



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**ANTIMONATES GLASS OPACIFIERS IN HISTORY: A NEW INSIGHT
THANKS TO THE HIGH RESOLUTION SPECTROMETER**Experiment****number:**

EC-544

Beamline:	Date of experiment: from: 27/01/2010 to: 01/02/2010	Date of report:
Shifts:	Local contact(s): M. Cotte	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):**M. Cotte^{1,2*}, I. Biron^{1*}, S. Lahlil^{1*}, J. Szlachetko^{2*}, J. Susini², N. Menguy^{3*}**

(1) Centre de Recherche et de Restauration des Musées de France, UMR 171 CNRS, Paris, France

(2) ESRF, Grenoble, France

(3) IMPMC Institut de Minéralogie et de Physique des Milieux Condensés, Univ. Paris 6 et 7, Paris, France

Report:Purpose:

Following a work done in 2008-2009 on the analysis of calcium antimonates used as opacifiers in ancient glasses technology¹⁻² (report EC-281), our aim, in the present experiment, was to extend this research on the complex family of lead antimonates. These yellow compounds have a predominant role throughout history as they are found from the 3rd millenium BC in Mesopotamia, until modern times. They were used as glass colorant and opacifier but also in the glazed decorations of ceramics and later as painting pigments. In this study, three opaque glass productions were analyzed: Egyptian glass of the 18th dynasty (1570-1292 BC), Roman mosaic tesserae and beads from Aquilea and Rome (2nd c. B.C –5th c. AD) and Nevers lampworking glass figures (18th c. AD) (Fig.1).

Our objectives were to determine to which extent the crystal composition and the Sb and Sn speciation could be specific of the different productions. The possibility to get clues about the ingredients used for the glass manufacturing was also assessed.

Samples:

Were studied: Four Egyptian opaque decorated glass shards dating from the 18th dynasty (1570- 1292 BC) and coming from the Louvre museum(Fig. 1a), for yellow roman mosaic tesserae -one coming from Aquilea (181 BC to 452 A.D), one from Rome (390 AD), and two from Saint-Romain en Gal (2nd-3rd AD), (Fig. 1b), two green opaque glasses from Nevers figurines dating from the 18th c. A.D and coming from the Museum of Decorative Arts of Paris are studied (Fig. 1c). For all the samples, micro-sampling (0.2 x 0.5 cm²) were taken, embedded in resin and polished. Additional SEM and Raman analyses were performed.

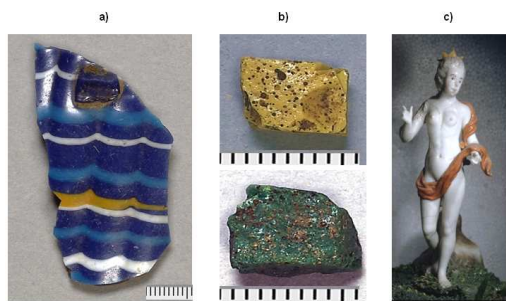


Fig.1 Opaque coloured glass productions. a) Shard of the 18th Egyptian Dynasty (inventory number AF12707 © C2RMF/ D. Vigears); b) Yellow and green Roman mosaic tesserae from Aquileia (2nd c. BC –5th c. AD) (© C2RMF/ D. Vigears); c) Figurine of Diane made of Nevers lampworking glass (35470A © C2RMF/ D. Bagault).

