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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.

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: XANES and XRD mapping of a series of paint samples obtained from Van Gogh paintings: understanding the factors that influence the darkening of chrome yellow.**	**Experiment number**: EC-1051
Beamline: ID22	**Date of experiment**: from: 12/09/2012 to: 18/09/2012	**Date of report**:
Shifts: 15	**Local contact(s)**: Rémi Tucoulou	*Received at ESRF:*

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Report:

Introduction:

Lead chromate-based compounds [$PbCrO_4$, $PbCr_{1-x}S_xO_4$ and (1-y)PbCrO4·yPbO] are commonly known as chrome yellow (CY) pigments and were widely used by Vincent Van Gogh and his contemporaries. These pigments show a limited stability under light and other types of environmental factors, causing the bright yellow colour to become brownish. It is striking that only some Van Gogh paintings suffer from this darkening effect while others do so to a far lesser extent. Previous Cr-K edge XANES investigations at ID21 beam line of photochemically aged oil paint models made up of different chrome yellow varieties [1,2] and two paint-microsamples from paintings by Van Gogh [3] demonstrated that the CY alteration is caused by the reduction of Cr(VI) to Cr(III). We also found that not all the chrome yellow forms show the same photochemical stability [2] and that Van Gogh effectively used different types of this class of pigments [4]. The presence of several Cr(III) compounds, such as amorphous $Cr_2O_3·2H_2O$ and either sulfate-based [$Cr_2(SO_4)_3·H_2O$, $KCr(SO_4)_2·12H_2O$] or organo-based materials, [e.g., Cr(III)-acetate or Cr(III)-acetylacetonate] were mainly found as a superficial thin layer (2-3 μm) in the model paints composed of the S-rich orthorhombic $PbCr_{1-x}S_xO_4$ solid solution. Similar alteration products were identified in between the surface of the yellow paint and the S-rich areas of the outer varnish layer of several orginal paint micro-samples. In this work, we have performed μ-XRF/μ-XRPD experiments to verify our assumption that the CY darkening phenomenon only takes place to a significant extent in the case that the CY paint consists (largely) out of $PbCr_{1-x}S_xO_4$.

Experimental:

Combined μ-XRF/μ-XRPD scanning experiments have been performed at the nano-imaging endstation of the ID22 beam line (ESRF), using a photon energy of 29.6 keV. The beam was focused to ca. 0.2 x 0.2 μm^2 (hor. x vert.) employing two graded multilayer coated surfaces mounted in crossed KB configuration. Diffraction signals were recorded in transmission geometry with a FReLoN2k area detector, with 51 x 51 μm^2 pixel size. X-ray fluorescence signals were recorded using a Si-drift detector. Elemental and phase distribution maps were collected from model and real paint samples with 0.3 x 0.15 μm^2 (hor. x vert.) step size and an acquisition time of ≤10 sec/point. XRF spectral fitting was performed using the PyMCA software package [3] while the ensuing XRD data was analyzed with the XRDUA software [4]. Measurements were performed on aged model (3) and historic (1) samples and real paint samples (3) originating from different Van Gogh paintings.

Results:

Next to a number of artificially aged model samples, the following original samples were investigated at ID22NI:

- ”*Falling Autumn Leaves*”, 1888, Kröller-Müller Museum (results shown in Figure 2);
- “*The Bedroom*”, 1888, Van Gogh Museum; and
- “*Sunflowers*”, 1889, Van Gogh Museum.

