



## 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://www.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.



<b>Experiment title:</b> A spatially resolved study by $\mu$ -XRF and $\mu$ -XANES spectroscopy analyses at S K-, Cu K and As K-edges to understand the degradation process of Cu-/As-based oil paint systems.	<b>Experiment number:</b> HG-199	
<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: 02/11/2022 to: 07/11/2022	<b>Date of report:</b> 01/03/2023
<b>Shifts:</b>	<b>Local contact(s):</b> Olivier Mathon	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> * Letizia Monico, CNR-SCITEC, Perugia, Italy * Sara Carboni Marri, Department of Chemistry, Biology and Biotechnology, University of Perugia, Italy * Annelis Riós-Casier, Faculty of Design Sciences, Antwerp University, Belgium		



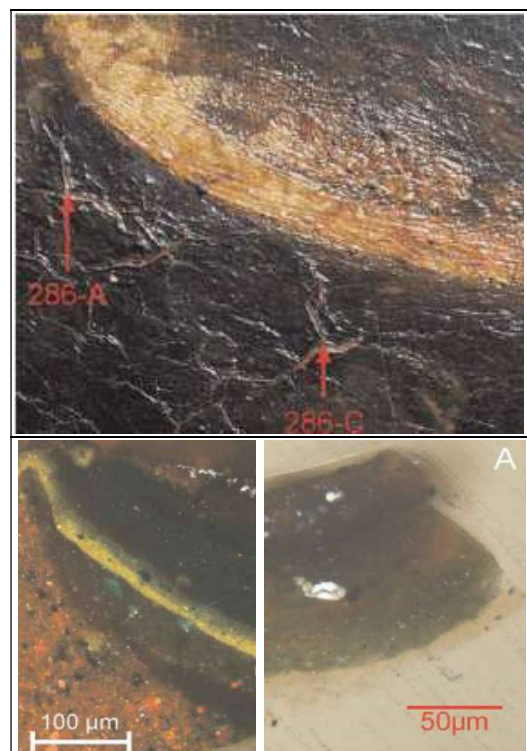
<b>Experiment title:</b> A spatially resolved study by $\mu$ -XRF and $\mu$ -XANES spectroscopy analyses at S K-, Cu K and As K-edges to understand the degradation process of Cu-/As-based oil paint systems.	<b>Experiment number:</b> HG-199	
<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 25/11/2022 to: 28/11/2022	<b>Date of report:</b> 01/03/2023
<b>Shifts:</b>	<b>Local contact(s):</b> Marine Cotte	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> * Letizia Monico, CNR-SCITEC, Perugia, Italy * Sara Carboni Marri, Department of Chemistry, Biology and Biotechnology, University of Perugia, Italy * Steven De Meyer, Department of Physics, Antwerp University, Belgium		

## 1. INTRODUCTION

During the two experiments, we investigated the alteration products of the copper and arsenic-based pigments Emerald Green ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$ ) and Scheele's Green (hereafter called "EM" and "SH", respectively) [1,2] in the oily medium after their exposure to artificially aging conditions (combination of humidity and light). The alteration phenomenon of these compounds, but in particular of EM, most widely used between impressionist and post-impressionist painters, have been observed in micro-samples taken from Théodore Rousseau's "Descente des Vaches" (1834-1835) (Figure 1). FT-IR analyses and As K-edge XANES imaging of these samples have identified  $\text{Cu}^{2+}$ -carboxylates and  $\text{As}^{+5}$ -compounds as possible degradation products of EM [3,4].

Despite the research already done, understanding the degradation mechanism of EM and SH paints still remains limited and more systematic research is required on the intrinsic properties of the pigments and the role played by the additives/synthesis residues, the binding medium and environmental agents.

To understand how the additives/synthesis residues and environmental parameters (light and/or humidity) affect the chemistry of EM and SH oil paints, we have performed  $\mu$ -XRF mapping and  $\mu$ -XANES analysis at Cu K-edge (ID21) and at As K-edge (BM23) on a series of artificially aged model samples made with EM and SH synthesized powders and with historical EM powders.



**Figure 1.** Enlargement of the sampled area (bottom left corner) of the painting "Descente des Vaches" by Théodore Rousseau (top); fragments taken from a sampled area (bottom).

## 2. EXPERIMENTAL

The list of samples that we have analyzed at beamlines ID21 and BM23 is reported below:

*a) EM and SH-based model samples (24 in total):* synthesized or historical powders mixed with linseed oil (4:1 weight ratio) before and after exposure to different aging conditions (combination of light and relative humidity); table 1 below summarized all the samples analyzed.