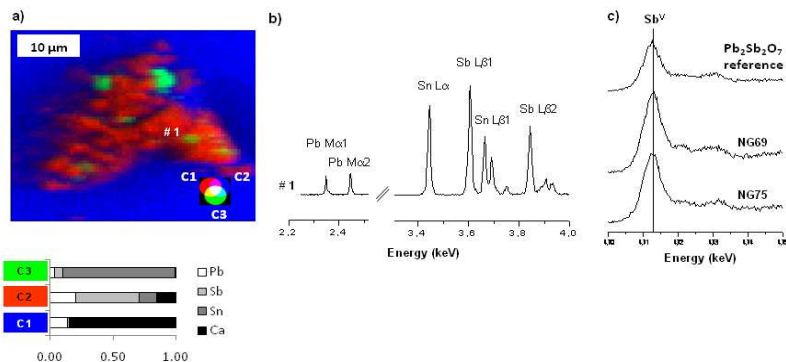


Fig.2 Nevers glass lead-tin-antimonate opacifiers a) μ -XRF analysis of polished fragments and principal component maps obtained by NMF analysis of the Pb, Sb, Sn and Ca maps. The relative intensities of the emission lines of these 4 elements are plotted in the bar chart, for the three main components. In RGB are plotted these three main phases (sample NG69): C1, the vitreous soda-lime silica matrix (blue), C2, lead-tin-antimonate crystals (red) and C3, crystals containing mainly tin (green); b) an example of μ XRF spectra acquired with the WDS c) μ -XANES spectra performed at the Sb L_1 edge (average of five measurements) on the crystals (reference sample $Pb_2Sb_2O_7$ and samples NG69, NG75).

Methods:

The lead antimonate crystals are rather small ($\sim 20\mu\text{m}$ max), but, as observed, sometimes very heterogeneous (Fig. 2a). It was therefore essential to use a submicrometric beam. The beam size was reduced to $0.8 \times 0.4 \mu\text{m}^2$ (horizontal \times vertical) thanks to Fresnel zone plates.

The second technical challenge was related to the possible additional presence of tin, with lead and antimony in the crystals. Sb and Sn have emission L-lines which are quite close and which can hardly be differentiated with EDS detectors. Besides, the Ca present in glass matrix also complicate this lines identification as the Ca K-lines are falling in the same region (3.5-4keV). For this reason, the high spectral resolution provided by the WDS at ID21 was very useful (Fig. 2b). It was in particular necessary to determine with high accuracy to presence or absence of tin, and was also fully exploited for the acquisition of μ XANES at the Sb and Sn K-edges (Fig. 2c). For this measurement, a Si(111) crystal was chosen, giving access to both Ca, K-, Sb, Sn L- and to Pb M-lines.

For data processing, we have exploited recent possibilities offered by the PyMCA software for statistical analysis. In particular, we wanted to extract relative composition (in Sb, Sn, Ca and Pb) of the different principal components identified in the crystals. This approach was useful in order to compare the composition of one sample with another, one production with another.

μ XANES spectra were collected at the Sb and Sn L_1 -edges. As demonstrated in previous publications¹⁻², direct identification of the oxidation state can be obtained working at these edges.

Results:

One of the most important results is that lead antimonate production evolves throughout History. Differences between the three productions could be clearly highlighted and hypotheses about glass manufacturing are drawn³. In particular, our results show that a very homogeneous process has been used to produce lead antimonate crystals in all the Egyptian yellow glasses studied whereas Roman glasses show various heterogeneities at different scales, indicating that no strict recipe was used. On the other hand, a more controlled process than in Roman time is used for Nevers modern glasses, likely based on the Muranese recipe books. In one atypical sample, it was even possible to observe Sb in 2 different oxidation states, which was interpreted as the result of a mixture of reactants and products in a single aggregate.

Specially for the Roman and Nevers glass productions, the heterogeneity observed from one sample to another, but also within the same sample, and even more within a single crystal aggregate (e.g. Fig. 2a) clearly shows that a production cannot be unequivocally associated to a single chemical composition. This work emphasizes the necessity of using high resolution micro analytical techniques to investigate this type of materials. Since tin is commonly found with a mixture of Pb and Sb, in other productions of opaque glass or in yellow glass-based pigments dating from the 16th–late 19th cent. AD [16, 18-27], this methodology can be applied to the study of yellow pigments for painting or glazed ceramics. Here we have seen that one cannot conclude about the raw materials, the recipe and the process used according to the measurement on a single area of the artefact. It is of main importance to collect data of this type to find out more on the original recipe and the raw materials employed.

Results have been presented to the SR2A 2010 conference and an article was submitted in Dec 2010 to JAAS.

References

1. S. Lahlil, I. Biron, M. Cotte and J. Susini, *Appl. Phys. A*, 2010, 100, 683-692.
2. S. Lahlil, I. Biron, M. Cotte, J. Susini and N. Menguy, *Appl. Phys. A*, 2010, 98, 1-8.
3. S. Lahlil, M. Cotte, I. Biron, J. Szlachetko, N. Menguy and J. Susini *J Anal Atom Spectrom*, submitted.