Is it possible to integrate the p-XRF data from several sources? Method application to large collections of Iron Age glass

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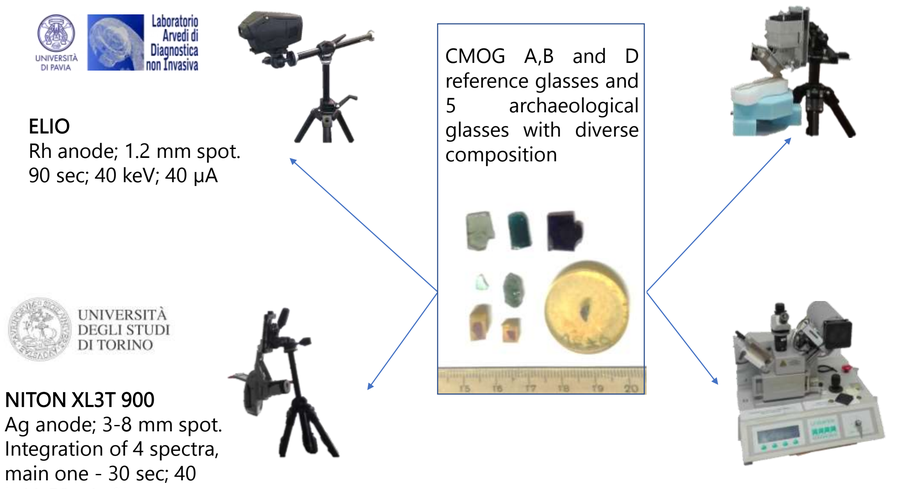
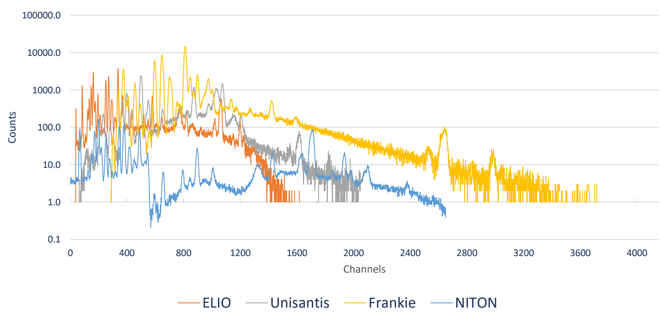
Introduction

The INGOT-EL project (INvestigation of Glass Origin and Technology in Etruscan Lands) aims to bring new evidence on glass production and circulation by analysing a large set of glass beads uncovered in many Iron Age burials in central Italy. One of the first steps of the investigation accounts for a non-invasive in-situ approach with portable X-Ray Fluorescence (p-XRF) equipment operating in several archaeological museums involved in the research. XRF is one of several analytical techniques that show high degree of sustainability during research - it is non-invasive, low-cost, relatively fast method that might be implemented in the field, making it safer for the objects under analysis and the institutions that keep them [1]. It is capable of yielding quantitative data of the accuracy and precision that is useful for the chemical characterisation of glass, studying of its technology and, in specific cases, provenance of raw glass. Several units of portable XRF spectrometers were used while working with different collections. The first and very acute question that rose was: to what extent the data produced by different units can be compatible with each other. Using quantitative approach in data handling and several XRF units made this research more sustainable due simpler logistics and increased quality of analytical information for each acquisition.

Materials and methods

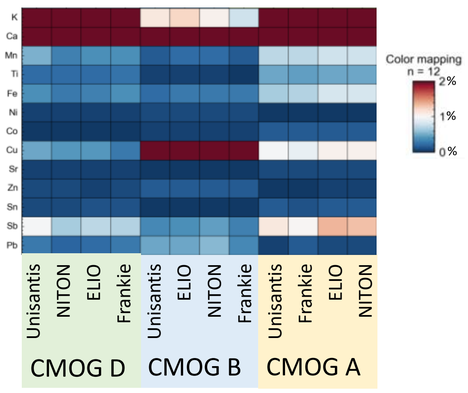


Round robin analysis

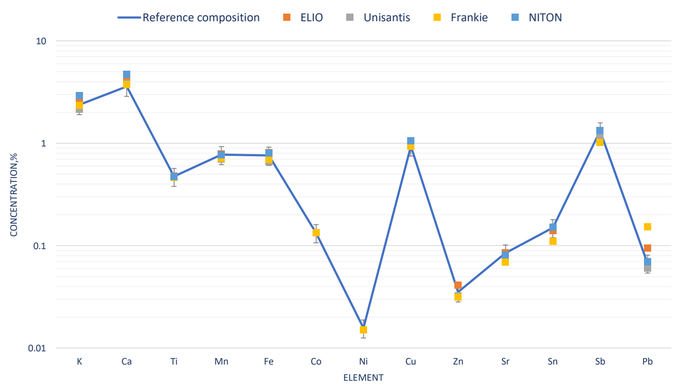


Spectra of CMOG A glass reference produced by 4 spectrometers used in the study. They have different number of channels and feature different peaks of their X-ray sources.

Data transformation



Compositional matrix of 3 CMOG glasses obtained with 4 XRF units. Repeatability without systematic bias.



