NON-INVASIVE ANALYSES ON GLASSES: PRODUCTION AND METHODOLOGICAL ISSUES OF A LABORATORY PROJECT

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Our leading field project MEMIP09 (Medieval Enamels Metals and Ivories in Piedmont) is focused on 11^{th}-14^{th} century Limoges enamels and their 19^{th} century copies, and an outstanding amount of data has been collected thanks to the possibility to use a non-invasive approach.
Indeed, the joined use of portable X-ray Fluorescence (p-XRF) and UV-VIS Fibres Optical Reflectance Spectroscopy (FORS) is a strategic key to accede to a large amount of artworks otherwise inaccessible to common analytical techniques requiring sampling procedures. However, objections have been moved to the actual reliability of quantitative data produced with p-XRF, as frequently they are considered as semi-quantitative data, especially when performed on problematical samples where inhomogeneity, heterogeneity, roughness or the presence of superficial patinas have to be faced.
Consequently, specific issues due to the non-invasive approach have raised collateral research-lines to improve the reliability of quantitative data. The main target is to overcome the very limited number of solid certified materials for glass matrices, which are fundamental to predict matrix effects. A laboratory research has been opened in order to produce medieval-like enamels to use as reference materials in order to overcome the lack of adequate standards.

This paper will present the preliminary results and issues of the production and characterization of the laboratory samples.
The compositions are focused on medieval-like enamels and the references are medieval Limoges characteristics such as taken from literature [1].
We explored different heating curves with melting temperature in the range 1000-1200°C using various base glass compositions: 1) soda to potash content in silica lime glass, 2) glass base compositions calculated to represent the two main categories of Limoges enamels [1], 3) PbO content variations up to 30% wt.
Then, we produced glass opacified with SnO_2. Historical recipes report the addition of a Pb-Sn calx (Pb_2SnO_4) to a glass frit or glass powder [2][3]. We decided to start from glass raw reagents, Pb and Sn content being introduced either as PbO and SnO_2 either as mixtures of $PbO/SnO_2/Pb_2SnO_4$. According to XRPD results, the only crystalline phase detected in these samples is SnO_2. The opacification level is related to the PbO and SnO_2 content in the matrix and to their ratio (Fig. 1).

Fig.1 Samples with increasing PbO and SnO_2 content: SV26, SV16, SV17.

After that, we aimed producing opaque glass by melting SnO_2 opacified glass to transparent glass. However, we encountered problems of replicability of the correct opacification level [4]. No information on SnO_2 crystallization in similar matrices could be obtained from literature, though a number are present on lead glazes [5][6].
Consequently, we did a number of experiments to improve our knowledge respect to SnO_2 behavior. We focused our attention on the heating step, performing HT-XRD from room temperature up to 850°C. XRPD was applied on quenched samples to investigate temperatures from 800 up to 1100 °C and on the melting dwell. According to XRPD data, SnO_2 is already present from 800°C but further investigations are needed. First, we need to understand SnO_2 particles behavior at this range of temperatures and just below. Second, it is fundamental to define whether a dissolution of SnO_2 occurs or not, at which extent, and which is its contribution respect to particles size.

Parallel to the production of the laboratory samples, we set up a characterization protocol based on SEM-EDS and P-XRD.
In order to evaluate the elements' trend after the heating cycle, we used the nominal compositions obtained from weighted raw ingredients as reference parameter to EDS-analysis, with a main interest to eventual significant loss of Na_2O.

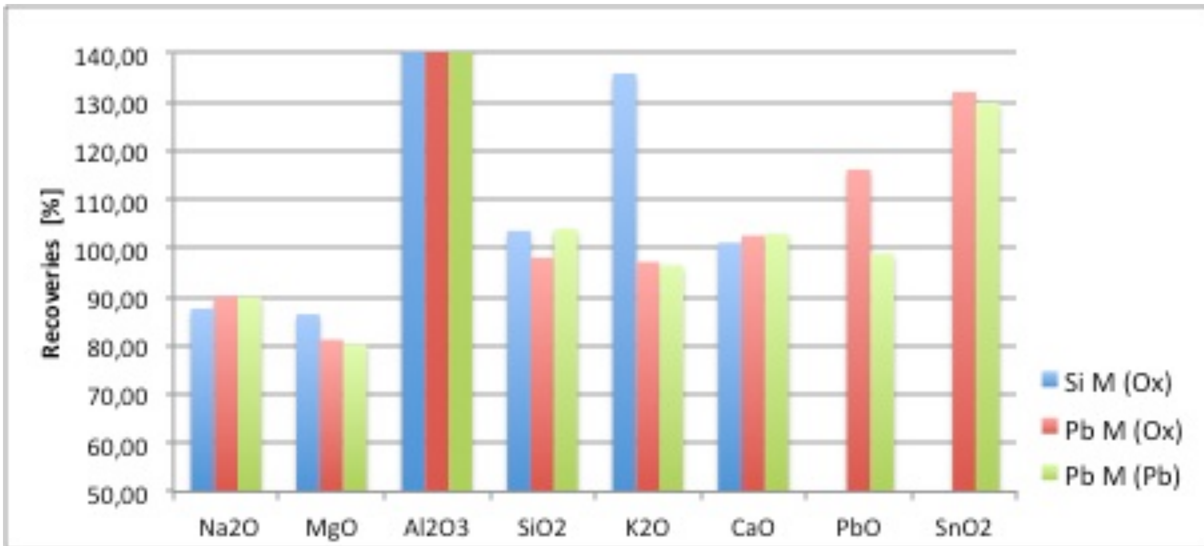

Fig. 2 Recoveries of data obtained with EDS respect to nominal compositions.

Fig. 2 presents recoveries obtained on Si-based glasses (Si M) and on Pb-containing glasses (Pb M). We observe an attended decrease of light elements (Na_2O and MgO) due to volatilization during the heating treatment but it is quite moderate (10%), and a crucible influence on Al_2O_3 content is also clear.
Two different calibrations have been applied, the first (Ox) uses geochemical standards for EDS, the second (Pb) includes a Pb-containing certified glass. The last was applied in order to correctly predict the matrix effect of lead in the glass matrix, as the geochemical standards could not fit properly.
The preliminary results of this project underline the complexity of laboratory production and characterization phase. However, a relevant amount of experience has been collected and it will be useful in order to define the set-up of the other typologies of opaque glasses. In fact, the production is intended to include all colours found in medieval enamels.

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