

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.



	Experiment title: A study of the distribution of Mg and S compounds	Experiment number: EC1060
	Beamline: ID21	Date of experiment: from: 7/2/2013 to: 12/2/2013
	Shifts: 15	Local contact(s): Dr. Marine Cotte
Date of report: 28-2-2014 <i>Received at ESRF:</i> 28-2-2014		

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Report:

Recent research suggests that paints that contain magnesium carbonate added as an extender undergo deterioration that leads to the formation of hygroscopic compounds of magnesium sulphate hydrate. The primary reaction known is the formation of magnesium sulphate heptahydrate (espomite) from magnesium carbonate ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$) present as an extender in the oil paints (G. Silvester, A. Burnstock, L. Megens, T. Learner, G. Chiari, K.J. van den Berg. A cause of water-sensitivity in modern oil paint films: the formation of magnesium sulphate. *Studies in Conservation* 59;1 (2014) 38-51). The source of sulphur for the formation of these hygroscopic magnesium compounds may be from atmospheric sulphur dioxide or alternatively from the residual sulphurous side products from pigment preparation. The sulphates compounds are present on the surface of paintings and paint samples produced by manufacturers. The paintings and samples exhibit significant sensitivity during cleaning treatments using water and protic solvents.

The aim of the experiment was to detect using μ -XANES the presence of sulphur-containing compounds in oil paints. Question was whether these compounds are formed primarily on the surface and if so to what depth. An additional aim was to investigate to what extent atmospheric sulphur dioxide had reacted with the organic surface layer, the 'skin of medium'.

Experiment

Samples were prepared into thin cross sections from paints using a microtome at ID21 (E. Pouyet et al., The combination of FTIR and X-ray micro-spectroscopies for the analysis of thin sections of paintings at the ID21 beamline, European Synchrotron Radiation Facility. Poster presented at the TECHNART conference Amsterdam, 2013) and perpendicularly applied on a sample holder to allow for μ -XANES and μ -XRF point analysis and mapping in transmission.

Samples were used from a series of original Winsor&Newton student quality oil paintouts on canvas, applied in dec. 1964/jan 1965. Oil paints contained pigments such as lead chromate yellow, prussian blue, raw sienna, lead carbonate white, chromium oxide green. Most prominent fillers were barium sulphate and magnesium carbonate.

Existing cross sections from oil paints from paintings and from paint reconstructions embedded in polyester resin were also microtomed and applied on the sample holder.

For μ -XANES and μ -XRF analysis the monochromatic primary beam was obtained through a fixed-exit Si(111) double crystal monochromator. Energy ranges were typically 2.46-2.53 eV for S. μ -XANES spectra were recorded in the fluorescence mode and decomposed as a linear combination of a set of sulphur reference compound spectra.

μ -XRF signals were collected in the horizontal plane perpendicular to the incident beam direction with an energydispersive Silicon Drift Diode detector to create elemental maps. X-ray fluorescence spectra were fitted using the PyMCA software. Batch fitting of the XRF spectra corresponding to each pixel of the 2D maps yielded elemental maps.

While experiments were also planned on μ -FTIR, initial results were too limited and the rest of the time was focussed on the XANES and XRF experiments.

Results

μ -XANES and μ -XRF analysis of cross sections of paints showed thin surface layers of sulphur-rich surfaces. Initial analysis of standards (not shown) indicated potential to distinguish between Ba (optimal K-Edge energy 2.4846 keV) and hydrated Mg sulphates (2.4836 keV).

Figure 1 shows the maps of a chrome yellow paint sample (containing lead chromate, barium sulphate and magnesium carbonate) which was partly surface cleaned. Although S appears to be evenly distributed (1a), the Mg sulphates are more prominent on the uncleaned paint, whereas it has been removed on the cleaned part, revealing barium sulphates underneath (1b).

