

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.



	Experiment title: XAFS analysis for the structural characterization of alteration compounds in chrome and zinc yellow paints by X-ray fluorescence yield and total electron yield detection modes	Experiment number: A08-1-1074
Beamline: ID21	Date of experiment: from: 03/06/2021 to: 09/06/2021	Date of report: 28/02/2021
Shifts: 18	Local contact(s): Francesco d'Acapito	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): * Letizia Monico, CNR-SCITEC, Via Elce di Sotto 8, 06123, Perugia, Italy * Laura Cartechini, CNR-SCITEC, Via Elce di Sotto 8, 06123, Perugia, Italy		

1. Introduction

In the art conservation field, the darkening of chromate-based yellows in 19th-20th century paintings is a long-standing issue.[1]

In this proposal, a combination XANES/EXAFS spectroscopy measurements collected at the same time in X-ray fluorescence yield (FY) and total electron yield (TEY) detection modes at the Cr-K edge, has been successfully exploited to determine the semi-quantitative abundance and chemical nature of $\text{Cr}^{3+}/\text{Cr}^{5+}$ compounds, arising from the alteration process of chrome yellow ($\text{PbCrO}_4/\text{PbCr}_{1-x}\text{S}_x\text{O}_4$, with $0 < x \leq 0.8$; hereinafter called as “CrY”), K_2CrO_4 , and zinc yellow pigments ($\text{K}_2\text{O} \cdot 4\text{ZnCrO}_4 \cdot 3\text{H}_2\text{O}$; henceforth indicated as “ZnY”) in the oil binder. We have analyzed a set of artificially aged oil chromate-based oil paint mock-ups composed of light sensitive CrY (i.e., mainly orthorhombic $\text{PbCr}_{0.2}\text{S}_{0.8}\text{O}_4$), K_2CrO_4 and ZnY pigments, the latter in-house synthesized by following different receipts. First explorative Se K-edge XAFS spectroscopy measurements have been also carried out on a series of $\text{CdS}_{1-x}\text{Se}_x$ pigment powders with different x values.

2. Experimental

The following set of samples have been investigated at BM08-LISA at ESRF:

• Cr K-edge XAFS spectroscopy

- not aged/aged chromate-based oil model paints (ca. 20 in total) obtained by mixing linseed oil with either light-sensitive $\text{PbCr}_{0.2}\text{S}_{0.8}\text{O}_4$ (mainly orthorhombic), or K_2CrO_4 , or zinc yellow ($\text{K}_2\text{O} \cdot 4\text{ZnCrO}_4 \cdot 3\text{H}_2\text{O}$) (1:4 weight ratio).

- set of Cr-reference powders (7 in total).

• Se K-edge XAFS spectroscopy

- set of $\text{CdS}_{1-x}\text{Se}_x$ pigment powders with different x values (4 in total)

Paint mock-ups were analyzed as fragments fixed on carbon adhesive tape and then directly mounted on Al-plates. This kind of sample preparation has allowed us to perform simultaneously XAFS measurements in two different detection modes: i) TEY and ii) FY. Reference powders were instead analyzed by transmission mode XAFS as pellets that were prepared by mixing about 33 mg of cellulose with 4–28 mg of sample.

For both paint mock-ups and reference powders, measurements were carried out under vacuum conditions, using a Si(311) double-crystal monochromator, an averaged beam size ($h \times v$) of $\sim 70 \times 200 \mu\text{m}^2$ and a photon flux of ca. 10^8 ph/s.

For Cr K-edge analysis, spectra were recorded by scanning the primary energy of the beam with the following steps: 5.8892- 5.9692 keV, step: 10 eV; (ii) 5.9742- 6.0496 keV, step: 0.25 eV; (iii) 6.0499- 6.5375 keV, step: from 3 to 9 eV. Se K-edge profiles were acquired by scanning with energy with the following steps: (i) 12.4648–12.6388 keV, step: 5 eV; (ii) 12.6438–12.7227 keV, step: 0.5 eV; (iii) 12.7232–13.9016 keV, step: from 2 to

7 eV. Cr and Se samples were employed as calibrants and a spectrum was collected at the same time as the sample in order to guarantee the energy scale stability, which resulted to be better than 0.01 eV.

For each sample, a total of n. 2 -4 spectra were acquired.

