Influence of degradation in the production of quantitative data by using portable-XRF on glassy matrices of Limousin composition

Chiara Gamarra[1], Angelo Agostino, Maurizio Aceto, Gaia Fenoglio, Maria Labate, Lorenza Operti

[1]University of Turin, Department of Inorganic Chemistry, chiara.gamarra@gmail.com

Introduction

Commercial portable X-ray fluorescence (p-XRF) instrumentation offers the advantages of performing nondestructive, *in situ* analyses but, when sampling or sample preparation on cultural heritage materials is precluded, reliability of its quantitative results can be compromised due to the presence of deterioration processes.

For this reason, a validation of quantitative p-XRF analyses is essential: the present work aims to validate the quantitative p-XRF analyses performed on artificially altered medieval-like Limoges enamels. In particular, our research focuses on cobalt blue enamels opacified with tin oxide, one of the most employed in medieval Limousin ateliers (Biron *et al.*, 1996).

Glass degradation processes are strongly affected by environmental conditions, especially pH. Leaching phenomena of network modifiers prevail for pH<9, whereas at pH>9 the corrosion of the network predominates. Accelerated weathering treatments (i.e. immersion tests in acidic and basic solutions) were thus performed on a set of laboratory-synthesized samples for variable times of exposure, simulating natural deterioration processes (Greiner-Wronowa *et al.*, 1999; De Bardi *et al.*, 2013). Samples were analyzed with p-XRF before and after accelerated weathering treatments, in order to evaluate possible compositional variations linked to the presence of deterioration. Since temperature plays a fundamental role in the reaction kinetic, tests were also performed at high temperature.

Morphological and compositional surface changes were monitored by Scanning Electron Microscopy coupled with Energy Dispersive X-ray analyses (SEM-EDX). Finally, possible structural variations of glassy matrices were preliminarily undertaken by performing in-depth analyses with confocal micro-Raman instrumentation.

Morphology of weathering

The glassy matrix studied shows a great resistance to the weathering treatments applied: in particular, room temperature reactions are too slow to appreciate variations, and longer times of exposure would be required.

Basic and acidic attacks show specific morphologies of weathering.

The most deteriorated samples are those exposed to a basic environment, because the attack is directly at the expense of the network formers. Deterioration starts in correspondence of surface irregularities, like scratches and lapping marks, forming deep tunnels (see Fig. 1).
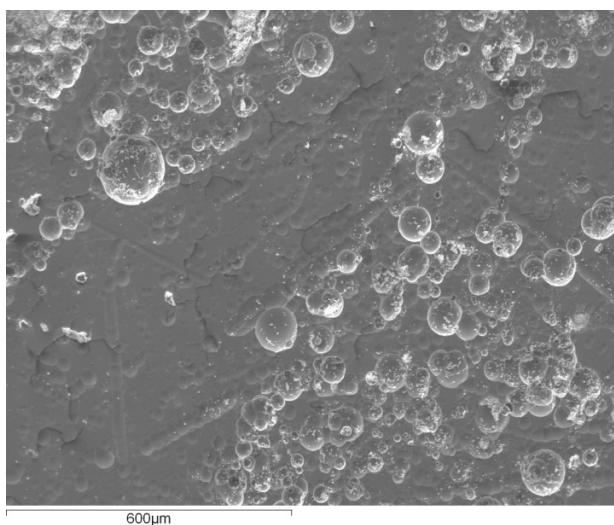

Fig. 1: SEM SE image of sample exposed for 48 hours to NaOH solution at 70 °C (100x).
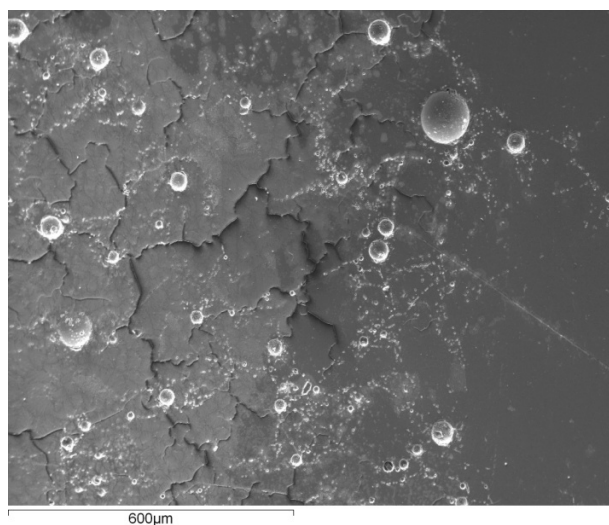

Fig. 2 : SEM image of sample exposed for 48 hours in H_2SO_4 solution at 70 °C (100x).

Samples exposed to acidic solutions generally appear in better conditions: first signs of deterioration are isolated and elongated pits that, with the progress of deterioration, interconnect forming a crizzled network. The most altered samples also register a beginning of surface lifting. This weathering morphology is the consequence of the substitution of modifier alkaline ions with protons, causing a contraction of the leached layer (see Fig. 2).

