

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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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: DYNAMICS OF LATE 19TH/EARLY 20TH C PIGMENT ALTERATION:

Experiment number:

How long will Van Goghs vibrant colours remain intact ? The alteration of Lead chromate yellows.

EC-504

Beamline: ID21	Date of experiment: from: 12/02/2010 to: 16/02/2010	Date of report: 31/08/2010
Shifts: 12	Local contact(s): M. Cotte	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

- * L. Monico, University of Perugia, Italy
- * G. Van Der Snickt, University of Antwerp, Belgium
- * K. Janssens, University of Antwerp, Belgium
- * J. Dik, Delft University of Technology, Netherlands
- * M. Cotte, ESRF, France

1. Introduction

The alteration of chrome yellow (PbCrO_4), a bright yellow pigment intensively used in both industrial and artistic paints, is a well-known phenomenon which has been studied continuously since its invention in the first decades of the 19th C. Although recent literature agrees that this degradation involves a reduction reaction of Cr(VI) to Cr(III), the exact alteration process and the ensuing degradation products remain enigmatic. In addition, depending on the application of the pigment and the atmospheric circumstances, several agents can induce the reduction of CrO_4^{2-} , consistent with the high standard reduction potential of the $\text{CrO}_4^{2-}/\text{Cr}^{+3}$ redox couple ($E^0 = 1.477 \text{ V}$):

- UV-Visible light, heat, contaminants [1,2,3,4]
- atmospheric gasses, such as SO_2 [5] and H_2S [6],
- soil constituents (e.g., amino, humic and fulvic acids) and Fe(II) [7,8]
- sulfides and sulfates [9,10],
- organic matter [11,12],
- semiconductors particles in aqueous solutions [13,14,15]
- H_2O_2 in acidic aqueous solutions.[16,17]

Even though the associated discoloration of the pigment creates a severe threat towards paintings from the end of the 19th C and the beginning of the 20th C (in particular for paintings by Van Gogh), the reduction of original Cr(VI) and the resulting Cr(III)-degradation products have not yet been characterised experimentally.

2. Overview of investigated materials

Both artificially aged model samples, (prepared by applying a thin layer of paint on glass microscopy slides) and two paint cross-sections taken from paintings by Vincent van Gogh (*Banks of the Seine*, F293, 1887 and *View of Arles with Irises*, F409, 1888, see Figure 1) were examined at ID21 by means of μ -XRF and μ -XANES analyses around the Cr-K edge.



Figure 1. Photographs of (left) *Banks of the Seine* (F293), 1887 and (right) *View of Arles with Irises* (F409), 1888 by Vincent van Gogh, Van Gogh Museum, Amsterdam.

(a) Artificially aged model samples.

After UV-visible irradiation and heating of various model systems, the paint taken from a historic paint tube (ca. 1914) proved to be particularly prone to discoloration. A pre-characterization by means of different analytical techniques (μ -XRD, μ -Raman and FT-IR spectroscopy), revealed that this lead chromate paint was particularly rich in lead sulfates. The latter were present in a very fine-grained/amorphous form. Both SR μ -XANES point measurements and SR μ -XRF maps performed on imbedded samples (Figs 2A and 2B) revealed the presence of Cr(III) species (up to 65%), in amounts more significant in the brown discoloured area (Figs 3C, black spectrum). This result was demonstrated by a clear decrease of the intensity of the Cr pre-edge peak at 5.993 keV and a shift of the absorption edge toward lower energies (Fig.3C). However, also on the still-yellow areas of the materials, the reduction of Cr is observed, albeit to a lesser degree than at the surface (around 30-40%) (Fig.3C, red spectrum). By means of a combination of EELS and μ -XANES, the exact nature of the Cr(III) compounds could be identified: the observed spectral data are consistent with the presence of $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. Moreover, as Figure 2D demonstrates, a fit of the μ -XANES measurements demonstrated the possible presence of an additional compound, such as $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ or $(\text{CH}_3\text{CO}_2)_7\text{Cr}_3(\text{OH})_2$ [Chromium(III) acetate hydroxide].

