



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: X-ray Raman investigation of the organo-Cr and organic compounds formed during photodegradation of yellow painters' pigments	Experiment number: HG-119
Beamline: ID20	Date of experiment: from: 31/01/2018 to: 06/02/2018	Date of report: 01/03/2020
Shifts: 18	Local contact(s): Chr. Sahle	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): * Koen Janssens, University of Antwerp, Belgium * Letizia Monico, Università degli Studi di Perugia, Italy- University of Antwerp, Belgium		

1. INTRODUCTION

Chrome yellow ($\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ with $0 < x < 0.8$; CY) is a family of pigments prone to degradation when used by artists in the form of oil paint, i.e. when intimately mixed with lipidic binding media [1]. (In acrylic binder, a lower reactivity is observed). The alteration comprises a reduction of Cr(+VI) to Cr(+III) while the binding medium is subject to oxidation. Both photo-induced as well as thermal ageing may induce this phenomenon, which causes the original orange-yellow colour of the chromate paint to turn brown/olive green.

Next to Cr(+III) and Pb(+II) ions, one may expect a mixture of sulfate, oxalate and (long chained) carboxylate anions with ability to form complexes/soaps with metal cations to be present. Depending on the degradation circumstances, the newly formed secondary reagents form a series of identified as well as unidentified compounds, including metal (hydrox)oxides (e.g., Cr_2O_3), metal salts (e.g., $\text{KCr}(\text{SO}_4)_2$) and metal-soaps. These are present in a superficial alteration layer of ca 3-20 μm thickness. Many secondary compounds are hard to identify (by XRD) because they are not crystalline and do not show a distinct Raman signal. Previous K-edge XANES investigations of the Cr(+III) compounds present, yielded spectra consistent with mixtures of $\text{Cr}(\text{OH})_3$, Cr_2O_3 , $\text{Cr}(\text{SO}_4)_2$ and Cr(+III)-carboxylates.

Also FTIR measurements are consistent with this. S-XANES measurements reveal sulfates in this layer. We proposed to perform X-ray Raman measurements ($E_0=6.5$ keV) in different geometries (regular vs. grazing incidence/emission) to directly probe the K-edges of C [3] and the $L_{2,3}$ edges of Cr [4] to obtain contrasting information between the upper alteration layer and the original paint underneath. By probing different depths below the surface, we wanted to reveal the difference in "average" redox state of the binding medium between the top few micrometers and the material below.

[1] L.Monico et al., *Angewandte Chemie Int. Ed.*, 54 (2015) 13923-13927. [2] H. Tan et al., *Angewandte Chemie Int. Ed.* 52 (2013) 11360-11363. [3] U. Bergmann et al., *Chemical Physics Letters*, 369 (2003) 184-191. [4] Nyrow A. et al., *J. Anal. At. Spectrom.*, 31 (2016) 815-820. [5] J. Jiminez-Mier et al., *Phys. Rev. A* 72 (2005) 052502.

3. RESULTS

Due to excessive beam damage to the paint samples, no meaningful results could be collected.