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*

## Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

### Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

## Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** "High energy resolution XAS to unravel lead pigments darkening and possible plasma reconversion on wall paintings" | **Experiment number**: HG-191 |
|---|---|---|
| **Beamline**: BM16 | **Date of experiment**: from: 15/11/2022 to: 21/11/2022 | **Date of report**: 1/02/2023 |
| **Shifts:** 18 | **Local contact(s)**: Mauro Rovezzi | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

**Maria Amelia Suzuki*** - Institute of Heritage Science ISPC-CNR

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**Report:**

***Experimental details***

The aim of the experiment was the investigation of the Pb speciation of lead based wall painting mock-ups treated with chemical and physical treatments (cold plasma and others) and compare the artificial alteration with naturally altered lead pigments coming from hystorical wall paintings. All of the investigated samples consisted of lead pigments applied with a casein binder on a lime based mortar substrate (dimensions 2 x 2 x (0.2-0.5) $cm^3$). Three different lead based pigments were investigated:

1) lead white ($2PbCO_3 \cdot Pb(OH)_2$) with a thickness of ca. 30-50 μm;
2) red lead ($Pb_3O_4$) with a a thickness of ca. 100 μm;
3) plattnerite ($PbO_2$), which is a common lead pigments alteration, with a thickness of ca 200 μm.

The case studies consisted of small fragments of 2 x 2 x 1 $mm^3$ and a powder (measured in a borosilicate glass capillary of 1 mm diameter) of altered lead pigment from a $17^{th}$ century wall painting from Sicily.
The samples were allocated in the experimental chamber attached to a holder with adhesive tape the experimental investigation proceeded operating X-ray Absorption Spectroscopy in Fluorescence mode carried out at the Pb $L_3$ edge (13035 eV). A Pb foil was allocated in the transmission geometry to check alignment every certain set of measurements. A set of consecutive XAS were performed in the same area to control, at the specific setting, the occurence of potential radiation damage. Once defined the operating condition, several spectra were acquired in different spots around the surface sample to evaluate the homogeneity of the treatment. The Pb standards were measured in fluorescence and prepared in pellets of boron nitrate at 5-10%. No particular experimental issues occurred. A total of ca. 2 h and a half of beam lost occurred. Never the less, all the samples were successfully investigated (24) as well as a set of relevant standards (11). For some of the samples, although the very thick Pb layer (paint layer varying between 50-200 um), the transmission signal was also detected and registered.

List of the investigated samples

| Sample name | Sample type | Type and number of measurements | Sample name | Sample type | Type and number of measurements |
|---|---|---|---|---|---|
| MC-TQ | Pristine paint | 12 FLUO | BC-4h_V | Alteration | 12 FLUO |
| PC-TQ | Pristine paint | 12 FLUO | BC-12h_V | Alteration | 12 FLUO |
| BC-TQ | Pristine paint | 12 FLUO | BC-8m_NBis | Alteration | 12 FLUO |
| MC-1h | Alteration | 12 FLUO + 12 FLUO low deg | BC-1h_N_Bis_barc | Alteration | 12 FLUO |
| MC-12h | Alteration | 12 FLUO + 12 FLUO low deg | BC-4h_NBis_barc | Alteration | 12 FLUO |
| BC-8m_V | Alteration | 12 FLUO | BC-12h_NBis | Alteration | 12 FLUO |
| BC-1h_V | Alteration | 12 FLUO | PC-PLN | Reconversion | 60 FLUO |
| BC-12h_NBis_barc | Alteration | 12 FLUO | PC-CW | Reconversion | 26 FLUO |
| BC-1h_V | Alteration | 12 FLUO | BC-8m_NBis_barc | Alteration | 12 FLUO |
| BC-12h_NBis_barc | Alteration | 12 FLUO | BA-P-1 | Case study | 12 FLUO |
| BA-P-4 | Case study | 1 FLUO | BA-P-2 | Case study | 18 FLUO |
| BA-P-5 | Case study | 3 FLUO | BC_8m_V_raddam | Radiation damage test | 10 FLUO |
| MC_4h | Case study | 3 FLUO | MC_1h | Radiation damage test | 10 FLUO |

***Preliminary survey of the obtained results***

For the lead oxides (both red lead and plattnerite mock-ups) the preliminary analysis of the XANES spectra provided significant information. The XANES acquired at the previous allocated beamtime at BM08 were of difficult interpretation as the XANES of all the most significant lead oxides compounds for our experiment presented very similar spectra **(FIG1a**). Thanks to the higher energy resolution we have been able to distinguish in a clear way the majority of the lead oxides (**FIG1b**).

For the red lead, the plasma treated samples do not show significant variation from the spectra of the pristine reference mock-up (**FIG 2a**). In the previous beamtime a small difference was observed between the Total Electron Yield (TEY) spectra and the fluorecence spectra (**FIG2b**), suggesting a very superficial enriched layer of Pb(IV) (in agreement with the type of plasma treatment applied). The comparison of the results of both data sets is very useful to evaluate the significance of small spectral changes and provide insights on the in depth stratification by comparing the spectra acquired in Fluorecence, transmission and TEY mode.

