EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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.

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

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** Study of the alteration state of the blue smalt pigment in faded paintings by Caspar David Friedrich to virtually reconstruct their original	**Experiment number**: HG/157
Beamline: ID21	**Date of experiment**: from: 24/08/22 8:00 AM to: 28/08/22 8:00 AM	**Date of report**:
Shifts: 12	**Local contact(s)**: Marine COTTE	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Introduction and aim of the experience:

The experiment at ID21 focuses on the understanding of the alteration state of the blue smalt pigment in several micro-samples collected on paintings by a famous German 19th c's painter Caspar David Friedrich (CDF, 1774-1840) from the collections of the Alte Nationalgalerie, Staatliche Museen zu Berlin-Stiftung Preußischer Kulturbesitz (ANG) and other paint samples from the Louvre Museum, Paris. Preliminary analyses showed that the blue smalt pigment is fundamental for the impression of these paintings, which are heavily discolored today.

The Co colored potash glass called smalt was basically used as a blue pigment between the 15th and the 18th c. It is known to be unstable over time, going from a deep blue hue to a grey-yellow color. The color change is related to a loss of K^+ ions leading to a change in coordination of tetrahedral Co^{2+} ions towards octahedral coordination. The CDF paintings under investigation correspond to one of the latest use of this pigment we know of and they present smalt in a partly degraded state. The aims of these measurements was twofold: first we wanted to quantify the degradation state of smalt in the paint layers and second we wanted to improve our understanding of the alteration mechanism by identifying precisely the Co- and K-based degradation products. Submicronic XRF was combined with high resolution Co and K-edge microXANES mapping of the smalt grains and other products present around the smalt grains to determine the coordination state of Co and K in the present phases in order to relate their chemical state to the degradation process.

Materials and methods:

For this experiment 22 historic paint samples have been brought to ID21 including six samples from two paintings of CDF from the collections of the ANG and 16 samples from paintings of the Louvre Museum. In addition to these samples, thirty model samples prepared with smalt pure or mixed with cerussite or

hydrocerussite in linseed oil or egg and artificially aged were brought. Model samples were first analyzed in unfocused mode and then in focused mode on thin section prepared at the beamline.

