



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: Vermilion alteration revisited by means of Full-field Hg-L ₃ edge EXAFS	Experiment number: EC904	
Beamline: BM23	Date of experiment: from: 23 rd of November 2011 to: 29 th of November 2011	Date of report: <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Olivier Mathon	
Names and affiliations of applicants (* indicates experimentalists): Marie Radepont^{a,b*}, Marine Cotte^{a,c*}, Koen Janssens^{b*}, Barbara Fayard^{d*}, Emeline Pouyet^{c*}, Sakura Pascarelli^c, Jean Susini^c, Yvan Coquinot^a. (a) Centre de Recherche et de Restauration des Musées de France, UMR 171 CNRS, Paris, France (b) University of Antwerp, Department of Chemistry, Antwerp, Belgium (c) ESRF, Grenoble, France (d) Laboratoire de Physique des Solides, UMR 8602 CNRS, Paris, France		

Report:

Purpose

The aim of this experiment was to develop a transmission “full-field” Hg-L edge EXAFS mapping experiment and to use it on degraded paint samples of red vermilion in order to identify and discriminate the different degradation compounds.

Experiment

Instead of using a micro-beam as it was previously done for the study of the alteration of vermilion¹, the experimental set-up was based on an existing project of full-field XANES one² (see Fig.1) and improved to be applied at the Hg-L₃ edge to our type of samples.

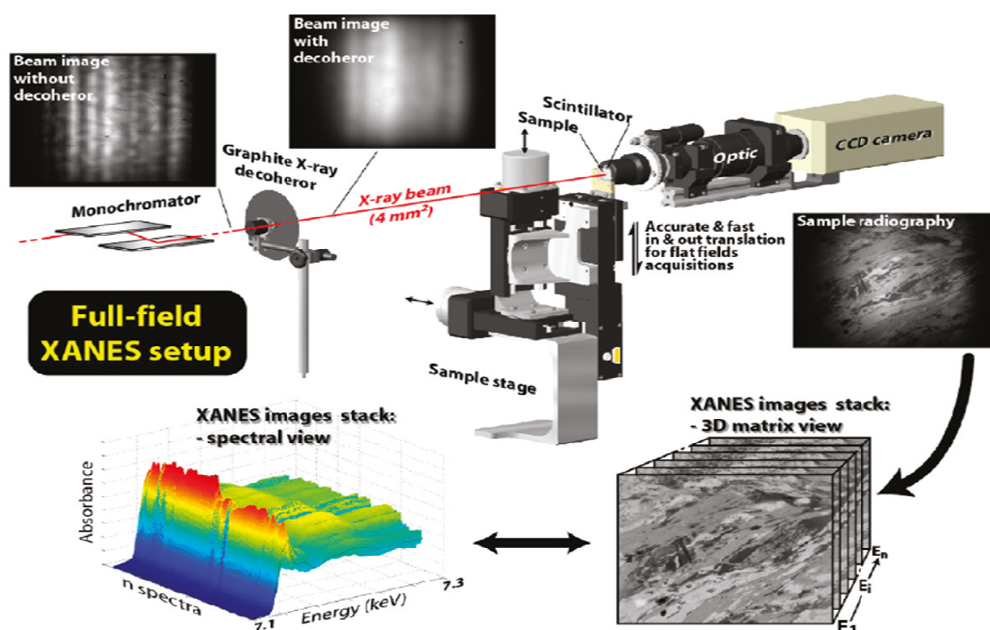


Fig. 1 : Full-field XANES setup principle on which we based our experiment.²

After assessing the best parameters to perform these analyses (bender, slits, acquisition conditions...), we performed transmission mappings on model samples. Different thicknesses of cross-section were tested to establish a protocol for the sample preparation, and we focused on samples with several layers of mercury compounds with different states of oxidation ($\text{Hg[II]S}/\text{Hg[II]SO}_4/\text{Hg[I]}_2\text{Cl}_2/\text{Hg[II]Cl}_2$) to assess the possibility to differentiate these compounds, in full 2D mode.

Then, samples artificially aged were tested to obtain XANES and EXAFS spectra on pigment and degraded layers.

