

## 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.



pigment particles in the heterogeneous paint layers (Figure 2). XANES spectra (fluorescence mode; microbeam) were subsequently gathered on such selected particles (Figure 3), specifically utilizing the microbeam to remain localized solely on ultramarine. The spectral profiles indeed relate to those from the heat-treated samples with the spectra of the Potter sample (red trace) and the Steen sample (blue trace) most like those of the 750 °C and non-heated samples, respectively. Significantly, these relationships suggest that paint containing pigment heat-treated to 750 °C is less susceptible to degradation than that containing unheated pigment. Such a discovery motivates the need for further studies of historical paint samples.

In addition to these generally positive results, there were a few obstacles faced during the measurements that complicate the interpretation of the data described above. Notably, issues arose relating to beam damage when employing analyses with a microbeam (e.g. for all analyses of the historical samples). For instance, Figure 4 presents spectra gathered from the unheated pigment sample with either the microbeam (red trace) or the macrobeam (blue trace). Beam damage is recognizable by the appearance of a peak at 2478.0 eV, attributed to sulfite formation; this type of beam damage is not uncommon in sulfur K-edge XANES as sulfate is susceptible to photoreduction. When exposed to the microbeam, a peak at 2470.7 eV also becomes prominent relative to the spectral shape observed using the macrobeam. Importantly, this newly produced peak is at the same peak position as the peak defining differences between the heated and unheated samples measured solely with the macrobeam (recall Figure 1). Such an artifact also hinders our interpretation of spectra from the historical samples, which were only measured with the microbeam and produce relatively intense sulfite peaks. Lastly, the detection of these artifacts in the pigment samples were not consistent from particle to particle suggesting an inherent heterogeneity within and between the pigment particles due to sulfur speciation and associated minerals. The avoidance of beam damage and characterization of heterogeneity would be best achieved employing full-field XANES on thin sections of embedded paint samples.

### Output:

‘New insights into the Ultramarine Sickness’, K. Keune, ChemCH2016 conference, 6-8 July 2016, Antwerp, Belgium (invited lecture).

‘Ultramarine Disease’, A. Gambardella, Internal meeting AkzoNobel, 6 October 2015, Deventer, Netherlands.

‘Ultramarine Sickness as Explored by S K-edge XANES’, A. Gambardella, Gordon Research Conference, 31 July -5 August 2016, Maine, USA (poster).

### Figures:

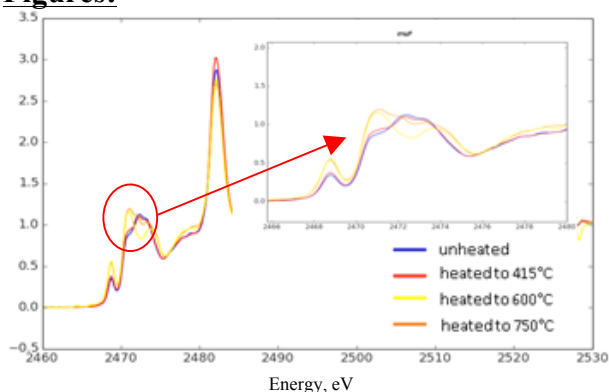


Figure 1. XANES spectra (fluorescence mode; macrobeam) of heat-treated ultramarine pigments.

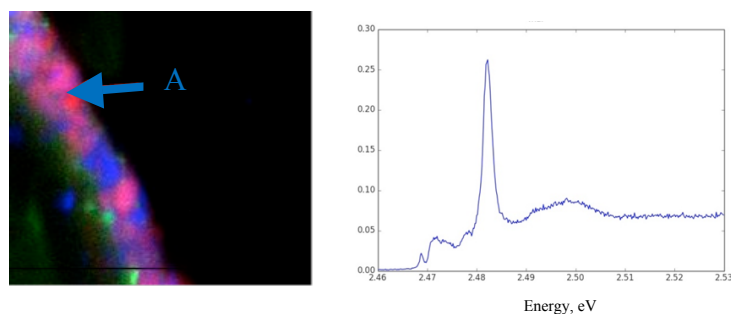


Figure 2. (left) Identification of lazurite particle with  $\mu$ -XRF in the cross section of Jan Steen painting (1650) (Cl (green), Si (blue), S (red)) and (right) XANES spectrum (fluorescence mode; microbeam) of that particle.

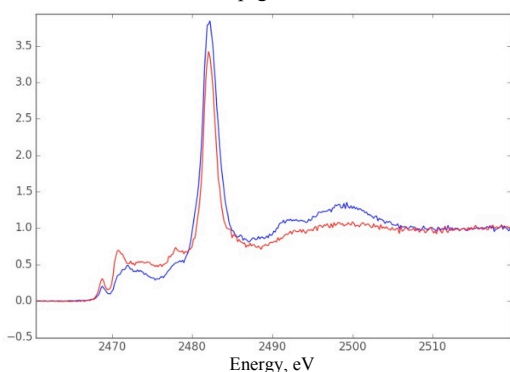


Figure 3. XANES spectra (fluorescence mode; microbeam) of degraded and intact ultramarine in paintings by Jan Steen (blue) and Paulus Potter (red), respectively.

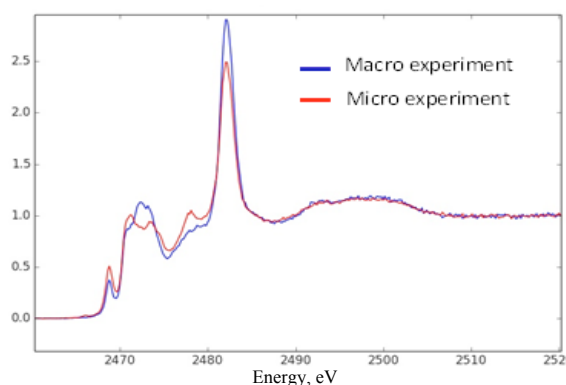


Figure 4. XANES spectra (fluorescence mode) of unheated ultramarine pigment using microbeam (red) and macrobeam (blue).