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

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.

ESRF	**Experiment title:** Investigation of the influence of historical prepared ultramarine on the 'ultramarine sickness' by the sulfur speciation	**Experiment number**: HG-94
Beamline:	**Date of experiment**: from: 02 Feb 2017 to: 06 Feb 2017	**Date of report**: 1 March 2018
Shifts: 6	**Local contact(s)**: Dr. Marine Cotte	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Katrien Keune*, University of Amsterdam, Rijksmuseum, The Netherlands

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Objective & Expected Results:

Oil paint with the exclusive blue pigment ultramarine is often found to be degraded. This degradation phenomenon, known as "ultramarine sickness", is observed for instance in Dutch paintings by Jan van Eyck (1390-1441) and Jan Steen (1626-79) with ultramarine from its natural source, lapis lazuli. Our research aims to identify the mechanism of such degradation so that we may ultimately determine a means for better preserving works containing ultramarine. The degradation mechanism is not well-understood, and we hypothesize that the ultramarine pigment catalyzes this degradation phenomenon. Because historical records describe various methods of pigment preparation, we are also interested in identifying markers in the pigment that correspond to the method of preparation and determining if a relationship exists between pigment preparation and the state of degradation.

Sulfur K-edge XANES was chosen to investigate the potential link between the historical preparation of the ultramarine pigment and the "ultramarine sickness." According to literature, there is a correlation between heat treatment, the blue hue, and sulfur speciation. Our previous studies (HG62) show a relationship between the sulfur species in and the heat pre-treatment of the ultramarine. In the most recent beamtime, samples from intact and degraded ultramarine paints were studied to correlate the "ultramarine sickness" with the profile of sulfur species and thus with the pre-treatment of the pigment. Besides the micro-beam mode, the full-field set-up was applied to both historical and lab-prepared samples to overcome beam damage, enhance the signal to noise in averaged spectra, and investigate heterogeneity.

Results:

Sulfur K-edge XANES spectra were gathered in three modes—micro-beam (fluorescence), attenuated micro-beam (fluorescence), and full-field (transmission)—on a total of 30 historical paintings (samples prepared as cross-sections) from Dutch collections of the Rijksmuseum Amsterdam and the Mauritshuis in the Hague. In addition, each of the 4 pigments prepared from heat-treated lapis lazuli rock (i.e. no heat, 415, 600, and 750 ˚C), which were analyzed with defocused and micro-beam modes in the previous beamtime, were measured under full-field mode. Lastly, samples taken from painted mock-ups of linseed oil with the non-heated or the 750 ˚C pigment following accelerated aging were also measured under full-field mode.

Unlike raw pigment samples, pigment grains within paint layers, which are surrounded by potentially interferring sulfur signals, require a small beam spot size for analysis. The micro-beam provides this focused spot size, however, as observed briefly in our previous beamtime, it can produce artifacts due to damage. In our current work, we further studied the susceptibility of lazurite to beam damage from the micro-beam. 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. Consecutively gathered spectra from a single lazurite grain within a historical paint layer using the microbeam (Figure 1) shows the presence and increase of the peak at 2478.0 eV (sulfite) upon initial and prolonged irradiation, respectively. Also, upon initial exposure to the microbeam, the peak at 2470.7 eV—characteristic for the sulfur composition in lazurite—again appears over-represented with respect to the spectral shape typically observed using the defocussed beam.

To avoid beam-damage while keeping the small spot size, the historical paint samples were measured with the attenuated micro-beam. This mode, however, results in spectra with low signal to noise, and thus, it was thus necessary to gather and average multiple spectra for a given sample. Prior to collecting XANES spectra, we first performed micro-XRF measurements on each sample to identify the location of ultramarine pigment particles in the paint layers. Figure 2 shows the averaged spectra for 21 historical paint samples. The peak near 2469 eV and the envelope of peaks between 2470 and 2475 eV are characteristic for lazurite and, as concluded from our previous results, are influenced by pigment treatment. The dotted lines in Figure 2 help highlight variation in the spectral patterns between samples and reveal that sample SKA3988_6b is most different from the others. Comparing the spectra to those from the previous beamtime, the spectral profile of SKA3988_6b is consistent with pigment from non-heated rock while the other spectral profiles are more consistent with spectra from pigment of rock heated to some degree. To determine the utility of sulfur speciation as a marker for ultramarine degradation, we are currently looking more closely at the visible state of degradation in the corresponding paintings and how such relates to the observed spectral profiles.