**Table 1.** List of the paint mock-ups analyzed.

Oil paint mock-ups	Not aged	Aging conditions		
		UVA-Vis light (T=25° C, 45% RH)	UVA-Vis light (T=25° C, 95% RH)	95% RH, 40° C
EM-historical (x2)*	X	X	X	X
EM-synthesized (x 3)	X	X	X	X
SH-synthesized (x1)*	X	X	X	X

\*EM= Emerald green; SH= Scheele's green

*b) set of Cu-, and As-reference powders and of pigment powders used to prepare mock-up samples (ca. 20 in total).*

All model paint mock-ups were investigated as embedded resin thin-sections (thickness of ca. 5  $\mu\text{m}$ ) both at beamline ID21 and BM23 Each reference powder was analyzed as a thin film (thickness < 50  $\mu\text{m}$ ) fixed on sulfur-free tape.

• *ID21-experimental set-up.*  $\mu$ -XRF and  $\mu$ -XANES measurements at Cu K-edge (8.978 keV) were performed at the scanning X-ray microscope (SXM) end-station using a fixed exit double-crystal Si(111) monochromator. The incident beam was focused with Kirkpatrick-Baez (KB) mirrors down to a diameter of ca.  $0.5 \times 0.5 \mu\text{m}^2$  (h $\times$ v). The energy calibration was performed at the Cu K-edge by setting the position of the peak maximum of the first order derivative spectrum of copper foil at 9.00545 keV.

XRF signals were acquired in the horizontal plane and at 69° with respect to the incident beam direction using a single energy-dispersive silicon drift detector (Xflash 5100, Bruker).

Single point  $\mu$ -XANES spectra were acquired in XRF mode by scanning the primary energy around the Cu K-edge (8.95-9.2 keV; energy step: from 0.5 to 1 eV).

Full spectral XRF mode XANES mapping experiments were performed by tuning the energy of the incident beam around the Cu K-edge. Maps of the same region of interest were collected by employing 20-30 ms/pixel at ca. 120 different energies with a variable energy step (from 1 to 4 eV).

• *BM23-experimental set-up.*  $\mu$ -XRF and  $\mu$ -XANES investigations at As K-edge (11.8667 keV) were performed using a fixed exit double-crystal Si(111) monochromator and an incident beam with a diameter of ca.  $3 \times 3 \mu\text{m}^2$  (h $\times$ v). XRF signals were collected by means of both a 13-element Ge detector and Si drift-diode array detector.

$\mu$ -XANES spectra were recorded in XRF mode by scanning the primary energy across the As K-edge (11.83-12 keV; energy step: 0.5 eV). The XANES spectra were recorded by following a line across the thin-section, with 5  $\mu\text{m}$  step in the bottommost side of the paint (bulk area) and with 2.5  $\mu\text{m}$  step in its uppermost part (i.e. closer to the surface).  $\mu$ -XRF maps of the same region of interest were collected using 200 ms/pixel at the three following energies: (i) 11.8759 keV and (ii) 11.87961 keV to favor the excitation of As<sup>3+</sup> and As<sup>5+</sup>-species, respectively and (iii) 12.0 keV to obtain the XRF intensity of all As-species.

ATHENA [5] was employed to perform the normalization of the XANES spectra, while the processing of the elemental maps was performed using the PyMca software.