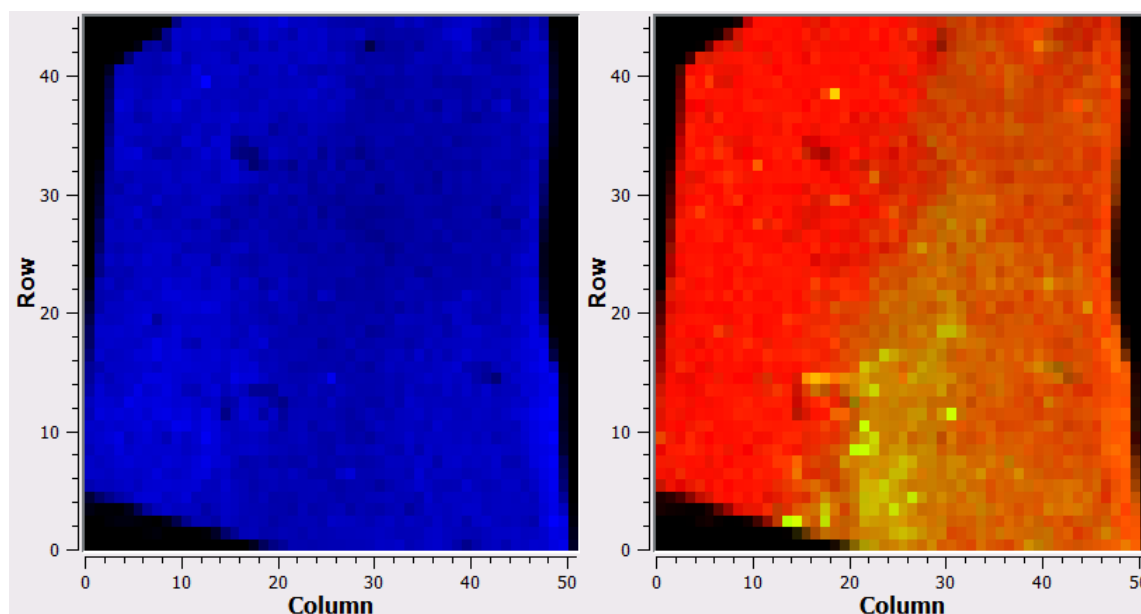


Figure 1. K-Edge μ -XANES mapping of the surface of a partially cleaned chrome yellow Winsor&Newton paint. a) S, at 2.53 keV; b) red: S, at 2.4836 keV; yellow: S, at 2.4846 keV.

Mg carbonate containing paints were found to contain hydrated Mg sulphate on the surface, in layers of typically 3-5 μ m. However these sulphates are most prominent on relatively lean paints.

Figure 2 shows the images of chrome yellow in cross section. The paint shows a thin layer of Mg sulphate on the surface. The Mg sulphate particles are clearly detected in μ -XRF combining the fluorescence signal for S (blue) with those of Mg (green).

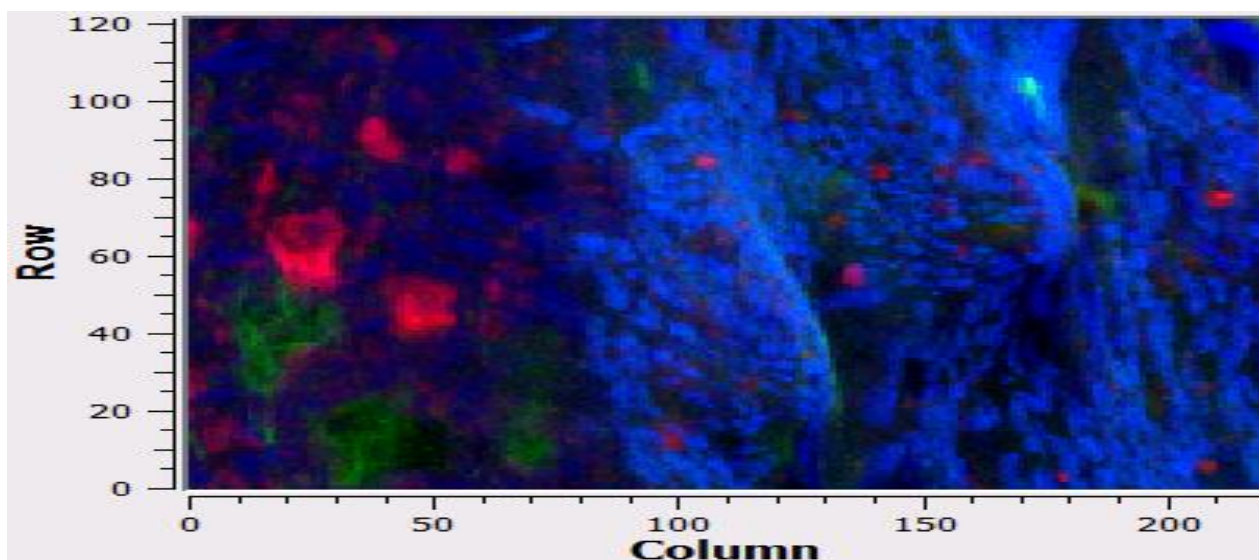


Figure 2. K-Edge μ -XANES/XRF mapping of the cross section of a chrome yellow Winsor&Newton paint. left hand side: bulk below surface, containing aluminium containing additive, Mg from Mg carbonate and S from Ba sulphate; right hand side: surface (the sample is slightly tilted showing the surface). Green: Mg, Blue: S; light blue: Mg and S; Red: Al.