Table 1 : List of analysed samples

Historical samples			
Sample	Artist	Painting	Date
Cpe_CDF_Monk_P3	CDF	Monk by the Sea	1808-1810
Cpe_CDF_Monk_P7	CDF	Monk by the Sea	1808-1810
Cpe_CDF_Monk_P9	CDF	Monk by the Sea	1808-1810
Cpe_CDF_Abbey_P2	CDF	Abbey in an Oak Forest	1808-1810
Cpe_CDF_Monk_P4	CDF	Abbey in an Oak Forest	1808-1810
Cpe_CDF_Monk_P15a	CDF	Abbey in an Oak Forest	1808-1810
Cpe_2177	WEENIX	Départ d'une troupe orientale	1621-1660
Cpe_2177	FLORIS	Dieu rassemblant et protégeant son peuple par la grâce du crucifié	1562
Cpe_2281	Giorgio VASARI	L'annonciation	1512-1574
Cpe_2719	MAZZOLA-BEDOLI	La Nativité avec St Benoit	1552-1555
Cpe_4811	MAZZOLA-BEDOLI	La Nativité avec St Benoit	1552-1554
Cpe_4812	Luca GIORDANO	La mort de Sénèque	1634-1706
Cpe_6063	Luca GIORDANO	La mort de Sénèque	1634-1705
Cpe_6064	VERNOESE	Les Noces de Cana	1562-1563
Cpe_6486	VERNOESE	Les Noces de Cana	1562-1563
Cpe_6595	Salvator ROSA	Le christ ressuscité	1660-1662
Cpe_6732	VERNOESE	Les Noces de Cana	1562-1563
Cpe_6770	VERNOESE	Les Noces de Cana	1562-1563
Cpe_6849	RUISDAEL	Le Coup de Soleil	1660
Cpe_7716	RUISDAEL	Le champ de Blé	1660
Cpe_7850	RUBENS Pierre-Paul	Saint Dominique et saint François d'Assise préservant le monde de la colère du Christ	1618-1620
Cpe_8691	Nicolas POUSSIN	L'enlèvement des Sabines	1637
Cpe_8849	Nicolas POUSSIN	L'enlèvement des Sabines	1637
Cpe_8850	BRUEGEL	L'adoration des Mages	1564-1638
Cpe_12575	WEENIX	Départ d'une troupe orientale	1621-1660
Model Samples			
Sample	Pigment	Medium	Ageing time
S_Huile_0	Smalt	Linseed oil	0 h
S_Huile_1	Smalt	Linseed oil	10 h
S_Huile_2	Smalt	Linseed oil	24 h
S_Huile_3	Smalt	Linseed oil	48 h
S_Huile_4	Smalt	Linseed oil	240h
SH_Huile_0	Smalt + Hydrocerussite	Linseed oil	0 h
SH_Huile_1	Smalt + Hydrocerussite	Linseed oil	10 h
SH_Huile_2	Smalt + Hydrocerussite	Linseed oil	24 h
SH_Huile_3	Smalt + Hydrocerussite	Linseed oil	48 h
SH_Huile_4	Smalt + Hydrocerussite	Linseed oil	240h
SC_Huile_0	Smalt + Cerussite	Linseed oil	0 h
SC_Huile_1	Smalt + Cerussite	Linseed oil	10 h
SC_Huile_2	Smalt + Cerussite	Linseed oil	24 h
SC_Huile_3	Smalt + Cerussite	Linseed oil	48 h
SC_Huile_4	Smalt + Cerussite	Linseed oil	240h
S_Oeuf_0	Smalt	Egg	0 h
S_Oeuf_1	Smalt	Egg	10 h
S_Oeuf_2	Smalt	Egg	24 h
S_Oeuf_3	Smalt	Egg	48 h
S_Oeuf_4	Smalt	Egg	240h
SH_Oeuf_0	Smalt + Hydrocerussite	Egg	0 h
SH_Oeuf_1	Smalt + Hydrocerussite	Egg	10 h
SH_Oeuf_2	Smalt + Hydrocerussite	Egg	24 h
SH_Oeuf_3	Smalt + Hydrocerussite	Egg	48 h
SH_Oeuf_4	Smalt + Hydrocerussite	Egg	240h
SC_Oeuf_0	Smalt + Cerussite	Egg	0 h
SC_Oeuf_1	Smalt + Cerussite	Egg	10 h
SC_Oeuf_2	Smalt + Cerussite	Egg	24 h
SC_Oeuf_3	Smalt + Cerussite	Egg	48 h
SC_Oeuf_4	Smalt + Cerussite	Egg	240h

XRF mapping:

Samples have been analyzed under vacuum at the ID21 beamline with a submicrometric beam. The Co and K µXRF maps have be acquired at the Co- K-edge energy and have been used to select locations for the µXAS measurements. For each sample a first quick mapping has been performed to select the region of interest. These maps were several hundred micrometers wide and high depending on the size of the sample and were recorded with a step size of 2x2 μm^2 and a dwell time of 0.02 s.

Then a high-definition map was performed in the most interesting zone. These maps were 99x99 µm^2 with a step size of 0.5x0.5 µm^2 and a dwell time of 0.05 s.

µXANES:
µXANES at the Co K-edge has been performed on all samples and 6 samples were also analyzed with µXANES at the K K-edge (four historical samples and two model samples)
µXANES at the Co K-edge were recorded between 7670 and 8050 keV with a step size of 0.5 eV and a dwell time of 0.1 s.
µXANES at the K K-edge were recorded between 3580 and 3730 eV with 500 steps of 0.3 eV and a dwell time of 0.1 s.

Preliminary results:

Model samples:
We first analysed model samples by µXRF and XANES at Co K-edge on unfocused mode to verify their global alteration state (Figure 1). As it is shown on the Figure 1, µXANES spectra are similar in a series with same composition but different ageing time even if the visual aspect the series show that colour have changed. Smalt must have weathered at least at the surface, but the unfocused beam and the penetration of X-rays at this energy must have averaged the signal between the smalt at the surface of the samples. Thin sections of model samples were prepared to analyse them at a microscopic scale.
µXANES has been performed on these thin sections (figure 1C) and the difference between the spectra could be clearly evidenced showing that the smalt has weathered.