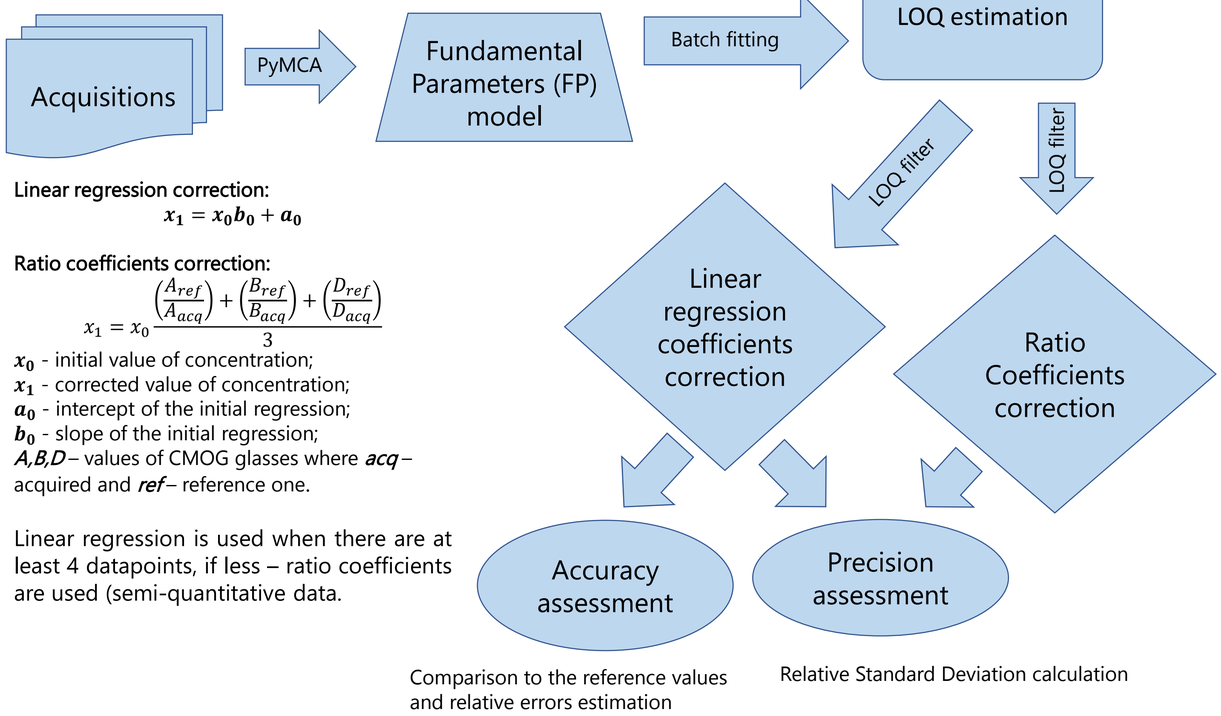
Comparison of the compositional data provided by 4 spectrometers of the CMOG A reference glass. Error bars represent 20% deviation.

Workflow for a single instrument

At least 3 acquisitions of all reference materials in different points.

Model is improved by adjusting it to match the reference spectrum, calculated by PyMCA software [2].

Estimated as the concentration that creates more than 10σ increment of the background area.



Linear regression correction:

$$x_1 = x_0 b_0 + a_0$$

Ratio coefficients correction:

$$x_1 = x_0 \frac{\left(\frac{A_{ref}}{A_{acq}}\right) + \left(\frac{B_{ref}}{B_{acq}}\right) + \left(\frac{D_{ref}}{D_{acq}}\right)}{3}$$

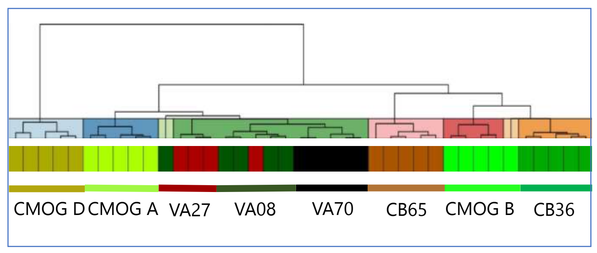
x_0 - initial value of concentration;
x_1 - corrected value of concentration;
a_0 - intercept of the initial regression;
b_0 - slope of the initial regression;
A,B,D – values of CMOG glasses where ***acq*** – acquired and ***ref*** – reference one.

Linear regression is used when there are at least 4 datapoints, if less – ratio coefficients are used (semi-quantitative data.

Comparison to the reference values and relative errors estimation

Relative Standard Deviation calculation

Reproducibility assessment



Hierarchical cluster analysis of the quantitative portion of the data. 5 datapoints of the same material are the reference value and 4 results from each XRF unit. Their placements together means sufficient reproducibility of the results. VA08 and VA27 datapoints are partially mixed because of the similar composition.

CONCLUSION

- Analysis of archaeological glass with pXRF can provide reliable quantitative information.
- Data from different pXRF units can be considered together but they require adjustment of the quantification algorithm using matrix matching reference materials.
- Differences in hardware do not play important role, unlike the common processing workflow.
- Improving the compositional range of the set of reference materials can improve the quality of data.

References:

[1] Liritzis I. et al. (2011). Portable XRF of Archaeological Artifacts: Current Research, Potentials and Limitations. In: Shackley, M. (eds) X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology. Springer, New York

[2] V.A. Solé, E. Papillon, M. Cotte, Ph. Walter, J. Susini, A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, Spectrochim. Acta Part B 62 (2007) 63-68.

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