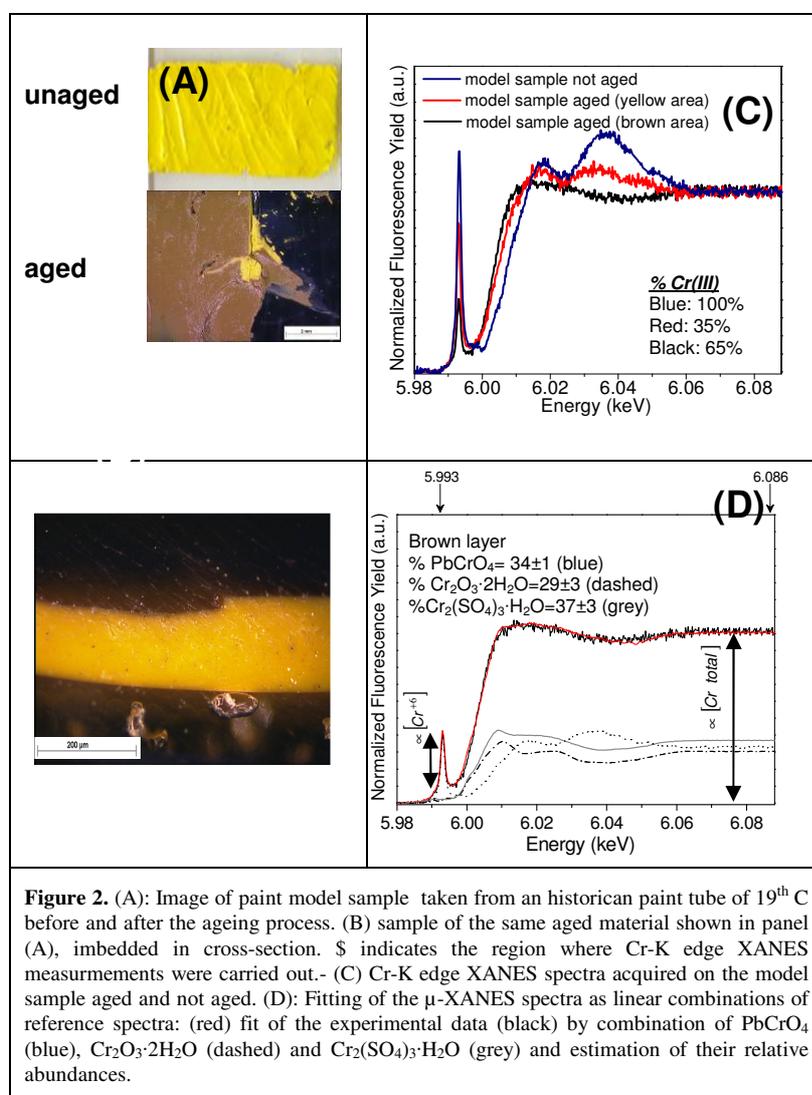
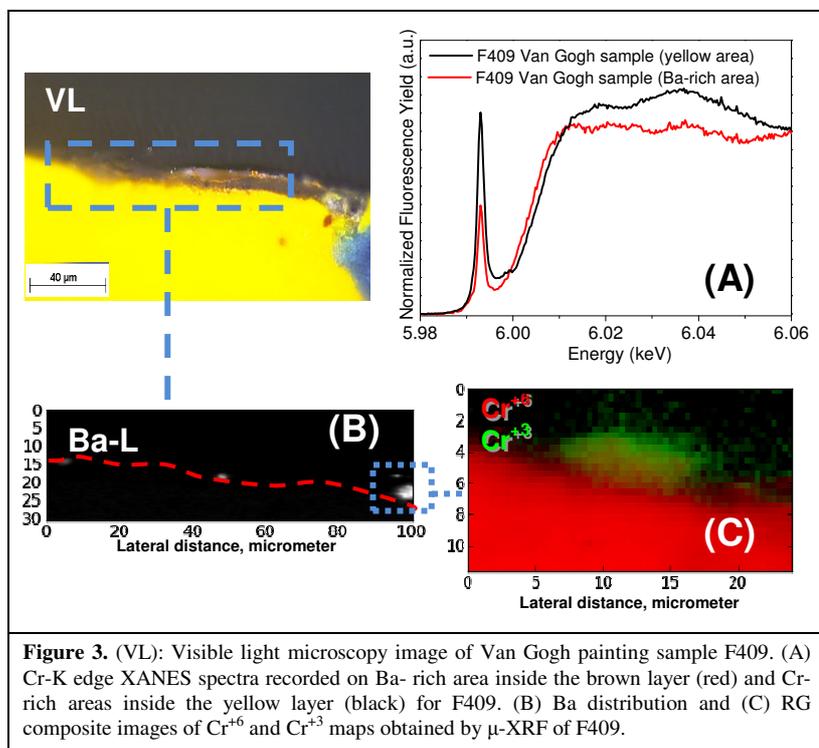