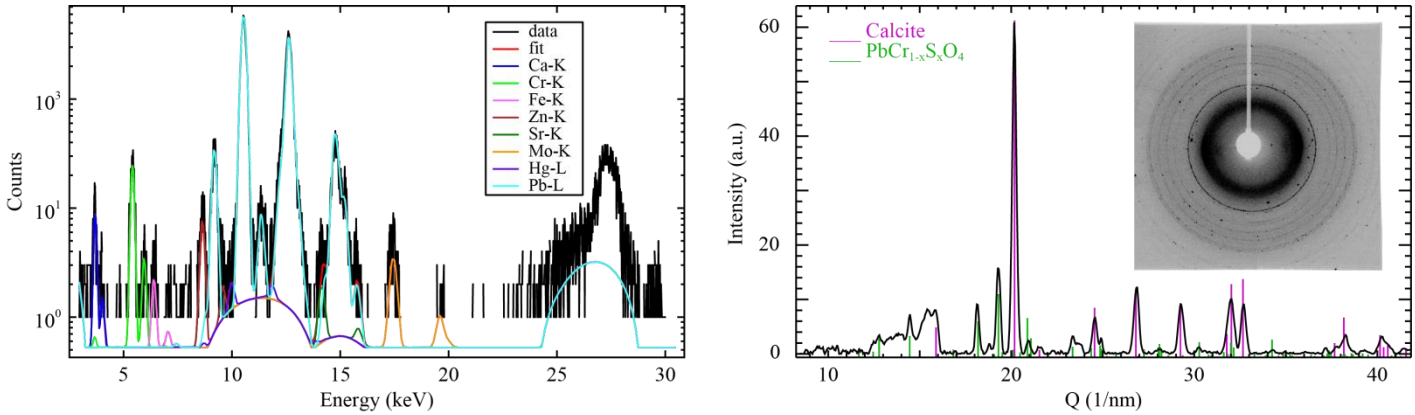

Figure 1 XRF spectrum (left) and X-ray diffractogram (right) collected from the yellow area of the cross-section from “Falling Leaves/Les Alyscamps” with a measurement time of 3 seconds. The calcite signals visible on the diffractogram originate from a piece of paper embedded together with the paint-microsample.

As an illustration of the measurement results, in Figure 1 an XRF spectrum and an X-ray diffractogram, collected from the lower area of the sample discussed in Figure 2 are shown. This sample (from “*Falling Leaves/Les Alyscamps*”, V. Van Gogh, 1888) was previously investigated with XANES at ESRF-ID21 and showed the presence of several islands inside the S-rich areas of the varnish which contain Cr(III) species (dashed lines). Although it was possible to locate these islands again using µ-XRF, no evidence of diffracting species attributable to Cr(III) compounds in these regions was found. This result suggests the amorphous character of the Cr(III) compound formed.

Due to the small thickness of the alteration layers it was necessary to employ a sub-micrometer beam for the analysis of the degraded pigments. The very small beam size resulted in ‘grainy’ phase distribution maps obtained (see $PbCr_{1-x}S_xO_4$ map in Figure 2) on paint samples originating from real Van Gogh paintings. On the superimposed diffraction image obtained in the yellow paint layer, it can be seen that the chrome yellow compound used in this paint fragment is the monoclinic coprecipitate $PbCr_{1-x}S_xO_4$ (Figure 2, bottom). This coprecipitate is very similar to the synthesized model paint sample s3b for which the coprecipitate is known to be $PbCr_{0.76}S_{0.24}O_4$. The paint fragment from “*The Bedroom*” showed the presence of monoclinic $PbCrO_4$ and both monoclinic $PbCrO_4$ and coprecipitate were found in the sample from the “*Sunflowers*” painting.