Finally, original altered samples coming from a fresco of the Monastery of Pedralbes (Spain) were analyzed. These samples were previously analyzed by other techniques^{1,3}.

Results

Apart from technical problems that should be fixed for future measurements (the sample was moving during the analysis and the beam structure is not well corrected with the flat-field acquisition), the image quality was quite good. From these images we extracted sum spectra corresponding to specific areas and comparable to the ones of references analyzed before.

The XANES parts of the spectra were smooth enough to be able to see the energy of the white line, but the EXAFS parts were too noisy to have interpretable oscillations. It appeared that the flux at BM23 was insufficient for such an EXAFS approach, and therefore, the data analyses were focussed on the XANES region. It also appeared that beam variation with time is a real issue. Therefore, for future experiments, it would be better to consider the acquisition of multiple short scans, instead of the acquisition of a single long scan.

On the model samples, it was possible to differentiate spectra of sulfides ($\alpha\text{-HgS}$) and sulfates (HgSO_4) (see Fig. 2). Sample preparation appeared as a limiting factor. Different thicknesses had been prepared in order to choose the best one. However, heterogeneity of the density, granulometry and therefore absorption made this choice difficult (cf. Fig. 2: HgS is poorly absorbing while HgSO_4 is almost completely absorbing X-rays). On the artificially aged samples, the degraded layers were not concentrated enough to be able to identify the compound present.

On the original samples, only vermilion ($\alpha\text{-HgS}$) was clearly detected.

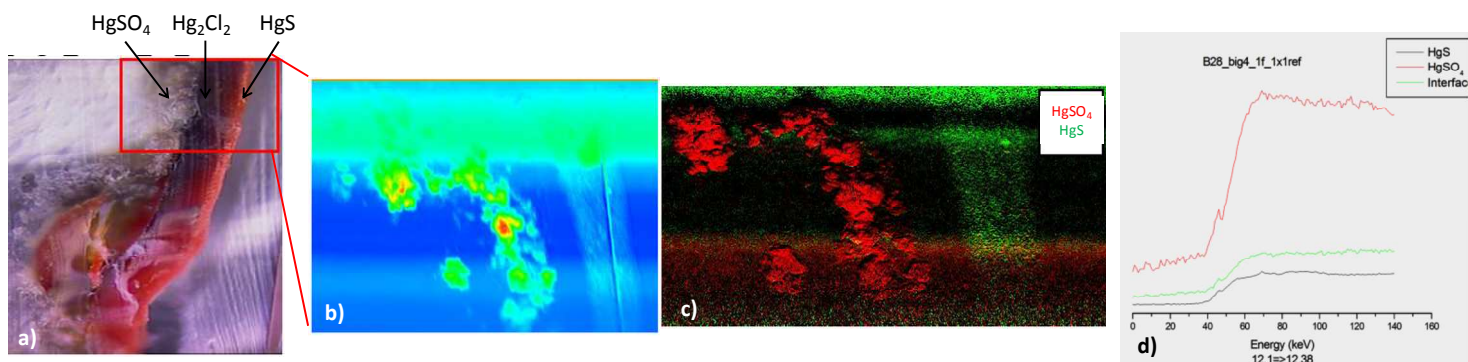


Fig.2: (a) Visible image of a model sample composed by 3 layers ($\text{HgS}/\text{Hg}_2\text{Cl}_2/\text{HgSO}_4$). (b) ROI image showing the sum of the spectra on the area analyzed (represented by the red square on (a)). (c) Map of HgS (green) and HgSO_4 (red) layers corresponding to specific energies selected by differentiating characteristics of each spectrum (d) of HgS (black) and HgSO_4 (red).

Multiple consecutive spectra were acquired to see if the analyses induced a degradation, but no difference was observed between them.

The analysis of data has still to be improved to have a better normalisation and correct the heterogeneity of the beam. With this improvement we hope to obtain more information on the original samples from the data acquired during this experiment.

[1] Marie Radeponet et al., 2011, Journal of Analytical Atomic Spectrometry.

[2] Vincent De Andrade et al., 2011, Analytical Chemistry.

[3] Marine Cotte et al., 2008, Journal of Analytical Atomic Spectrometry.