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ESRF

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.

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https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

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The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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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.

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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:** Micro-XANES and FTIR investigation of degraded smalt from Baroque painters	**Experiment number**: HG- 9
Beamline: ID21 (SXM)	**Date of experiment**: from: 07/05/2013 to: 13/05/2011	**Date of report**: 22/01/2013
Shifts: 18	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

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Report:

Introduction:

Smalt, a ground blue cobalt-containing potassium-based glass, was used in European painting from the middle of the 16th century. Prominent painters such as Rembrandt, Rubens, El Greco and Veronese used it frequently. First intended as a substitute for the expensive natural blue pigment *ultramarine*, it was soon seen to discolour in oil media. Such a discolouration can significantly influence the colour balance and therefore the complete appreciation of a painting. E.g. 'Homer'(see Fig. 1), currently a fairly monochrome earth-tone painting by Rembrandt, is likely to have been painted in a much more 'regular'/colourful manner than its current state allows to assume.

Figure 1: Homer (Rembrandt, 1663;Mauritshuis, Den haag, NL)

Since smalt is a glass-based pigment, its degradation process is similar to the degradation of historical window panes. K-leaching from inside the grain, creates a discoulered K-poor rim around a core that retains its original blue colour.

It was demonstrated by Figueredo et al. [1] and Robinet et al. [2] that this degradation process is accompagnied by the change in chemical environment of Co, namely from a tetrahedral towards an octahedral coordination. Moreover Figueredo et al. suggested that in the Co-K pre-edge two separate contributions can be distinguished at ~7709 eV and ~7712 eV of respectively Co^{2+} in tetrahedral coordination and Co^{2+} and Co^{3+} in a octahedral coordination.

The main aim of the experiment was to test if it a similar trend in the pre-edge can be seen in the degradation of smalt in paintings, in order to better understand the degradation process.

Quality of measurement/data:

A Si(111) double crystal monochromator was used, having an energy resolution ($\Delta E/E$) of about 10^{-4}. A transmission XANES spectrum of a metallic Co foil was recorded to provide an accurate energy calibration for all the recorded spectra; the first inflection point of the Co-K edge was set to 7709 eV [3]. All reference materials were measured in transmission mode without focusing and with a pinhole of 200 µm, resulting in a photon flux of $9x10^9$ ph/s.

The thickness of all embedded smalt samples only allowed measurement in fluorescence mode with the sample oriented at 45° to the incoming beam; the fluorescence signals were collected using a Silicon Drift Detector at an angle of 45° with respect to the sample surface. KB focusing optics were used for the X-ray mapping en XANES point analysis, resulting in a spot size of 0.6 x 0.3 μm^2 (hor. x vert.) and a photon flux of $1.8x10^9$ ph/s.
Spectra were collected from 7.65 keV to 7.9 keV (7.65 keV - 7.70 keV, 0.7 eV/step, 0.25 s/step; 7.70 keV - 7.72 keV, 0.2 eV/step, 0.25 s/step; 7.72 keV - 7.74 keV, 0.5 eV/step, 0.19 s/step; 7.74 keV - 7.9 keV, 0.7 eV/step, 0.1 s/step).
Prior to XANES point measurements, detailed X-ray maps were recorderd using step sizes down to 0.3 x 0.3 μm^2 (in general 1 x 1 μm^2) , with dwell times of 150 ms – 600 ms, depending on the necessary resolution needed to visualise the Co present and the time needed to record the X-ray maps.

Status and progress of evaluation:

For XRF mapping, the PyMCA software package was used for the fittting of the XRF spectra. After scanning the surface of the resins with the focused x-ray beam, the X-ray fluorescence spectra of the Si drift diode array are fitted with PyMCA and the resulting elemental maps can be calculated from the fitted intensity. For the XANES measurement, a point of interest is scanned with a X-ray beam varying in energy. ROI fitting around the Co Kα line (~6.6 – 7.2 keV) was performed.
All acquired spectra, transmission and fluorescence, were normalised by means of the software package ATHENA. An edge-step normalization was performed by a linear pre-edge subtraction and by regression of an (in general) third degree polynomial beyond the edge [4].

Results:

Samples were analysed from several smalt containing paintings (Table 1). Amongst others, Co XANES was performed on grains of a completely decolourised (brown) sample (Rembrandt, Homer) and on blue (Van Dyck, Portrait of Quinten Simons) and dark blue grains (Holbein, Nobleman with hawk) (Fig. 3). Prior to any XANES measurements, X-ray maps were recorded on cross-sections of embedded paint samples. In this manner smalt grains could be located, being cobalt containing potash-glass. The latter implies that during degradation, K can leach out of the glass network. Therefore the elements of interest to examine the degradation were mainly Co and K. Si-K and Pb-M maps were used to localise the grains (Fig. 2), since often it is difficult to interpret the Co-K distribution maps due to the higher information depth.

Painter	Painting
Jan Steen	A pig belongs in the sty
Unknown artist	Trippenhuis ceiling
Rubens	Education of Mary
Sebastiano del Piombo	Ritratto di Michelangelo
Giovanni Pellegrini	Dwindling Night
Anthony Van Dyck	Portait of Quinten Simons
Rembrandt	Homer
Holbein	Jane Seymour
Holbein	Nobleman with hawk

Table 1: Overview of the origin of all the measured paint samples.