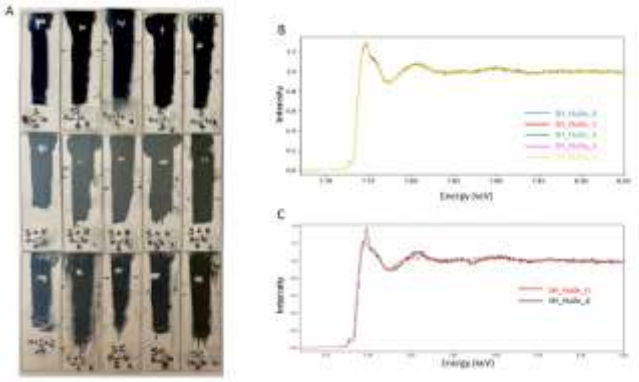

Figure 1: A: Photo of 3 series of model sample (S_Huile, SH_Huile, SC_Huile). B: XANES spectra of SH_Huile series with an unfocussed beam. C: µXANES spectra of SH_Huile_0 and SH_Huile_4 on thin section.

Historic samples:
Each historical sample has been first analysed by µXRF mapping. Elemental maps were obtained at the 7.7 keV, these maps allowed to locate smalt grains (Figure 2). On the Figure 2B Co, Si and K distributions are shown. Si and K maps are well defined and allow to distinguish the grains, although the Co map is blurred. The penetration of X-rays at this energy may be the cause of the problem. Actually when we compare the XANES spectra at the Co K-edge from the centre of a K rich grain and from the edge of the same grain poor in K the distinction between them is not as clear as expected (Figure 2A). Co K-edge XANES can be a good way to characterise the global alteration state of smalt pigment in a paint layer but does not seem to be able to evaluate the state of a grain in a thick section at a microscopic scale. However, it is possible to see a clear difference between spectra of smalt grains with different alteration state at the K K-edge: the more altered a grain is the more intense the white line of K edge is and the intensity of the second peak increases as well (Figure 2C). Furthermore, the analysis of the free K ion in the oil medium shows that it reacts with other components of the paint forming salt and possibly soap. A further investigation of these species at the K K-edge would be interesting to determine with which component of the paint leached K reacts in order to better understand the factors responsible for the alteration of the pigment.

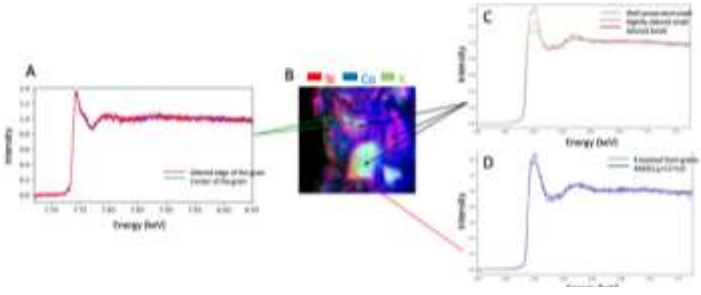

Figure 2: A, Co K-edge XANES spectra of the K rich centre and the K poor edge of a grain. B, XRF map of Si, K and Co. C, XANES spectra at the K K-edge of different smalt grain. D, XANES spectra at the K K-edge of free K in the paint layer

Conclusion

During the experiment on ID21, several historical and model samples were analyzed by µXRF and µXANES. Elemental maps were acquired on all samples with µXRF and µXANES at the Co K-edge evidencing smalt grains. These measurements have allowed to characterize the global alteration state of the pigment in each sample, but the penetration of X-ray at Co K-edge prevents an analysis at the scale of a grain. To get rid of this problem, thin sections of model samples were prepared at the beamline but for this was not possible for valuable historical samples. K K-edge XANES was then realized on some of the historical samples. At this energy, X-ray penetration is lower, and this has allowed to characterize in these samples the alteration states of grains. Furthermore, XANES spectra of K which has leached from the smalt grains show that it is found in new structure such as salts. Further investigation of these structures should allow us to learn what K-ions react with in the paint layers and give us more information on the causes of smalt alteration.