Quantitative analyses

With respect to the reference composition of untreated samples, EDX analyses on altered samples register compositional variations for samples exposed at high temperature treatments for at least 12 hours, both in acidic and basic environment. In particular, those exposed to basic solution reveal a silicon oxide and a lead oxide loss, whereas samples treated with acidic media reveal a loss of its main network modtifier, that is sodium oxide, introduced in the structure as flux. Results are in agreement with the expected behaviour.

p-XRF measurements on weathered samples, instead, do not show analogous trends: all the compositional variations in the measurements pursued after accelerated weathering are always included into the 2σ error of the reference composition of untreated samples.

In conclusion, according to the applied protocol, no correlation exists between deterioration and variation of oxides concentration obtained with p-XRF. This implies that p-XRF response, in these specific conditions of deterioration, is not affected by the presence of a deterioration process. It has to be considered that all possible compositional variations detected are included within the instrumental error. For this reason possible compositional trend evaluations are precluded.

Raman spectroscopy: preliminary study

The silicon tetrahedron, SiO_4, is the main constituent of a traditional glass network structure, and it can also be considered as a single vibrational entity (Mc Millan, 1984). When a modifier ion enters the structure, the tetrahedra network opens: the number of bridging oxygens between silicon atoms diminishes, and the quantity of non-bridging oxygens (NBO) increases. In the structure of a modified glass will thus coexist different vibrational entities: Q4 with 4 bridging oxygens,

Q3 with 3 BO, Q2 with 2BO, Q1 with 1BO, and Q0 for isolated tetrahedra.

The Raman spectrum of a glass is influenced by these vibrational units, and can be divided into three main areas: low-wavenumber range, centred at 500-600 cm^{-1}, deriving from bending Si-O-Si (i.e. BO bonds); medium wavenumber range, centered at about 800 cm^{-1}, associated to motions of silicon atoms against its tetrahedron cage; high-wavenumber range, extended between 850 cm^{-1} and 1220 cm^{-1}, associated to Si-O stretching modes (see Fig. 3).

In literature (Colomban, 2003), the polymerization index (I_p), i.e. the ratio between areas under 500 cm^{-1} and 1000 cm^{-1} bands, is reported as a good marker of the polymerization degree of a glassy system. It is possible to suppose that variations of this parameter depend on structural variations of the glass, as a consequence of the weathering treatment. Preliminary analyses on the considered samples did not show significative I_p changes among treated and untreated samples, but further studies are required.

Moreover, Raman spectroscopy was used for the identification of crystalline phases in the samples. Tin oxide opacifier precipitates were recognized and spectra deconvolution allowed distinguishing their contribution from the glassy matrix signal.

To confirm the potentiality of Raman spectroscopy on weathered glassy matrices, further studies on more deteriorated samples would be required. For these reason, these can be considered only as preliminary considerations of a wider study.
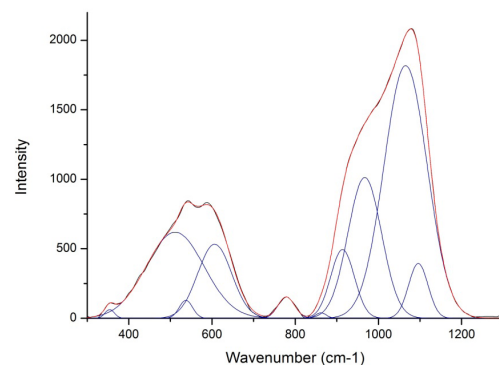

Fig. 3: Example of Raman spectrum collected from untreated sample.

Conclusions and future work

Data obtained reveal that: I. p-XRF is a proper technique to acquire quantitative information on enamels with the composition considered and with moderate alteration processes, such as musealized objects; II. data from historical samples can as a consequence be considered reliable.

Comparing XRF data of treated and untreated samples, it is evident that oxides concentration of weathered samples is included within 2σ deviation of reference concentrations of untreated samples. This means that it is not possible to distinguish analyses performed before and after treatments.

The same instrumental setup and validation protocol can be safely applied on all enamels of the Limousin palette, both medieval and XIX-century, in order to understand differences in their behaviour and responses to weathering.

Raman spectroscopy results can only be considered as preliminary observations, though encouraging. Confocal μ-Raman analyses, indeed, reveal information both on molecular structure of the glassy system and on the identity of mineral precipitates. In order to understand spectroscopic variations in Raman spectra attributable to weathering processes, further analyses on samples subjected to stronger weathering conditions would be required.

References

Biron, I., Dandridge, P., Wypyski, M.T. 1996. Techniques and materials in Limoges enamels, in: *Enamels of Limoges: 1100-1350*, O'Neill, J.P. (ed.). New York: Metropolitan Museum of Art.

Colomban, Ph. 2003. Polymerization degree and Raman identification of ancient glasses used for jewelry, ceramic enamels and mosaics. *Journal of Non-Crystalline Solids*, 323: 180-187.

De Bardi, M., Wiesinger, R, Schreiner, M. 2013. Leaching studies of potash-lime-silica glass with medieval composition by IRRAS. *Journal of Non-Crystalline Solids*, 360: 57-63.

Greiner-Wronowa, E., Paluszkiewicz, C., Stoch, L. 1999. Applying FTIR spectroscopy in the study of archeometric sensor glasses. *Journal of Molecular Structure*, 511-512(1): 199-204.

McMillan, P. 1984. Structural studies of silicate glasses and melts - applications and limitations of Raman spectroscopy. *American mineralogist*, 69: 622-644.