EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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.

![ESRF]	**Experiment title:** **Role and fate of sulphur in the degradation of arsenic sulphide paint layers**	**Experiment number**: HG-67
Beamline: ID16B-NA	**Date of experiment**: from: 11/09/2015 to: 14/09/2015	**Date of report**:
Shifts: 9	**Local contact(s):** Jussi-Petteri Suuronen	*Received at ESRF:*

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Report:

Purpose

The aim of this experiment was to identify and localize the arsenic degradation products in various types of binding media using XANES and energy mapping. This research aims to demonstrate the role of the binding media and the type of pigment (natural or artificial) on the degradation process of arsenic sulfide pigments (As_2S_3, orpiment, As_4S_4, realgar and g-$As_{xx}S_{yy}$).

Experiment

After optimizing the analytical conditions (slit position, beam size, alignment, …), we started with measuring reference samples of both natural pigments (orpiment and realgar – arsenic sulfides) and potential degradation products (pararealgar, arsenic (V) sulphide, potassium arsenate (arsenic V), arsenic (III) oxide, arsenic (V) oxide and arsenic[0]) to assess the possibility to differentiate these compounds.

Then, naturally aged samples from 1) a Japanese tower in Brussels, Belgium, 2) an Egyptian canopic jar from the Royal Museum of Art and History, Brussels, Belgium, 3) a 17th-18th-century "Chinoiserie" from a private collection, and 4) a 17th-century Dutch painting samples (Seghers) from the National Gallery of Denmark were analysed.

Four energy maps (pre- and post- edge as well as arsenic (III) and arsenic (V) white lines) and XANES line scans were performed on each samples in order to locate and visualise the degradation phases.

Results

From the analyses of the reference materials, four different energies were observed for the different arsenic oxidation states: 11.868 (As^0), 11.869 (As^{+3} sulphides), 11.871 (As^{+3} oxides) and 11.875 keV (As^{+5}) (Fig.1.). The some of the energy differences between the different oxidation states were too small to choose them all and so, two energies characteristic for non-degraded arsenic sulphide (11.869 keV) and degraded arsenic sulphate (11.875 keV) were selected and used for energy mapping on the historical samples. Two other energies (pre- and post-edge energies at 11.860 and 11.92 keV respectively) were also selected for the energy maps.
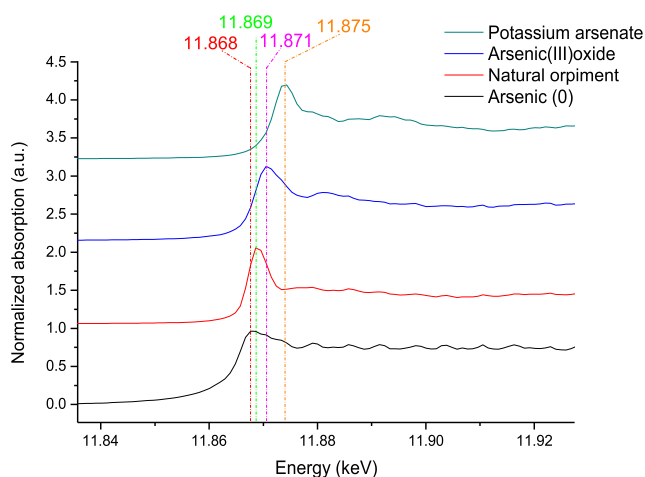

Fig.1. XANES spectra of reference materials and their associated white lines. The white lines for As^0 and As^{3+} oxide are too clase to the other ones to be chosen for energy mapping.
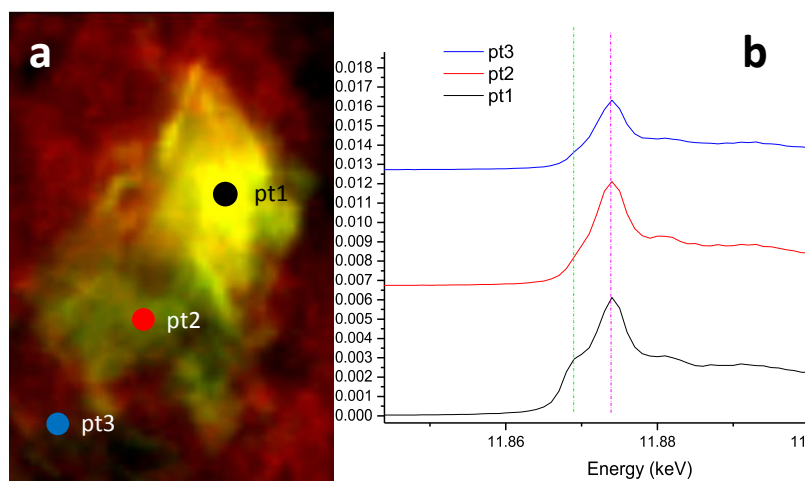

Fig.2. Energy map presenting partially degraded arsenic sulphide (yellow/green) and fully degraded and diffused arsenate (red) (a) and XANES spectra assocated with these regions (b) showing the presnece of arsenic3+ in the inner part of the pigment particle but its absence on the outter part.

While the XANES spectra obtained for both the reference materials and the historical samples were quite noisy, it was still possible – as shown in Fig. 1 – to identify different white lines for the non-degraded and degraded materials. In the first part of the experiment, several spectra were acquired for short amount of time (zap mode) in order to maximize the signal to noise ratio (S/N) but, the noise appearing to be systematic (with no improvement of S/N), another approach with a single spectrum was chosen for the last sample (scan mode) with better S/N than with previous mode. Since the flux of the beamline being too low to allow the use of the I_0 detector, the normalisation of the XANES spectra was done using the sum intensity of the Fe Kα lines.

Before starting the analyses on historical samples, multiple consecutive spectra were acquired to see if the analyses induced degradation, but no difference was observed between them.

On the historical samples, it was also possible to differentiate and localize non-degraded arsenic sulphide and degraded arsenate (Fig.2).

Differences were observed in the degradation based on the medium: pigment in lacquer showed a lower level or no degradation compared to pigment in oil.

The data still has to be analysed more in depth and/or processed in the hope of getting more information on the historical samples.