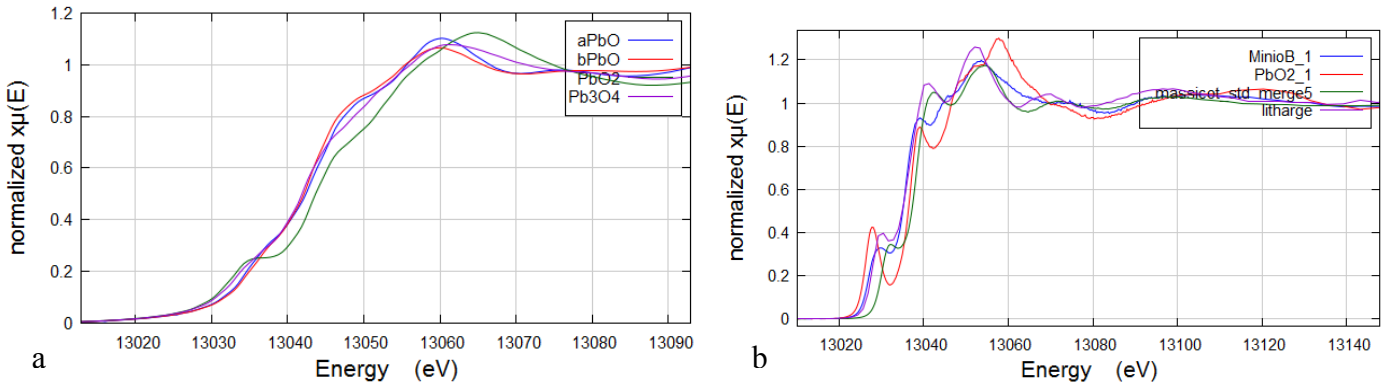


**Figure 1. a) the standard lead oxides of interest acquired at BM08; b) the same standards acquired at BM16.**

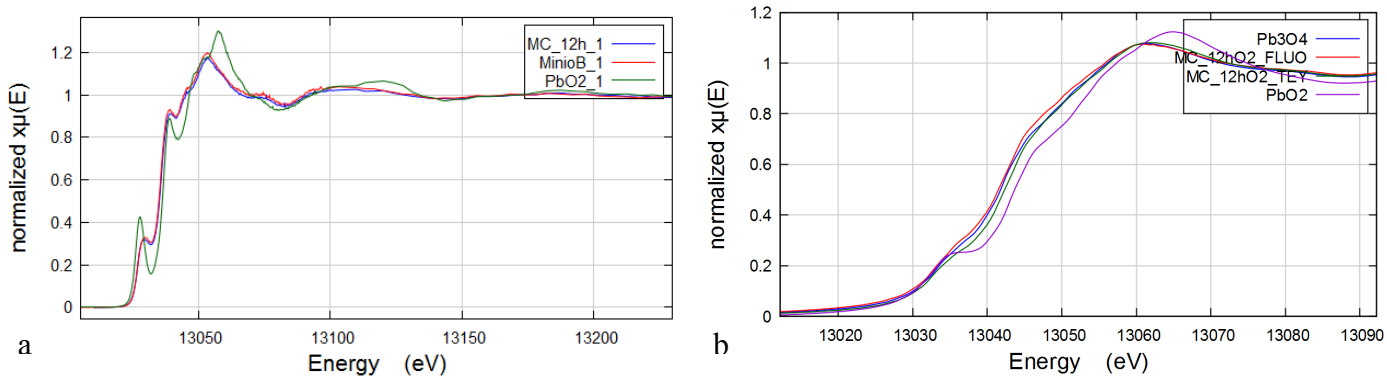


**Figure 2. a) the XANES spectrum obtained at BM16 in fluorescence mode of red lead treated with plasma (sample MC-12h) and the pristine red lead and plattnerite for comparison. b) XANES spectrum of the same mock-up both in fluorescence and TEY mode and the relevant standards.**

In the case of basic lead carbonate mock-ups the XANES give significant information suggesting a structural change of the carbonate to oxides maintaining the lead(II) oxidation state, but the artificial alteration do not cause further transformation to plattnerite.

Regarding the case study with potentially altered lead white, the signals obtained are very poor due to a very small amount of Pb in the painting layers and from the low signal-to-noise spectra acquired on the fragments there is no clear suggeston of the presence of Pb(IV) as alteration product of lead white but it could be present in a very small percentage below the detection limit.

***Preliminary conclusions***

Performing XAS on the treated mock-ups provided description of the structure and chemical nature of Pb to cheracterize the effects of physico-chemical artificial and natural lead pigments alteration. The comparison of the data sets acquired with the fluorescence and TEY signals at BM08 and the fluorecence spectra at high sectral resolution of BM16 and the complementary in-house XPS measurements on the mock-up suggests a higly superficial action of the plasma and different alteration products depending on the starting lead based pigment.