements has been established in 0.08 wt% [1]. Nevertheless, a common procedure for a more accurate calculation of the LODs in the FESEM and SEM from experimental measurements procedures is carried out by considering that the LOD is determined as three standard deviations of the background [2]. According to this last method the averaged LOD value calculated from the experimental X-ray spectra obtained for the set of elements analyzed are in the range 0.07 - 0.1 wt%.

Quantitative measurements:

The standard deviation of the wt% values of the different elements is calculated by the Aztec software after applying the ZAF method of correction of interelemental effects on the intensity values for each element in each X-ray spectrum. Average precision values in this study were determined from the total of measurements carried out and are summarized in the table 1S expressed as average relative standard deviation values (RSD = (average standard deviation x 100%)/average mean value): Values obtained are in good agreement with those reported in similar studies of archaeological glass and ceramic materials [3].

Table S1. Average relative standard deviation values (RSD) calculated for the samples analyzed.

Element	RSD (%)
Mg	12
Al	1
Si	1
P	21

S	3
K	3
Ca	1
Fe	2

Accuracy of the FESEM-EDX instrument and applied method is calculated from NIST clay standard reference material (SRM 679-Brick clay) for considering the effect of the state of the sample (irregular and multi-mineralogical phase powder) in the accuracy provided by the analytical method. The values provided in the table thereafter correspond to the relative error, expressed in percentage (relative deviation, RD = (experimental observed composition – certified composition)/certified composition)x100 %. Results obtained are similar to those reported by other authors previously [3].

Table S2. Relative deviation (RD) calculated for the reference material SRM 679-Brick clay in the experimental conditions used in this study.

NIST brick-clay SRM 679 Brick clay powder		
Element	certified (wt %)	RD (%)
Al	11.01	3
Ba	0.0432	145
Ca	0.1628	45
Ce	105*	n.d.
Cs	9.2*	n.d.
Cr	109.7*	n.d.
Co	26*	n.d.
Cu	1.9*	n.d.
Hf	4.6*	n.d.
Li	71.7*	n.d.
Mg	0.7552	5
Mn	1730*	9
P	0.075	46
K	2.43	7
Rb	190*	n.d.
Sc	22.5*	n.d.
Si	24.34	2
Na	0,1304	4
Sr	73.4*	n.d.
Th	14*	n.d.
Ti	0.577	5
Zn	150*	n.d.
Fe	9.05	3
* value is in mg kg ⁻¹		
n.d.: not detected		

References

- [1] S. J. B. Reed, *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*. Cambridge University Press, Cambridge (1996).
- [2] M. Veritá, R. Basso, M. T. Wypyski and R. J. Koestler, X-ray microanalysis of ancient glassy materials: a comparative study of wavelength dispersive and energy dispersive techniques, *Archaeometry*, 36 (1994) 241-25.
- [3] P. Kuisma-Kursula, Accuracy, Precision and Detection Limits of SEM–WDS, SEM–EDS and PIXE in the Multi-Elemental Analysis of Medieval Glass, *X-Ray Spectrometry*, 29 (2000) 111–118. DOI: 10.1002/(SICI)1097-4539(200001/02)29:13.0.CO;2-W.