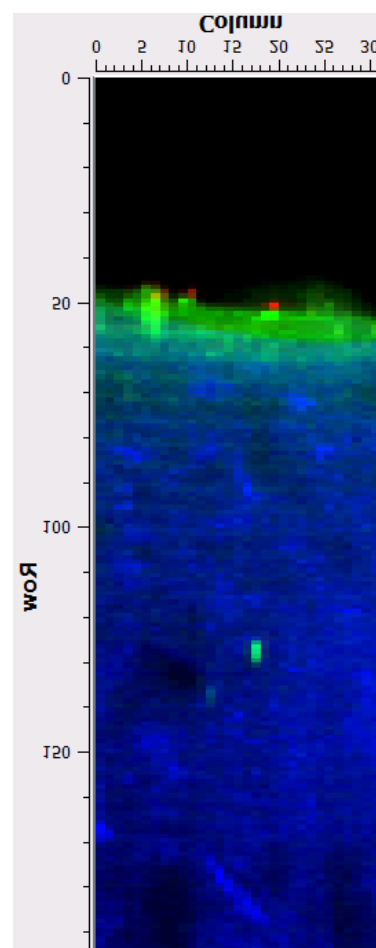
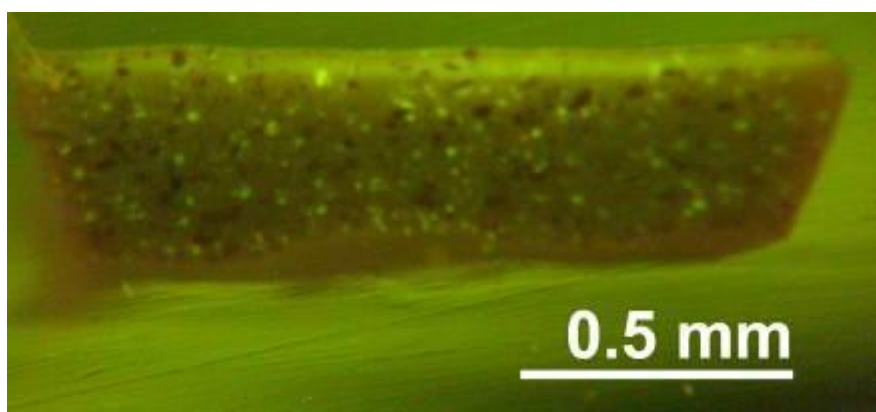


Figure 3. a) Micrograph of cross section in ultra-violet light, W&N raw Sienna, 1964/5. There is a strong fluorescence in UV light in a band below the surface of the paint. b) K-Edge μ -XANES/XRF mapping of the cross section (note: surface below); red = Sulphide at 2.4737 keV; green is sulphite at 2.4787 keV; blue is Mg. Please note that the sulphite is probably a sign of damage of sulphate by prolonged radiation.

Figure 3a shows a cross section of a relatively medium rich paint containing natural 'raw Sienna': hydrated ferric oxides and silicates, with Mg carbonate filler. Here, Mg sulphate is detected, also in its sulphite form, probably generated in the source due to radiation damage. In addition, sulphide is detected on the surface, not

associated with Mg. We speculate that this indicates the formation of an organic sulphide due to the reaction of the curing binding medium with atmospheric sulphur (W.H. Simendinger and H. Balik, Chemical reaction kinetics of sulfur dioxide and oxygen with unsaturated drying oils, Journal of Coatings Technology 66 (1994) 39–45). Further research to explore the influence of this side reaction on the properties of the oil paint and oil paint surface is required.

Summary of the outcomes

- The experiments were successful in that it was possible to detect $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ (epsomite) on the surface of oil paint containing MgCO_3 . No epsomite was detected in the bulk of the paint. This supports the hypothesis that epsomite is mainly formed from atmospheric SO_2
- Typical thickness of the layer containing epsomite crystals was few μm .
- Epsomite can be detected in the presence of other sulphates such as barium sulphates but not mainly by association with the elemental Mg mapping
- The epsomite was detected primarily on medium-poor paint surfaces containing MgCO_3 . A skin of medium forms a barrier for SO_2 to react with MgCO_3 .
- On medium-rich oil paints, an organic layer containing elemental sulphur, probably organic sulphide, was detected; layer thickness 1-3 μm .
- In thin sections of samples in polyester resin no sulphates could be detected, due to disturbance (dissolution) of the epsomite into the embedding medium. Since all samples were embedded in resin, these experiments failed. Making clean thin sections of paint was the only good approach. This experiment further exemplifies how critical sample preparation can be for such samples.

Some additional results were obtained at ID13 with $\mu\text{-XRD}$

All results are included in a manuscript which is in preparation, in collaboration with Ms E. Pouyet and Dr. M Cotte.

Outlook

The experiments showed great potential for the analysis of paint surfaces affected by atmospheric pollutants. Future applications for beamtime will study the effect of NO_x and SO_2 on paints containing pigments and fillers Zn, Pb and other elements and the effects of cleaning materials and procedures. The formation of sulphides and other products in the organic fractions will be explored further using FTIR, and investigated to what extent these fractions are removable in cleaning procedures.