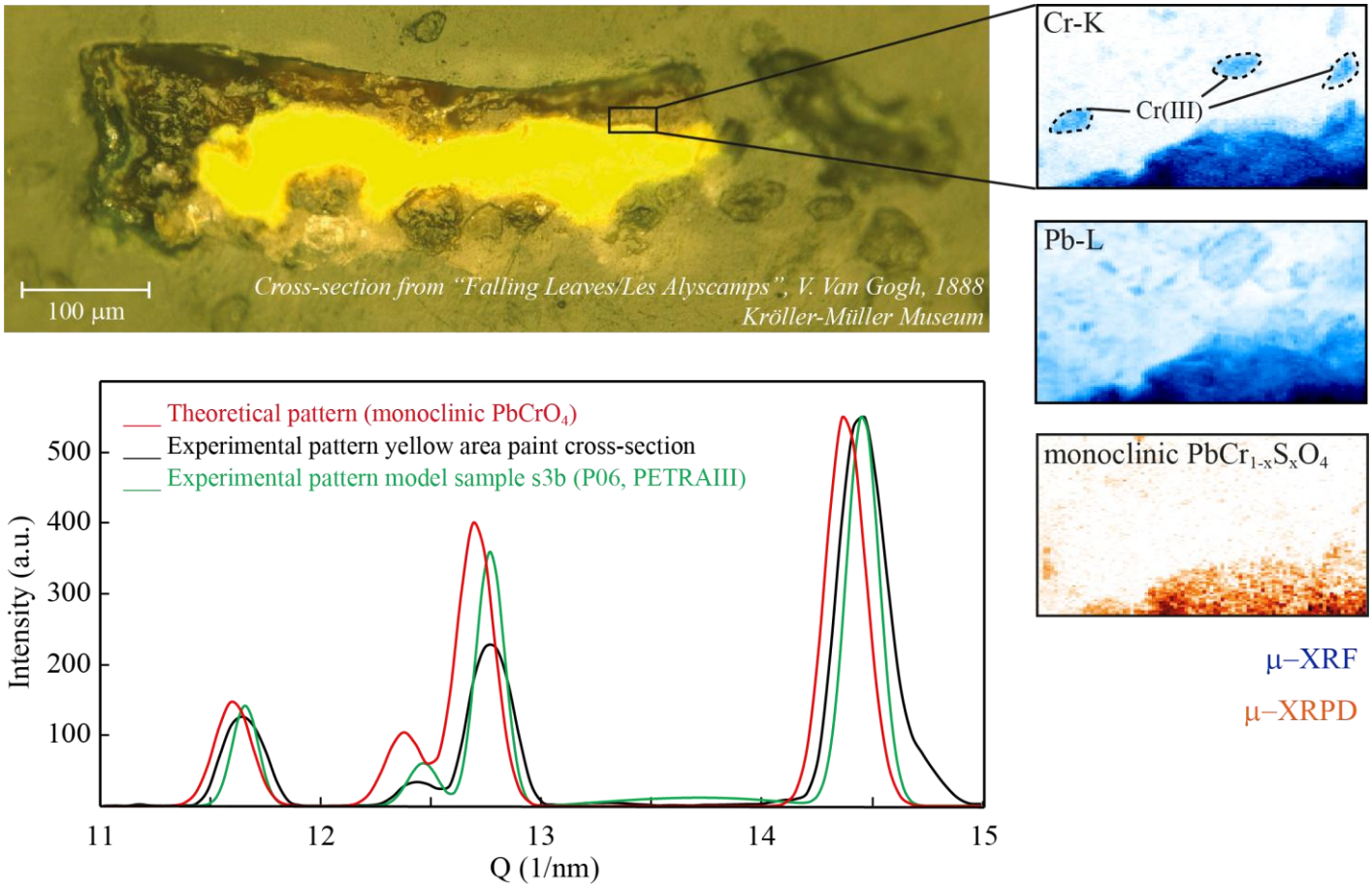

Figure 2 Optical microscope image (top) and elemental (blue) and phase distribution (orange) maps (right) from a cross-section of "Falling Leaves/Les Alyscamps", V. Van Gogh, 1888 (Kröller-Müller Museum). Previous XANES experiments showed the presence of Cr(III) species in islands located in the varnish (dashed lines). The integrated diffraction pattern (bottom) shows the presence of the monoclinic coprecipitate $PbCr_{1-x}S_xO_4$ (black), for which the diffraction signals show a shift to higher Bragg angles compared to monoclinic $PbCrO_4$ (red).The coprecipitate found is similar to the model paint sample s3b (green; previously measured at beam line P06, PETRAIII) with known composition $PbCr_{0.76}S_{0.24}O_4$.

References:

[1] L. Monico, G. Van der Snickt, K. Janssens, W. de Nolf, C. Miliani, J. Verbeeck, H. Tian, H.Y. Tan, J. Dik, M. Radepont, and M. Cotte, Anal. Chem. **83** (4), 1214-1223 (2011).

[2] L. Monico, K. Janssens, C. Miliani, G., Van der Snickt, G.; B.G. Brunetti, M. Cestelli Guidi, M. Radepont, and M. Cotte, Anal. Chem. **85** (2), 860-867 (2013).

[3] L. Monico, G. Van der Snickt, K. Janssens, W. de Nolf, C. Miliani, J. Dik, M. Radepont, E. Hendriks, M. Geldof, and M. Cotte, Anal. Chem. **83** (4), 1224-1231 (2011).

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[5] V. A. Solé, E. Papillon, M. Cotte, Ph. Walter, and J. Susini, Spectrochim. Acta Part B **26**, 63 (2007).

[6] W. De Nolf, and K. Janssens, Surf. Interface Anal. **42**, 411 (2010).