Full-field mode provided us the means to obtain averaged spectra with higher signal to noise relative to the attenuated micro-beam and still avoid beam damage. As this mode requires making thin-sections, which is microdestructive of our paint cross-sections, only 6 samples from historical paintings were analyzed. The 4 prepared pigment samples were also measured, producing averaged spectra from their full-field images consistent with the defocused results from the previous beamtime. In addition, averaged spectra of the aged mock-ups of the non-heated and 750 ˚C pigments were obtained and are very similar to their raw pigment counterparts, significantly showing the potential to use sulfur speciation as a marker for pigment preparation in aged historical samples.

In addition, full-field mode was an essential tool for exploring heterogeneity—between and, when possible, within lazurite particles both from historical samples and prepared pigment—as such details are not obtainable at the scale observed with defocused mode and are not reliable under micro-beam mode. This was necessary to ensure the statistical significance of differences observed between averaged spectral patterns. Close examination of the spectra comprising the full-field images of the 4 prepared pigment samples reveals heterogeneity of the spectral shapes within a sample, Figure 3. We are currently look more deeply into potential heterogeneity within the historical samples. As the samples are small, the lazurite particles are difficult to precisely select, and other sulfur-containing pigments are present, such analysis is requiring a robust statistical processing of the data.

Output:

‘Sulfur K-edge XANES to identify preparation of ultramarine pigment in historical paints’, *Manuscript in progress for Chem. Comm.* A. Gambardella, K. Schnetz, K. Keune.

‘The degradation of ultramarine paints: a catalytic process?’, K. Keune, Utrecht University, 1 February 2018 (invited lecture).

‘Ultramarine disease as influenced by pigment preparation’, A. Gambardella, ICOM-CC, 4-8 September 2017, Copenhagen, Denmark (poster).

‘Ultramarine degradation: toward understanding the mechanism and identifying markers’, A. Gambardella, 6th ALMA Conference, 31 May-2 June 2017, Brno, Czech Republic (presentation).

‘Analytical challenges in studying degradation processes in paintings: ultramarine disease’, A. Gambardella, Technart, 2-6 May 2017, Bilbao, Spain (presentation).

Figures:

Figure 1. Spectra gathered consecutively at the same spot on a lazurite grain with the micro-beam revealing beam damage.

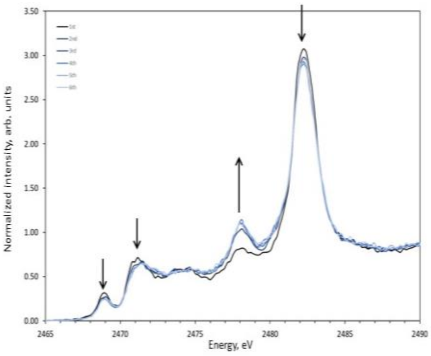

Figure 2. Example averaged spectra (approx. 10 each) for lazurite within historical paint samples from the attenuated micro-beam.

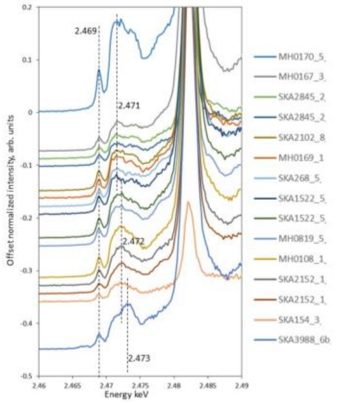

Figure 3. Example spectra from full-field mode averaged over two different lazurite grains in pigment from rock heated at 750 ˚C.