The ATHENA code [2] was used for the normalization and the processing of the XAFS data and the ARTEMIS code [3] for the quantitative fitting. Theoretical EXAFS paths were generated with the FEFF8.4 code.[4]

3. Preliminary and selected results

Cr-K edge XAFS spectroscopy data collected at the same time in FY and TEY detection modes from unaged/aged CrY, K_2CrO_4 and ZnY oil paint mock-ups (Fig. 1) clearly show the high selectivity of TEY mode measurements to probe the composition of the uppermost (about 100 – 200 nm) darkened layer. Here, with exception of ZnY paint (Fig. 1C), reduced Cr-species are the main constituents (Fig. 1, red line). The contribution of Cr^{6+} -species, arising from the innermost bulk yellow paint, is higher in the spectrum recorded in FY-mode (Fig. 1, black line), as shown by the pre-edge peak intensity increase at 5992.5 eV. [1] For the most altered CrY and K_2CrO_4 oil paint mock-ups (Fig. 1A,B), a loss of structure of the post-absorption features assignable to the Cr^{6+} reduction process [1] is also visible in the TEY mode spectra.

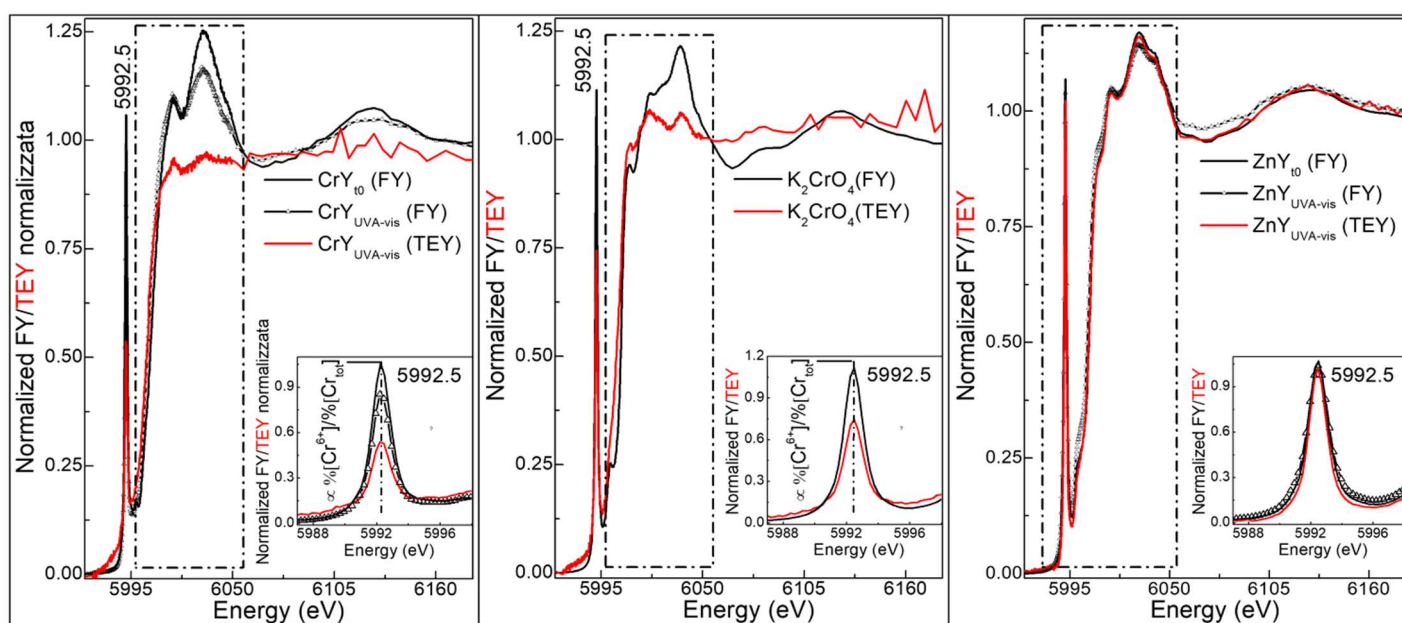


Figure 1. Cr K-edge XAFS spectra recorded in FY-mode (black) and TEY-mode (red) at BM08-LISA of ESRF from unaged and photoaged oil paint mock ups composed of (A) lead chromate-based yellow (CrY), (B) K_2CrO_4 and (C) zinc yellow (ZnY).

Quantitative fitting and theoretical processing of EXAFS data acquired from most of collected data are still ongoing.

Some results obtained from this experiment have been already published (see ref. [5] for further details); the rest of data is expected to be published in the future.

2. References

- [1] L. Monico et al., *ACS Omega* **4**, 6607 (2019), and references therein.
- [2] B. Ravel, M. Newville, *J. Synchrotron Radiat.* **12**, 537 (2005).
- [3] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, *Phys. Rev. B* **58**, 7565 (1998).
- [4] G. Kresse, J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [5] L. Monico et al., *The European Physical Journal Plus* (2022), DOI:10.1140/epjp/s13360-022-02447-7.