Figure 2. (A): Image of paint model sample taken from an historical paint tube of 19th C before and after the ageing process. (B) sample of the same aged material shown in panel (A), imbedded in cross-section. S indicates the region where Cr-K edge XANES measurements were carried out. (C) Cr-K edge XANES spectra acquired on the model sample aged and not aged. (D): Fitting of the μ -XANES spectra as linear combinations of reference spectra: (red) fit of the experimental data (black) by combination of PbCrO_4 (blue), $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (dashed) and $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ (grey) and estimation of their relative abundances.



(b) Van Gogh paint samples.

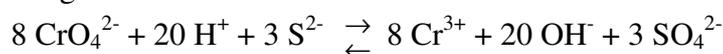
Analogous with the aged model sample, both XANES and XRF measurements revealed the presence of reduced Cr. As Figure 3 illustrates, Cr(III) species (ca. 60%) were particularly detected in the areas rich in Ba and aluminium-silicate compounds, while the surrounding yellow paint (without Ba) contained exclusively Cr(VI). At that time, BaSO₄ and aluminium-silicates were frequently added to paint in order to improve the viscosity.

3 The role of sulfates and sulfides on chromate reduction: scientific background

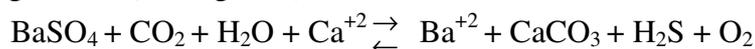
Considering the fact that the formation of Cr(III) was exclusively observed in (a) the PbSO₄-rich model sample and (b) the BaSO₄- and aluminium-silicate- rich areas of the Van Gogh paint samples, it is suspected that the sulfate and sulfide anions play a key role in the reduction process of lead chromate. According to literature, this phenomenon may be explained by one of different processes:

a) minerals and organic matter can act as catalysts, promoting an *in situ* reduction of Cr⁺⁶; additionally, this reaction is favoured under photochemical conditions.[12]

b) Absorption/desorption processes on mineral surfaces of aluminium silicate classes, such as kaolinite [Al₂Si₂O₅(OH)₄] [18] or Montmorillonite [(Na,Ca)_{0,3}(Al,Mg)₂Si₄O₁₀(OH)₂·n(H₂O)] in acidic conditions and in the presence of sulfide ions [12] can promote the reduction of Cr⁺⁶. The oxidation of the sulfides then leads to the formation of sulphur species in several oxidation states (e.g., S₂O₆²⁻, SO₃²⁻, SO₄²⁻, S⁰, and polysulfides)[10]. Since blanch fixe (BaSO₄) or lithopone (BaSO₄·ZnS) are often added to the paint as an extender, 19th C and early 20th C paint usually contains sulphur compounds. In case of sulfides (ZnS), a possible redox reaction involving chromate ions can be written as:



in which electrons released by sulfur are used to reduce chromium. studies have demonstrated that, even in the absence of sulfide species, S⁻² ions can be produced *in situ* from sulfates, after which chromate ions could react with sulfides to regenerate sulfate. According to Plummer,[19] this reaction occurs via the following redox equilibrium involving BaSO₄ (see Figure 4):



Otherwise, the formation *in situ* of S⁻² ions from sulfate and subsequent Cr(VI) reduction can be induced, in anaerobic condition, by the action of specific bacteria, known as sulphate reducing bacteria (SRB).[20]