### 3. RESULTS

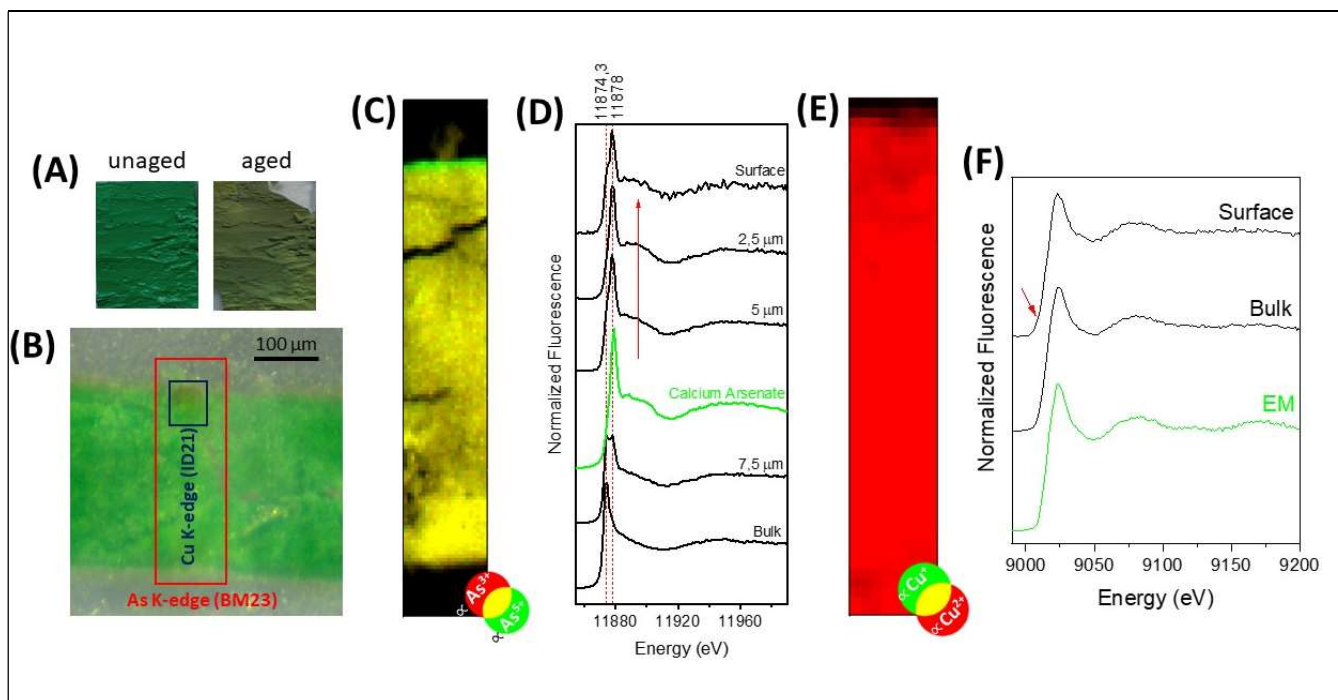
#### *Artificially aged mock-ups.*

As an example, Figure 2 shows the SR  $\mu$ -XRF and  $\mu$ -XANES results obtained from the EM-synthesized oil mock-up after photochemical aging with 95% of relative humidity (cf. Table 1),.

Before aging (results not reported), Cu- and As-speciation investigations reveal that, as expected, only Cu<sup>2+</sup> and As<sup>3+</sup>-species are present in the sample.

As a result of the aging, a strong discoloration of the original green color has taken place at the paint surface (Figure 2A-B). The As oxidation state maps (Figure 2C) along with  $\mu$ -XANES investigations (Figure 2D) reveal that a complete conversion from As<sup>3+</sup> to As<sup>5+</sup> has occurred at the surface, while As<sup>3+</sup>-species, related to the unaltered EM pigment, are dominant in the bulk green paint. These As<sup>5+</sup>-containing alteration products are ascribable to arsenates, as outlined by the similarities with the spectral features of calcium arsenate reference powder (green line in Figure 2D).

On the other hand, no evident changes are observed in the oxidation state of copper, that is present across the paint stratigraphy in the bivalent state (Figure 2E). Slight changes are only visible in the pre-edge region of the spectra recorded in the uppermost 5  $\mu\text{m}$  of the paint surface (i.e. where also As<sup>5+</sup>-compounds were found; see red arrow in Figure 2F), thus suggesting changes in the coordination of Cu<sup>2+</sup>.



**Figure 2.** (A) Photographs of emerald green oil paint mock-ups (left) before and (right) after the artificially aging treatment with UVA-Visible light and 95% of relative humidity. (B) Photomicrograph of a cross-section obtained from a fragment of the aged paint shown in (A). (C) Composite RG As-speciation maps (step size:  $2.5 \times 2.5 \mu\text{m}^2$ , exp. time: 200 ms/pixel) and (D) selection of As K-edge  $\mu$ -XANES spectra from the first micrometers below the surface and one spectrum (green) from a reference compound (data recorded at BM23). (E) Composite RG Cu-speciation maps (step size:  $1 \times 0.5 \mu\text{m}^2$ , exp. time: 20 ms/pixel) and (F) selection of Cu K-edge  $\mu$ -XANES spectra, one from the surface and another from the bulk, compared to the profile of reference EM powder (data collected at ID21).

Comparable results were obtained from the EM paints aged with UVA-visible light and environmental relative humidity; in the EM mock-ups aged in the dark and with high relative humidity, no arsenic oxidation has occurred instead but the formation of  $\text{As}_2\text{O}_3$  crystals was observed (data not reported).

Concerning SH mock-ups, they show a very similar reactivity with respect to EM samples, by revealing the formation of a superficial  $\text{As}^{5+}$ -rich alteration layer (in general thicker than the one of EM mock-ups) after treatment both in the presence and absence of light. In addition, in some of SH samples, the oxidation of  $\text{As}^{3+}$  to  $\text{As}^{5+}$  occurred along with the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  (data not reported).

Data processing is still under elaboration and the corresponding results will be published soon.

## REFERENCES:

- [1] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall. *Pigment Compendium: A Dictionary of Historical Pigments*. Elsevier Butterworth-Heinemann, 2004, p. 228. [2] C. Herm. *Emerald green versus Scheele's green: evidence and occurrence*. Proceedings of the 7th interdisciplinary ALMA conference, Bratislava, Slovakia, October 17–19, 2019 – Acta Artis Academica 2020, 189–202. [3] K. Keune et al., *Studies in Conservation* (2013), 58, 199–210. [4] K. Keune et al., *Heritage Science* (2016), 4, 10. [5] B. Ravel, M. J. Newville, *Journal of Synchrotron Radiation* (2005), 12, 537–541.