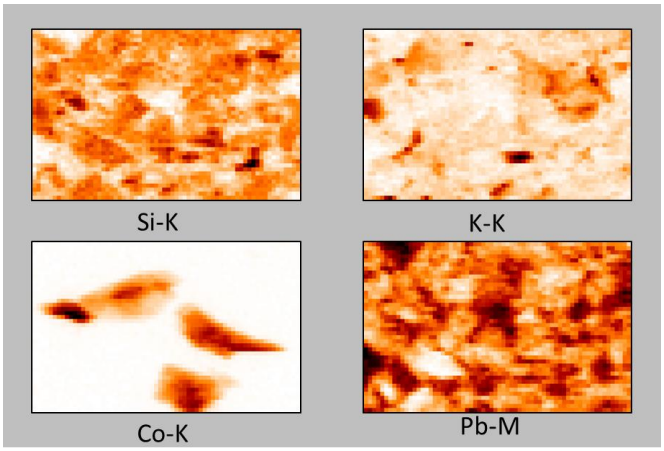

Figure 2: Elemental distribution maps of Si, K, Co and Pb of sample of Van Dyck.

In figure 3 (a-c) the visual microscopy images, as well as the elemental distribution maps of Si, K and Co (d-f) of the three described smalt grains are given. Complete and profound K-leaching can be observed in the grains of respectively the Rembrandt (Fig. 3f) and Van Dyck (Fig. 3d) samples, while no leaching is present in the Holbein sample (Fig. 3b).
A XANES spectrum was recorded on each of the examined smalt grains (Fig. 3g). Degradation can be observed as a lowering of the intensity of the

shoulder at ~ 7735 eV, but more clearly as a decrease in the pre-edge intensity at ~ 7709 eV. The latter is a less sensitive to possible normalisation problems. While the spectrum of the Holbein sample in the pre-edge region still resembles that of smalt, the Rembrandt and Van Dyck sample spectra clearly show alteration.

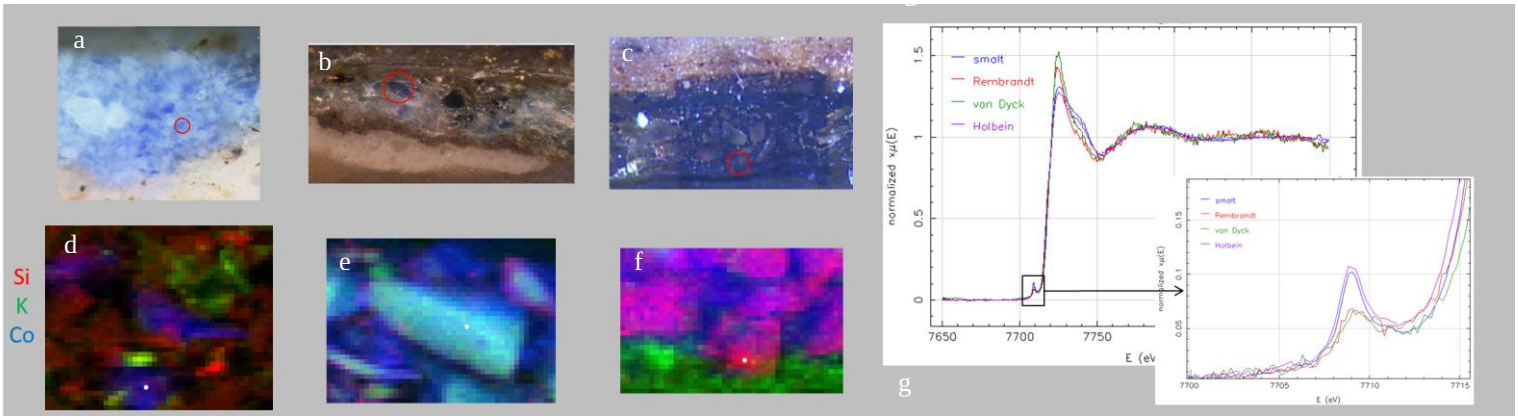

Figure 3: Visual microscopy images of embedded paint cross-sections from Van Dyck (a) , Holbein (b) and Rembrandt (c) are given; (d-f) show the Si-K, K-K and Co-K distribution maps of the respective paint samples; (g) shows XANES spectra recorded on each sample together with a smalt reference spectrum.

Conclusions:

A large number of smalt samples from different paintings/samples and of different quality were analyzed, however the two separate contributions, suggested by Figueredo et al., at ~7709 eV and ~7712 eV of respectively Co^{2+} in tetrahedral coordination and Co^{2+} and Co^{3+} in a octahedral coordination, were not found. It was therefore not possible (yet) to quantify the degree of degradation by e.g. the relative intensities of both contributions. Only the general trends found by Robinet et al. were observed.

References

[1] Figueredo, M.O., et al., A XANES study of cobalt speciation state in blue-and-white glazes from 16th to 17th century Chinese porcelains, Journal of Electron Spectroscopy and Related Phenomena, 185 (2012). [2] Robinet, L., Spring, M., et al., Investigation of the discoloration of smalt pigment in historic paintings by Co K-edge micro X-ray absorption Spectroscopy, Analytical Chemistry, 83 (2011) 5145–5152. [3] McMaster, W.H., Kerr Del Grande, N., Mallett, J. H. and Hubbell J. H., Report National Bureau of Standards, (1969). [4] Ravel, B. and Newville, M., Journal of synchrotron radiation, 12(2005), 537–41.