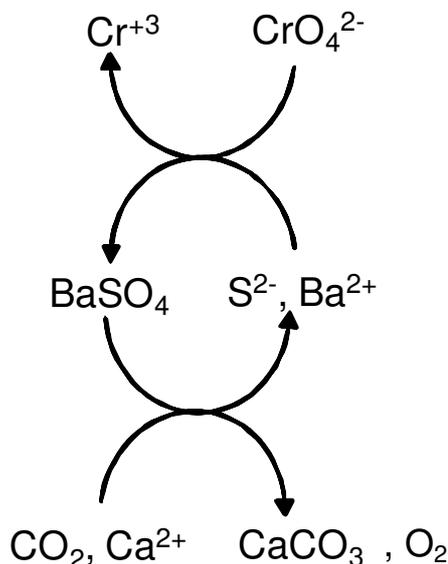


Figure 4. Possible 'catalytic' reaction for the reduction of chromates in the presence of BaSO₄ and CaCO₃, as suggested by Plummer. [19]

5. References

- [1] Cole, R. J.; *Paint Res. Ass. Tech. Pap.* **1955**, 199, 1-62.
- [2] Watson, V.; Clay, H.F. *Journal of the Oil & Colour Chemists' Association* **1955**, 38, 167-177.
- [3] Eibner, A. *Chemiker Zeitung* **1911**, 82, 753-755.
- [4] Haug, R. *Deutsche Farben Zeitschrift* **1951**, 5, 343-348.
- [5] Erkens, L.J.H.; Hamers, H.; Hermans, R.J.M.; Claeys, E.; Bijmens, M. *Surface Coatings International, Part B: Coatings Transactions* **2001**, 84, 1969-1976.
- [6] Somme-Dubru, M.L.; Genet, M.; Mathieux, A.; Rouxhet, P.G.; Rodrique, L. *J. Coat. Technol.* **1981**, 53, 51-56.
- [7] Loyaux-Lawniczack, S.; Refait, Ph.; Lecomte, P.; Ehrhardt, J. J.; Génin, J. M. R. *Hydrology and Earth System Sciences* **1999**, 3, 593-599.
- [8] Abdel-Samad, H.; Watson, P. R. *Applied Surface Science* **1997**, 108, 371-377.
- [9] Boursiquot, S.; Mullet, M.; Ehrhardt J. J. *Surf. Interface Anal.* **2002**, 34, 293-297.
- [10] Kim, C.; Zhou, Q.; Deng, B.; Thornton, E. C.; Xu, H. *Environ. Sci. Technol.* **2001**, 35, 2219-2225.
- [11] Mytych, P.; Ciésła, P.; Stasicka, Z. *International J. of Photoenergy* **2001**, 3, 181-186.
- [12] Tzou, Y. M.; Loepfert, R.H.; Wang, M. *J. Environmental Qual.* **2003**, 32, 2076-2084.
- [13] Navio, J. A.; Colón, G.; Trillas, M.; Peral, J.; Domènech, X.; Testac, J. J.; Padrón, J.; Rodríguez, D.; Litterc, M. I. *Applied Catalysis B: Environmental* **1998**, 16, 187-196.
- [14] Khalil, B.; Mourad, W.E.; Rophael, M.W. *Applied Catalysis B: Environmental* **1998**, 17, 267-273.
- [15] Ku, Y.; Jung, I.L. *Wat. Res.* **2001**, 1, 135-142.
- [16] Perez-Benito, F.; Arias, C. *J. Phys. Chem. A* **1997**, 101, 4726-4733.
- [17] van Niekerk, W.; Pienaar, J. J.; Lachmann, G.; van Eldik, R.; Hamza, M. *Water S.A.* **2007**, 33, 619-626.
- [18] Zachara, J.M.; Cowan, C.E.; Schmidt, R.L.; Ainsworth, C.C. *Clays and Clay Minerals* **1988**, 36, 317-326.
- [19] Plummer, L.N. *Economic Geology* **1971**, 66, 252-258.
- [20] Somasundaram, V.; Philip, L.; Murty Bhallamudi, S. *Journal of Hazardous Materials* **2009**, 172, 606-617.